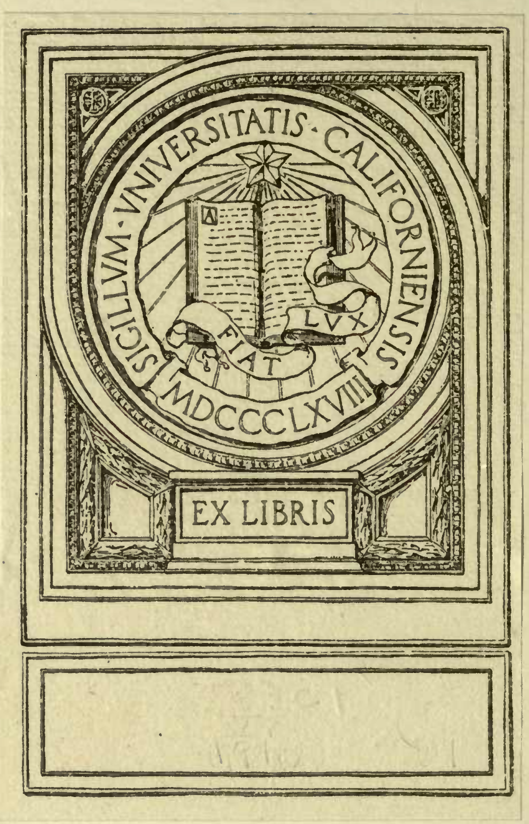

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WITH THE AUTHOR'S COMPLIMENTS

The Problem of International Congresses of Applied Chemistry

BERNHARD C. HESSE, PH.D.
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THE PROBLEM OF INTERNATIONAL CONGRESSES OF APPLIED CHEMISTRY

BERNHARD C. HESSE, PH.D.

The object of the following is to present in concise and impersonal form some of the lessons that seem to me to be read out of the experience obtained in preparing for and in participating in the conduct of the Eighth International Congress of Applied Chemistry. I am persuaded to the belief that these notes may be useful, because of the opinions to that effect expressed by most of such of my friends with whom I have discussed the subject, and to whom I have presented my views.

In reading these pages the fact must not be lost sight of that they in no wise deal with the social side or the factory-inspection, or the private entertainment side of such a Congress, or with anything that in any way deals with any "host and guest" aspect of these Congresses, all of which I regard as with perfect propriety not a matter of any concern whatever to these Congresses as an institution, but they are the pleasure and the reward of the host country alone. This article is limited strictly to the outline of, preparation for and conduct of the scientific or technical side, that is, the side of the actual hard work of the Congress about which all other functions are supposed to cluster and which is itself held out as being the real justification for the existence of these Congresses, and their real merit in aiding the progress of mankind.

My own conclusions, based upon what is contained in the succeeding pages, may, in part, be summed up as follows:

I. The International Congresses of Applied Chemistry of the past have been loaded down with such an overwhelming proportion of extraneous matter that their true business has been entirely submerged therein and the only remedy lies in curtailment of such matter and limiting the activities of the meetings to matter of international and debatable character all pre-arranged, leading discussions in print and the whole matter prepared for *viva voce* discussion.

II. Sectional meetings to be on alternate days and the intervening days to be used by sectional secretaries and participants in discussion in definitely making up the record of the meetings of the preceding days; all matter not in the hands of the sectional secretaries within a reasonable time, say, three working days after the close of the Congress to be denied admission to the printed record.

III. All manuscript *must* be typewritten and all other requirements of the printer fulfilled by all authors otherwise the papers to be returned without exception by the Committee to their authors.

IV. The only way that the persistent and thoroughly correct demand of members for rapid delivery of the printed proceedings can be complied with is to require all participants to be prompt in supplying their manuscript; rapidity of execution requires efficiency in organization and contributing members are part of such an organization and they must all discharge their respective duties at the same efficiency rate that they expect the officers in charge to achieve; no committee can print from nothing, nor can it proceed any faster than the slowest contributor.

V. The demands made upon the Congress for the treatment of scientific matter have grown out of all proportion to the financial ability of the Congress itself to do so; prudence and caution as well as a decent regard for financial propriety all demand that that part of the undertaking of the Congress be cut down to a dimension commensurate with its income.

The reasons for these and other conclusions will be made clear as this article proceeds.

Inspection of the Reports of all preceding Congresses, inclusive of the Eighth, discloses an evergrowing tendency to increasing bulkiness and with little or no increase in the efficiency or ripeness of the actual, crystallized work of these Congresses, namely, the discussions and the resolutions offered to and considered by the Congress, meeting as a whole in its last session and the Reports of Commissions or Committees created at a preceding Congress and directed to report at a subsequent Congress.

Everyone must be struck by the enormous amount of material brought together at the Eighth Congress and on suitable examination all will, no doubt, agree that more than 90 per cent of all such material (however valuable *per se* it may be), is not fitted for nor adapted to discussion in a meeting where international interests are supposed to be primarily or almost solely involved, and that these 90 per cent would have been written and published even without the stimulus of such a Congress, in one or more of the many channels of publication now so plentifully provided all over the world and in every language. The final result is that, in an endeavor to do seeming justice to the great bulk of material offered, the real and important work of the Congress, namely, the formulation of an expression of opinion on the part of the Congress on certain topics which are of international import, scope and interest is simply drowned in that bulk and therefore necessarily slighted and resolutions and reports are put through hurriedly and without due consideration by the various sections, trusting to the International Commission or to the Congress itself to take care of any imperfect work that may have been so performed.

Clearly, it is not the object of these Congresses to provide merely another vehicle of publication for papers that would be written and therefore published without the stimulus of the Congress, nor do men go to the expenditure of time, money and effort to attend such gatherings merely to hear papers read that would reach their library desks in due course and automatically. The object of these Congresses must be to bring into being a class of communications, and a class of results which cannot be created nor accomplished by the societies, associations and publications, now so plentifully at hand. The results that these Congresses must be intended for, are such results for whose accomplishment the direct personal contact and the direct attrition of minds of men of different and differing opinion on debatable and therefore discussible questions, is a prime requisite and essential so that out of these various opinions some order, some system, some agreement, some progress may arise. There is very little to be gained by discussing a paper which merely tells you the physical or chemical constants of a limited number of substances, certainly not enough to make it worth the while of any considerable body of men to travel across oceans and continents to attend the reading of such papers. There exists a plenty of publications ready and eager to take matter of that kind and which can be read with equal benefit in the quiet of one's own study.

In addition to these discussions of debatable questions there is the co-operative work needed for the solution of problems of international importance and the receipt and discussion of reports thereon by the Commissions appointed by preceding Congresses; like the resolutions above referred to these too are caught in the maelstrom of papers and suffer from want of discussion and do not receive that attention which they require and merit, yet these resolutions and these reports are the *only* work that depends upon and requires such gatherings for which the world does not now have ample volunteer and non-governmental machinery, and they have not held that prominence and that importance in past Congresses which their potential value justifies and demands.

It is easily manifest that past Congresses have not provided for the Commissions who are to report to them that machinery which is best adapted to the attainment of worth-while results, nor have they given to the results reported that attention and publicity to which their history and origin entitles them. To serve on such a Commission or Committee is wholly a labor of love on the part of those doing that work; the money grants made by the Congress appointing such Commission are wholly insufficient to give proper publicity even to the results, not to speak of the expenses due to organization and the actual performance of the needed clerical work if the work as a whole is to be well done. When such a Committee does report, its reports are not accessible to nor known to the members at large of the Congress while the paper of another who has not committed himself in advance to devote his time to the accomplishment of an allotted task in a given time has his paper prominently before the attending members and receives more than his proportionate share of attention, all to the detriment and the disadvantage of those who three years before bound themselves out, as it were, to perform work which from its own nature is largely a Cinderella-like piece of work. It is very easy for a Congress to say to a certain Committee that such and such work shall be done by the time the next Congress meets, but it is anything but easy to accomplish anything in the allotted time and present it in a form accessible for discussion and when it is presented for discussion those receiving the report should be acquainted with its nature sufficiently in advance to enable them to prepare a useful, helpful and creditable discussion and criticism, both destructive and constructive, of the report on which so much time, labor and thought have been spent. Perfunctory acceptance or perfunctory discussion or perfunctory discontinuance of labor voluntarily assumed in the belief that it is of wide and general importance and thereupon conscientiously performed with considerable sacrifice of time, effort and labor is not conducive to causing busy men, and they are generally the best men, to expose themselves to such sacrifice for so unsatisfying if not distinctly discouraging reward or treatment. If that kind of treatment of reports and of those who laboriously prepare them continues there can be but one result—men less qualified for the work will undertake it and reports of lesser and lessening value will be produced. If the value of such reports is to increase and these Congresses are more closely to approach the *only* field of real international usefulness open to them then more thought and more reflection must be given to the outline of the work to be performed when a Commission or Committee is created by those creating it or advocating its creation, more consideration and discussion must be given to the report when ready and the report itself must be more widely distributed and much more in advance of the meeting and finally more financial assistance must be given for the needful detail and clerical work; the same is true of resolutions expressing the conclusion or concensus of opinion of the Congress or any debatable subject or topic.

At this point it may be well to call to mind that of eighteen reports by Committees or Commissions that should have been made to the Eighth Congress only two were so made; further, that of twenty-five resolutions adopted by Sections only nine were placed before the Congress because of failure of the sponsors of the remaining sixteen to perform their respective duties.

Now, how can this be done? Merely to point out a fault without suggesting a remedy is an easy thing to do. I fully realize how difficult it is and perhaps how egotistical it may seem to propose such a remedy; nevertheless I will run the risk of error and misunderstanding and propose what seems to me to be one feasible plan at any rate, but I must not be understood to mean that I regard this as an *only* or a *complete* solution. It is brought up for the purpose of discussion in the hope that something will result from it which may in the future prevent these Congresses from falling within themselves due to their unwieldiness, bulkiness and poverty in results actually accomplished.

The plan is as follows:

I. Abolish all papers on promiscuous subjects.

II. Reduce the number of sections to four, say

    1. Inorganic.
    2. Organic.
    3. Analytical.
    4. Administrative.

III. Confine the work of each section to a stated program mapped out in ample time in advance of the meeting and limit their work to deliberation on reports submitted and resolutions to be proposed to the Congress as a whole.

IV. Have sectional meetings on alternate days only, *e. g.*, Monday, Wednesday and Friday with the Final General Meeting of the Congress on Saturday afternoon; Tuesday, Thursday and Saturday morning to be given up to sightseeing, works inspection and social and other matters generally and this time must be used by the sectional secretaries and participants in discussion in properly assembling and writing the minutes of each meeting and in preparing the proper matter for the daily paper of the Congress giving the text of the resolutions finally adopted by each section.

V. Monday, Wednesday and Friday afternoons to be given over, if desirable, to general lectures of the type heretofore held; these would provide ample opportunity for the broad presentation of chemical topics to the Congress and to the public in general.

VI. Sectional meetings from 10 to 12 and from 1 to 3; general lectures at 4.

The topics on which resolutions are to be proposed to the Congress are to be determined by the Committee in charge of the Congress in any way that may seem suitable to it; one way might be to present the Committee's views to each of the societies, institutions and associations represented by delegates at the last preceding Congress and to ask for criticisms of, subtractions from or additions to the list of topics so submitted and for suggestions of those who might be fitted to take part in the leading discussions; the suggestions of the Committee together with those received from these above defined organizations with respect to topics to be sent to the technical press on a stated day and left open for further criticism by the general chemical public until a certain other stated day; thereupon the Committee in charge of the Congress to select from all these topics those that it deems suitable for consideration and to announce the definite selection together with their numerical designation, their assignment to sections and their places upon the program not less than eighteen months in advance of the meeting and to send such statement to the various organizations and to the technical press. Further, this Committee should select for each debatable topic definitely put upon the program one individual to discuss the topic broadly but concisely in ten or fewer printed pages, say, not to exceed, 4,000 words; also to assign to each of two different view points of the subject one man who shall be limited to five pages or say not to exceed 2,000 words; (all those suggesting topics should also suggest the names of those who might be in position to discuss them to advantage, but these names should not be made public); the leader's article to be ready 120 days before the Congress meets and to be sent to the other two writers, and the other two articles to be with the Committee ninety days before the Congress meets. These individuals to be selected and announced one year before the Congress meets. These three contributions are each to carry with them a proposed resolution or proposed resolutions for submission to the relevant section and are to be based upon the matter submitted. Ninety days before the Congress meets no further suggestions of topics for resolution or report are to be received and no further memberships or delegateships accepted. This period of ninety days will all be needed to enable the Committees of the

Congress to make proper preparation for the prompt despatch of business and the proper social and other diversions; ninety days before the Congress meets each foreign central committee and organization should telegraph the Congress Committee the number of members it has obtained in its jurisdiction and how many of them will probably attend the meeting together with the probable number of accompanying ladies and should follow this telegram up with a typewritten list, in duplicate, of all members in its respective jurisdiction together with the post office address of each such member; the same should be done with respect to those members who have declared their intention of attending and so far as possible with their addresses while attending the Congress.

In selecting these topics and those who are to discuss them due regard must also be had to the reports to be received and acted upon and their respective places on the program.

Ninety days before the Congress meets all reports to be presented should be in the hands of the Committee; these reports together with all the discussion papers, are then to be printed and put in the mail for distribution to members of the Congress sixty days before the Congress meets together with a copy of the program in full, giving the date and time of day when each topic or report is to come up for action. In this way every member will have foreknowledge of all the principal points at his home not less than thirty days before the Congress meets and all who are interested will have ample time to prepare creditable and really valuable criticisms and discussions of definite subjects and topics; it might also be feasible to permit absent members to send in their criticisms in writing for presentation to the section in charge, but this seems to me to be of doubtful value.

The Committee in charge of the Congress will, of course, add to this printed volume a list of all the topics presented to it as subjects for discussion and which it did not accept so that the various sections can consider them also in laying plans for the succeeding Congress and after they have placed their recommendations with the Congress the latter, at the meeting of Saturday afternoon, can have the benefit of all these suggestions and of the various valuations placed upon them in deciding what shall be, in part, the leading topics for the next Congress.

At the sectional meetings themselves where the resolutions and reports are discussed suitable stenographic or reportographic minutes could be taken and after proper editing printed in a supplemental volume together with the final action on each topic, resolution or report.

This would result in a compact, concise and clear exposition of the real work of the Congress and free from all the distraction of extraneous and promiscuous papers; of smaller dimensions than its predecessors, doubtless and necessarily, but therefore all the more valuable and meritorious.

In the program proposed there are provided six meeting periods for each section or a total of twenty-four meetings of two hours each or a total of forty-eight meeting hours. If, in each two meeting hours one good resolution or expression of concensus of opinion can be adopted or one good report received, thoroughly discussed and further feasible work mapped out or a new commission established with ample and explicit working directions, the real and only field of international congressional work will have been covered in a fairly efficient manner and progress towards complete accomplishment and achievement of that real work, in the future will have been made. In this manner the attention of those in attendance at sectional meetings will be riveted on one, and only one, topic at a time and having two hours to make something out of the subject-matter, predigested as it were, and so placed before them and no further chance to consider the matter being offered, the probabilities are that proper consideration will be bestowed upon these subjects and the results are bound to be more nearly worth while than at any time in the past; at any rate, if under those conditions worth-while results be not accomplished the responsibility for such non-accomplishment cannot be shifted to the presence of distracting papers and the like. Each section would have before it just one piece of business to dispose of, two hours in which to do it and it would be known as being solely and alone responsible for the good or bad quality of the work turned out.

The responsibility of selecting worth-while topics and properly assigning them to the sections and disposing of them in the program would be wholly upon the Committee in charge of the

Congress and with only twenty-four items of business to arrange and provide for, it is clear that the chances of selecting good and worth-while topics and so disposing them in the program as not to clash or conflict with others the task is not so difficult as it might, at first glance, appear to be, certainly, not so difficult and unsatisfactory as trying to arrange 789 papers to suit as many authors and several times that number of auditors.

It may be objected that this would greatly reduce the attendance at the sectional meetings; if it reduces that attendance to all those actually interested and prepared to take part in the work no possible harm can come to the Congress and its work.

From the report of the Secretary of the Eighth Congress (Vol. 28, p. 471) the following table, which is self-explanatory, is deduced:

	Papers presented†	Papers read by authors	Per cent of papers not read by authors	Attendance	Participants in discussion	Per cent of attendance represented by participants in discussion
Sectional meetings,	546	286	47.6	3,956	610	15.42
Joint Sessions*	157	96	37.2	2,650	250	9.4
Grand total	703	382	45.6	6,606	860	12.9

* Not including three joint sessions at which discussion was not invited.

† A total of 789 papers was presented to the Eighth Congress; of these 703 were presented to the meetings by the authors, the authors' representative or by title, and 86 were not presented to the meetings in any form whatever, although printed in the Report.

Therefore almost half the authors did nor appear to defend or sustain their papers, 11 per cent did not even offer their papers to the meetings and only about one eighth of all persons in attendance made any remarks on the papers presented; surely those remaining seven eighths might just as well have been elsewhere so far as the real work of the Congress is concerned.

At the closing general meeting of that Congress fewer than 400 were in attendance and of these only 15 or 3.75 per cent took part in the discussions, *i. e.*, less than one per cent of all who had registered took part in the final deliberations of that Congress.

It further appears from the same report that eighty of the offered opportunities for meeting were not used and that not to exceed 217 of the 530 sectional meeting hours placed at disposal were utilized.

Further, that out of 217 actual meeting hours only 169 were used for reading and discussing papers, leaving 48 hours, at most, for the consideration of the total of twenty-five resolutions introduced and for the transaction of such other business as may have engaged the attention of the respective sections. It is perfectly safe to say, however, that these forty-eight hours were not nearly all used for discussion of resolutions.

It therefore seems not unreasonable to expect that a grand total of forty-eight hours of work devoted to a grand total of twenty-four different topics by four different sections, each working in meetings of two hours each on six topics and only one topic at a time for which it is wholly responsible will produce a concentrated and compendious and very much worth-while piece of work and one in which the real matter is not buried under or drowned in a mass of irrelevant matter, however interesting and otherwise valuable that matter may be.

This concentrated and classified program of the scientific work need in no way whatever interfere with any other of the functions incidental to such Congresses; quite the contrary, men who have undergone such concentrated and responsible work are all the more entitled to relaxation and enjoyment, and are all the more entitled to the privileges of factory and works inspection; they will have earned them many times over.

This plan of procedure would not only produce a final report of greater value, accessibility and utility than any of its predecessors, but would materially lessen the labors of the Committee in charge of the Congress and would permit it to concentrate more thoroughly on the actual and vital things needful for the accomplishment of the proper work of the Congress because these would thereby be greatly lessened in numbers and scope; necessarily with that it would prevent what cannot be, in the light of the preceding, anything but a waste of money and substance. The printing of 90 per cent of needless matter of the Eighth Congress called for the use of upwards of fifty-four tons of perfectly good white paper (representing in value 1,080 membership fees) and this, to all practical intents and purposes, is a waste of just so much good material and membership fees, a thing which chemists, above all other professionals, should not tolerate nor encourage. I am in a position to know that this unnecessary printing and the labor connected with the collection and handling of these papers, cost the Eighth Congress substantially 6,600 membership fees, whereas the paid-up membership was only 4,163 or roughly 63 per cent of these needless expenditures. If the policy that seems heretofore to have governed these Congresses continues these expenditures of time, labor, money and effort, above designated as needless will increase and sooner or later will assume far greater relative proportions with respect to income from memberships and therefore must inevitably destroy the support given these Congresses by chemists at large and finally these Congresses must of necessity; disappear, such disappearance could be regarded as nothing less than a calamity since the field for these Congresses does exist and there is need of the work they can perform.

Needless to say, no business enterprise could survive such disproportion between income and outgo and no institution, scientific or otherwise, that is operated on such inefficient lines has any real claim to support, encouragement or consideration from any source whatever. These Congresses have now passed through eight meetings and the institution as a whole is nineteen years or more old; it is not unreasonable to expect that a definite proper policy as to scope, commensurate with the income of and the actual interest in the institution, should be adopted. In this connection it may be useful to refer to a paper by Walter F. Reid (*Journal of the Society of Chemical Industry*, 1907, p. 75) in which he gives the total cost of some of these Congresses and their memberships.

	Total outgo, expressed in membership fees	Income, expressed in membership fees	Deficit, expressed in membership fees
1897 Vienna......	782	....	....
1900 Paris.......	1,200	1,751	551*
1903 Berlin......	15,000	2,533	12,467
1906 Rome.......	8,160	2,375	5,785

* Surplus.

(It might be helpful in framing a definite policy to ascertain just what things caused the surplus of 1900 to be thereafter turned into a deficit in each case greater than the total outgo of all preceding Congresses.)

Corresponding figures for the Seventh or London Congress of 1909 are not available. In the Eighth Congress the expenses for printing the proceedings were 7,000 membership fees, for propaganda 2,000, for stenographic and recording service 500, for registration, daily journals and delivery of original communications 300 or a total of 9,800 membership fees thus leaving for these items which are really legitimate strict Congress-business expenses a deficit of 5,628 membership fees. It is this sort of a deficit that calls for immediate, serious scrutiny and attention; unfortunately the Berlin and Rome figures are not capable of being distributed over strict Congress-business expenses on the one hand and expenses which are chargeable to hospitality, entertainment and the like, on the other; these latter are certainly not matters of concern to the Congress but the former most certainly are and they are the only ones here considered or in any way referred to.

The only remedy seems to lie in following the old adage: "Cut your coat according to your cloth" and that is precisely what the above proposed plan is peculiarly adapted for; the amount of preparatory work would be greatly diminished and also that of the preliminary printing; the amount of printing needed throughout would be greatly reduced and based upon the experience of the Eighth Congress it is safe to say that all the needful preliminary work could be done for 600 membership fees and all the printing necessary and all expense of reprints and placing of the volumes with the transportation lines and all strictly Congress work during the meeting could be done for 2,500 additional membership fees *i. e.* the entire expense of the Congress would be covered by 3,100 membership fees. Had the American Committee been at liberty to adopt some such plan as that proposed it is safe to say that there would have been a fund left of substantially 1,000 membership fees. What effective and useful work that sum of money would have enabled the Eighth Congress to initiate for the Ninth! What an entirely different economic position these Congresses would then occupy!

Instead of being dependent they would be independent; instead of justifying their existence by glittering generalities and of obtaining support and financial aid for them by appeals to national or civic pride they would be their own justification; the honor of being hosts to them would be spiritedly sought after; places on the Committees or Commissions to report to subsequent Congresses would be regarded as prizes to be struggled for and coveted and not, as now, accepted in a spirit of sacrifice for the good of the cause! The fact that all the organizations in the different countries would have an opportunity of shaping and directing or of helping in shaping and directing the program and of the work to be accomplished would greatly stimulate the interest in the work of the Congress and would make each one of them feel that it has a direct individual interest in the Congress; this would be equally true of individual chemists the world over. No doubt the Committee in charge would not be put in the embarrassing position of having 70 per cent. of its invitations to such organizations ignored and only 25 per cent. accepted; it would be spared the immense labor of sending out over 17,000 letters soliciting contributions of papers to the Congress and would be relieved of the work of writing up its aims and hopes from over 40 view-points and sending them out to the extent of over 300,000 pieces and of sending out over 120,000 application blanks for membership and to receive only 1-30 of them back as effective applications.

It is difficult to conceive that among the thousands upon thousands of chemists the world over that 4,000 of them would not discern it to be to their advantage to subscribe the same membership fee, as heretofore, to support an enterprise of the kind outlined; the volume or volumes containing the work of the Congress would be absolutely unique in chemical literature and would perform a function not now performed and which cannot be otherwise than of use to chemists wherever located and in whatever branch engaged and in so subscribing they would make it self-supporting and therefore self-perpetuating; it would be capable of continuous and powerful exercise of its influence and could be made to develop continuously and steadily along preconceived and clearly marked lines and be controlled by a continuous and continuing policy, itself capable of adaptation to changing conditions, none of which properties are possessed by the Congresses of the past.

In view of the fact that 11% of all the papers printed were not read at the Eighth Congress even by title and that on the average only 44.5% of those in attendance at the Congress were present at the reading of those papers, that the discussion of only 22% of all the papers presented was finally accepted for printing, it must be apparent that the reading and discussing of papers forms a very small part of the justification of those Congresses, nor can any great proportion of this justification be credited to reports and resolutions, for less than 22% of the time actually spent in meetings could have been used at the Eighth Congress for the discussion of such resolutions and reports and only 36% of all resolutions discussed in sections ever reached the Congress itself; nor can the meetings be credited with much attractive weight, for at the Eighth Congress the members utilized only 41% of the time made available for meeting in sections; finally, only 13.1% of those in attendance at the Congress had their remarks in discussions reported in the printed report, so this can not be credited with any very great attractive power.

At the Seventh Congress only 11% of all papers read were discussed and only 30% of the members in attendance at the Congress were present at the reading of papers.

Clearly, there must be some other justification in the minds of those attending these Congresses than the reading and discussing of papers and the discussing of reports. What can it be? The Eighth Congress planned to have a "Special Interests Registration Bureau" where attending members who desired to exchange information on special subjects could register and be immediately placed in communication with others interested in the same specialties and who had registered. Before carrying out this plan the prospective members were asked their opinion on this point at p. 12 of the Preliminary Announcement of March 6, 1911, of which 65,000 copies in five different languages were distributed throughout the world. They were asked to say if they cared for that kind of a bureau and if so what divisions and subdivisions they desired. The result was exactly three responses; one was indifferent and the other two thought it might be a good thing. It would seem, therefore, that personal interchange of opinion and information arranged and provided for in orderly, thorough and systematic fashion is likewise no justification for these Congresses in the minds of those attending.

Again less than 10% of the attendance participated in the excursions and factory visits, so these cannot form any great part of the attraction of these Congresses.

The Eighth Congress has therefore definitely determined that papers, reports, personal interchange of information, excursions and factory inspection are not singly nor collectively any very great determining factors in inducing attendance upon these Congresses and the puzzle of just what does constitute this real attraction and justification to those in attendance is passed on to the Ninth Congress in the hope that a correct and positive answer to it will then be obtained.

In the event that it should be considered unwise or not feasible to alter the policy governing the Congresses, experience with the Eighth Congress has shown that certain requirements and obligations, compliance with which has heretofore been left optional with members, should be made obligatory and mandatory.

1. Members should be *obliged* to have their names and complete post office addresses typewritten out or legibly printed by hand in their applications so that there will be no need of spending time deciphering them; writing should be absolutely barred for this purpose; to decipher the slovenly and indistinctly written applications for the Eighth Congress took four peoples' time for six weeks and cost 1.5 per cent. of the total income of the Congress from membership fees. It is simply ridiculous and absurd to place such a burden so willfully and recklessly upon a working staff and a Congress Committee both of which have other and more important things to occupy their attention. All applications not so made out should be rejected until so simple a requirement is complied with. Each member's own application should be so clear that it should be used for printer's copy direct.

2. Author's manuscript *must* be typewritten and in duplicate, both as to full paper and abstract, and all figures, drawings or illustrations must also be in duplicate. Handwritten manuscript is not only archaic but most difficult for the printer to follow.

All manuscripts should be provided with a protective front and a back cover and firmly fastened together, and each page numbered; the places that separate drawings are to occupy should be clearly indicated and all drawings should be clearly numbered and the number should appear at the space in the manuscript where the drawing belongs. Original and duplicate should not be sent in the same, but in separate packages; they should not be rolled or folded but should be sent flat; the printer will set from the original and proof-read against the duplicate; in this way danger of delay owing to loss or defacement of copy is avoided. Each document should bear in typewriting on the outside the author's name, the full address to which reprints are to be sent, the number of reprints wanted, the number of the author's or authors' Treasurer's receipt for membership in the Congress, the number of pages in the document, the number of separate drawings, if any; all drawings should be in india ink on white paper or may be tracings on tracing cloth; blue prints should not be sent for there is no generally adaptable method for reproducing them: the redrawing of blue-prints and slovenly or improperly-made drawings cost the Eighth Congress 1.5 per cent. of its income from membership fees. Further, all the different ways the title of the paper is to be indexed and cross-indexed in the final index to the Report, and if the author needs facilities for an exhibition lantern and if so what size slides he proposes to use; if he wants experimental facilities and if so what he needs, or if he needs space for the showing of exhibits and how much space is needed.

It is discreditable that so many authors, as actually did in the Eighth Congress, should send manuscript which was slovenly written, not paged nor fastened together and omit the author's post office address, the number of reprints wanted, the numbers of their figures and fail to show where the figures belong in the text or sent blue prints or slovenly made drawings; that there were no more mix-ups with the manuscript is certainly no fault of such authors; this indifference of authors to their own papers caused an immense amount of extra work for the working staff and for the Committee on Papers and Publications, both of whose time was pressingly wanted for something else than doing the work the authors themselves should have done and gave rise to a very large correspondence which was not only unpleasant but wholly avoidable in the first place by just a little forethought on the part of the authors, the necessity for which had repeatedly been brought to their attention. The Congress should have power, and it should be thoroughly understood that the power would be rigorously exercised, to return and reject any such manuscript peremptorily. That seems to be the only way to make such useless work impossible.

3. No paper should be considered unless its author or authors be members of the Congress at the time the paper is received; all papers should be short and concise otherwise the abstract only should be printed. It is doubtful if papers can be properly handled and printed, reprints provided and the volumes packed and addressed ready for forwarding for less than one membership fee for each printed page of text or illustration; if the expenses incident to propaganda and solicitation of papers are added the cost per printed page of text or illustration will be very close to 1.5 membership fees or 0.67 page per member. At the Eighth Congress there were 4,163 members whose fees would have provided for the printing of a total of 2,776 pages whereas the first twenty-four volumes alone, which were ready when the Congress opened, contained 5,143 pages of printed matter that had to be paid for; this amounts to 1.3 pages per member or twice each member's allotment; the total publication dealing with papers contains 6,500 pages or 1.5 pages per member or 2¼ times each member's allotment. There were 789 papers or an average of 8.2 pages per paper *i.e.* each paper used up 12.3 membership fees or 11.3 in addition to its own; the number of papers was 18.8 per cent of the membership. It is clear that if the individual papers of the future are to be of the same average length, that for each paper submitted there will have to be not less than thirteen members of the Congress if these Congresses are to pay their own legitimate expenses and not be dependent upon the bounty of their hosts to provide them with the naked necessities for transacting their business. Maintaining the present membership fee, there are only two ways of avoiding this situation: increase the membership or cut down the number and length of papers. Judging from the experience of the Eighth Congress the latter is the only way feasible; 4,000 or thereabouts seems to be the limit of membership.

4. If the papers are to be printed in advance, then ninety days before the Congress meets, no further papers should be received and no further memberships nor delegateships accepted. At the Eighth Congress 560 papers were received in time so they could be printed before the Congress met; 229 papers were received too late for such publication; there is no reason at all why all but a very, very few of these papers could not have been presented at the time the other 560 were; this procrastination of authors has caused a delay and an injustice to members and authors who have complied with the reasonable requirements entirely out of all proportion to any gain therefrom; memberships and delegateships can be determined upon and concluded ninety days before the meeting as well as at any other later time; last-minute members are rarely desirable or welcome.

With this thoroughly understood by all, the Committee in charge could have all the papers printed in advance and ready for distribution to those members in attendance and directly after the close of the Congress the volumes then ready could be forwarded to those members not in attendance; the membership list and organization list would be complete and printed and made a part of those volumes; the program could be made up and printed and mailed to every member sixty days before the Congress meets and every author would know that much in advance just when and where his paper would be up for discussion. The indexing work could be brought up to date and would merely need to have added to it the matter contained in the supplemental volumes which would contain the discussions, the general lectures, the joint-sessional addresses, the minutes of the last General Meeting, the errata sheet and the index.

Without some such definite agreement and understanding the Committee in charge will have its time and energies absorbed in attending to the late-comers and be practically forced to neglect or slight the work necessary properly to prepare for those who have been prompt and who attend, manifestly, an improper and wholly unjustifiable state of affairs and which most properly will cause dissatisfaction among those who have been prompt; but that dissatisfaction ought not be levelled at the Committee; the procrastinating and late-coming authors and members are the ones open to censure. The only means of avoiding such dissatisfaction is to have such an understanding and to stick to it. A gathering of this kind cannot be successful through the work of the Committee in charge alone; members *must* co-operate in the manner laid down by that Committee and not try to run the meeting each in his own way as so many evidently attempt to do. Members owe a duty to the Committee quite as much as the Committee owes a duty to the members and unless members will co-operate with the Committee in the way the Committee suggests, confusion and dissatisfaction must surely result and the cause thereof will most likely lie with the members themselves. It is, of course, unpleasant to write this paragraph but events at the Eighth Congress fully warrant and justify these remarks and they are here made in the hope that the unnecessary labors which the Committee in charge of the Ninth Congress may have to perform will thereby be much less than they otherwise would be.

5. The work performed by the Committee on Papers and Publications fully justifies the introduction of this check into the organization of these Congresses and should be retained. While it is true that the final selections of that Committee are not satisfactory to all nor thoroughly consistent, yet it is equally true that this Committee prevented much discreditable matter from being printed and given the prestige of the Congress. Papers of the rankest kind of advertising nature, of the most sophomoric and puerile character, of the most verbose quality and without point or conclusion were offered to and rejected by this Committee; elaborate papers on topics of the most limited or of no interest to chemists, papers made up largely of matters as old as chemistry itself, without any modern application were among those rejected; direct fraud, evasion and deception were practised by a number of would-be contributors from whom such acts would not and could not be expected or believed, but were detected and frustrated; papers published early in 1912 but which were offered in June 1912 in the hopes that the Committee would not know of such publication, were kept out; one author had persuaded a Sectional Committee to pass a ninety-three page printed book for publication, and this author had taken extreme care to obliterate from his submitted copies every trace that would throw any light on its origin or date of publication; he

overlooked, on one copy, to erase or deface the imprint of the printing house and through this the Committee located that publication and found it had been on the book-markets since 1909 and its preface written in October 1908! These are merely a few of the discreditable acts on the part of would-be authors that this Committee blocked and frustrated. There were many other cases where misrepresentation, falsehood, subterfuge and equivocation were resorted to in an attempt to have papers accepted, but which did not pass this Committee. The conclusion seems irresistible that most of these would-be authors regarded the publication of this Congress as a convenient dumping-ground for papers not elsewhere desired—a thing which the Eighth Congress in no uncertain terms had declared that it was not. Of course, this Committee was powerless to prevent certain instances of bad faith on the part of authors of accepted manuscripts who published such accepted matter in journals in other countries between the date of acceptance and the meeting date of the Congress; there is probably no way of adequately reaching such persons. These are harsh statements, but they are true and no doubt will cause as much astonishment to others as their actual existence did to the Committee.

The constructive work of this Committee has not been as uniform nor as satisfactory as that Committee itself wished, but this is due to the fact that no precedent was at hand except the vague one deducible from the nature of the papers printed by preceding Congresses and because wherever there was a doubt that doubt was resolved in favor of the author simply because of this vagueness; of course, the few guide posts to be found in the rules on papers and publications adopted by the Executive Committee of the Eighth Congress were followed but they did not cover very many cases. The problem of determining what papers should be received and what papers should not be received is a difficult one and a solution for it will probably not be readily found. Personally, I incline to the belief that no paper which does not show within itself and expressly stated, an application of the subject-matter communicated therein to a going industrial operation should be accepted and then only if the subject-matter be new since the last Congress and has not been elsewhere read or published; this is offered as a first approximation toward a solution and not for any other purpose.

It must be clear, however, that a Committee which, like this one, has to determine the nature of the material for which so heavy an expenditure as 1 1-2 membership fee per printed page is to be made, performs a necessary and useful function and is a Committee which should have for its guidance as distinct and definite a ruling as possible and power to follow that ruling regardless of any but itself.

6. The difficulty with discussions is to get a printable record of those discussions; many participants get up on their feet without knowing just what they want to say and make remarks which are too ephemeral for publication; others have something of more or less importance to say which may or may not be worth while perpetuating; to sift out the permanent from the ephemeral is the task of the Sectional Secretaries and this cannot be done in the meeting itself; the safest way is to obtain from each participant a statement of his remarks and then the participant must be asked for help in editing or cutting down those reports. Now the hard, cold fact is that the average participant does not like to be called upon in that way; he is at the Congress for, frankly, a holiday with labor, always irksome, as a distinct side-issue; he wants to meet his old friends, to make new ones and to see the sights and he is altogether too busy that way to bother with writing out or checking up the transcript of his remarks. The Secretary may enclose the most pleading note with that transcript or may make the most diresome and awful threats, but your average participant serenely pursues his way and leaves the Secretary to his troubles and gladly makes him a present of his own into the bargain and all the Secretary can do is to grin and bear it and be blamed and criticised afterwards because such participant's remarks did not appear.

The only remedy seems to be to give the average participant a little breathing time and to have sectional meetings on alternate days, say Monday, Wednesday and Friday from 10 to 12 and 1 to 3; this would give each section six meeting periods of two hours each or a total of twelve hours. With the papers printed in advance and the program made up and circulated sixty days in advance of the Congress the reading of papers is reduced to a mere formality; the discussion thereof is the only real business left for a sectional meeting. Aside from a few comprehensive but concise introductory remarks in which the debatable points or some of them are brought prominently forward, the author, if present, should not say anything before the discussion opens; at the close of the discussion the author should be given opportunity to answer criticisms or supply such additional information as may have been asked for. At the Eighth Congress about one half of the papers presented were discussed; the average time used in reading a paper was eight and one half minutes, in discussion the average time was twelve minutes per paper discussed. With the above mode of reading the papers the average time for reading need not exceed two, say, three minutes; in eighteen minutes two papers could on the average be presented and discussed, that is, on the average one paper every nine, say, ten minutes or six to the hour and twelve to the session or twenty-four to the day or seventy-two, in all, to the section. Tuesday, Thursday and Saturday morning could be available to the "average participant" in editing the transcript of his remarks or in writing them out; he would be deprived of his stock excuse that he has to rush off to another sectional meeting and must not neglect his other duties to the Congress for such clerical work which he can do later on just as well. At the Eighth Congress the participants did not get their edited remarks to the Sectional Secretaries until weeks and weeks after the Congress adjourned and it was almost six months before the last Sectional Secretary's report came into the Secretary's hands and all because of the shilly-shallying of the participants in discussion. Perhaps, with some such arrangement of the meeting time the average participant could be pinned down to his work, so that the Sectional Secretaries could all have their work cleaned up within a week after the close of the Congress for it must not be forgotten that each Sectional Secretary like Mr. Average Participant wants to meet his old friends and to make new ones and to see the sights and that the former is quite as much entitled to that relaxation as is the latter.

There should be a distinct and separate authoritative provision and widely published that all participants in discussion who do not have the corrected report of their statements in the hands of the Sectional Secretaries within three working days after the close of the Congress shall forfeit all right to have their remarks printed and that this provision is to be rigorously enforced. In the last analysis, this is the only way in which such procrastinators can be reached. As things are now the Secretary is criticised because he goes to press too soon by those lazy and indifferent persons and criticised for going to press too slowly by those who are not in attendance, an intolerable and wholly unnecessary condition.

7. Registration by sections should be abolished. At the Eighth Congress only 228 out of 1,883 or only 12 per cent registered by sections, and at no sectional meeting was a list of registrants for that section called for, nor was there any occasion for its use.

8. At the Eighth Congress a suggestion, made to it in the very best of good faith and which on its face gave every promise of the very best results, was followed, namely, of having existing foreign societies attend to all matters of the Congress within their own territory. This has not worked out as satisfactorily as the previous method of appointing one man or one society in each country as the organizer. "What is everybody's business is nobody's business" applies to this mode of procedure quite as well as to activities in other walks of life. Concentrate the responsibility upon one man, or one organization in each country and the results will be far more satisfactory. In order to prove this for the Eighth Congress it is only necessary to compare the elaborate organizations in some countries and the results of their work in membership, papers or attendance with the less elaborate organizations and their results in other countries and to see that, in efficiency, the latter far outstripped the former; in promptness and despatch the latter also were far superior to the former.

9. Chemists should appreciate, no matter on what plan or lines future Congresses may be conducted, that attendance upon these meetings is not necessary in order that they themselves may get the worth of the membership fee. The Proceedings of these Congresses go forward automatically, when ready, to each subscribing member and these are worth to each member at least as much as, if not many times more than, his fee. Chemists at large should appreciate that they are each contrib-

uting to these gatherings by subscribing even if they do not attend and that memberships beyond those in attendance are needed and *absolutely necessary* to make these Congresses a success and independent of bounty or charity; in fact, such subscriptions are just as essential to the success of these meetings as is attendance or contribution to the papers or the discussions. But, in order that these non-attending members be not unjustly treated it is necessary that *all* members and *each* member *without exception* do his share promptly, expeditiously and in conformity with the suggestions of those in charge; otherwise, as in the Eighth Congress the forwarding of the Proceedings to such non-attending members will be delayed to such an extent as to be virtually, though not intentionally but nevertheless, under all the circumstances unavoidably, a matter of injustice to and discrimination against such non-attending members who are each entitled to just as much consideration and courtesy as is any attending member and, as in the Eighth Congress, the Committee in charge will be utterly powerless to prevent such a condition, no matter how much it may have done in providing organization and working staff to carry out its work; if the work is withheld from it, no Committee can proceed. It should be remembered that such Committee is practically delivered into the hands of its lazy membership and such Committee can move no faster, as a whole, than the slowest moving member of the Congress; each member must do the whole of his share and do it promptly. Had this been done by all members of the Eighth Congress there would have been literally hundreds of membership fees of expenditures otherwise disbursed, now made available for constructive work for the Ninth Congress and the publications of the Congress would have been completed four months sooner than they actually were; the number of such lax members reaches an astounding and almost unbelievable total.

This brings me now to my final observation which is valid, no matter in which way future Congresses may be operated and that is that a very large proportion of the attending members fail to realize that all the officers and committee members of a Congress are also members of such Congress; that the services of these officers and committee members are given gratuitously to the cause and that the relationship is not that of master and servant or of employer and employee nor of guest and host, but of colleague and colleague earnestly striving, each in his own field of responsibility, to make the undertaking which is largely altruistic, a success; that the very least the member can do is to ascertain the plan laid out and follow and live up to that with as little interference with the working of the organization provided as is possible. Further, the organization of such Congresses thrown upon it is temporary, its work is over in a few days, the greatest load is at the very outset; the staff is temporary, is not and cannot be familiar with all the routine (for the simple fact that no man can guess or state what that routine is surely to be), or be familiar with all the members and all the minute details of the business as is the organization of a bank, a railroad or similar large institution dealing year in and year out with a large number of the same details at once, and if only a little forethought and the spirit of co-operation be exercised matters must and will straighten themselves out along the lines mapped out by those in charge. It is very easy to find fault and to criticise, but it is impossible to operate 2,000 or more different plans for accomplishing substantially the same thing at one and the same time, even though all these 2,000 or more plans singly, be equally good and as good as the plan decided upon.

All of the foregoing has been written in the hope and expectation that it will be of service and therefore no personal matters and no personal feeling, of both of which there is fortunately none on my part, appear therein. Some parts may be, and no doubt are, self-evident and obvious but it is the overlooking of the self-evident and the obvious that is the most common trait of men, inclusive of course, of chemists, and it is the self-evident and the obvious that so many fail to realize and consider and it is that overlooking which causes more delay and more disappointment than any other one thing and that is the justification for here bringing up those self-evident and obvious, that is, axiomatic things.

The Ninth Congress received but little discretionary power at the last General Meeting of the Eighth Congress; all it has power to do is to determine the number and scope of sections and to alter their identification-numbers. In all other respects precedent would require it to proceed along lines similar to those followed by the preceding Congresses. Any change in policy must first be sanctioned by the International Commission of Congresses of Applied Chemistry whose President is Professor Paul I. Walden, President of the Ninth Congress. This Commission is not expected to take the initiative in any change of policy; the desire, if any, for such a change must come from the members of these Congresses themselves. The members of the Eighth Congress owe it to the members of the Ninth Congress to acquaint the International Commission of Congresses of Applied Chemistry of any desires they may have in respect of such changes.

90 William Street,
New York, March 31, 1913.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION I.—ANALYTICAL CHEMISTRY.

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ORIGINAL COMMUNICATIONS

TO THE

EIGHTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY

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VOLUME I
SECTION I.—ANALYTICAL CHEMISTRY

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(Contributions from the Laboratory of the General Chemical Company)

A REVISED AND IMPROVED METHOD OF ACCURATELY DETERMINING ARSENIC—BASED ON THE GUTZEIT TEST

By **Walter S. Allen and Ralph M. Palmer**
Laurel Hill, N. Y.

INTRODUCTION

As a works control method for the quantitative estimation of small amounts of arsenic the Marsh test is obsolete; it is too tedious and too expensive. Hence has arisen the insistent demand for a rapid, accurate method, easy of manipulation.

The Gutzeit method, as a quantitative method, was tried in England after the epidemic in 1900 of arsenical poisoning from beer, but without much success. The first successful working out of the conditions necessary for a quantitative determination by this method appears to have been done by Sanger and Black[1] and published by them in 1907. Their studies showed that the Gutzeit "reaction can be made the basis of a simple and fairly accurate quantitative method, with no more than ordinary analytical precautions." Since the publication of the results of these researches the Gutzeit method has rapidly come into favor and has been used as a standard quantitative method in the laboratories of the General Chemical Company for four years.

INFLUENCE OF IRON ON THE ESTIMATION OF ARSENIC

Literature. In the course of our investigations of certain phases of this method some very interesting phenomena were observed which have a very important bearing upon its accuracy as a quantitative method. These phenomena have to do principally with the effect of iron, both when present as ferrous and ferric com-

[1] J. S. C. I. 26, 1115.

pounds. The effect of iron on the evolution of arsine has been looked upon both as beneficial and as injurious. A. H. Allen[1] recommends that zinc should contain a trace of iron in order that hydrogen may be regularly evolved. Gautier[2] precipitates the arsenic with ferric hydroxide and adds the solution of this precipitate, containing about .1 gram iron, directly to the Marsh generator. Lockemann[3] made use of the same procedure, although he preferred to precipitate the arsenic with alumina instead of ferric hydrate.

On the other hand several investigators ([4-5]) have shown by experiment that when iron is present in the Marsh apparatus the arsenic is incompletely evolved as arsine. In the experiments carried out by Parsons & Stewart[4] however, apparently the iron was always present in the Marsh apparatus in the form of *ferric* salts. Harkins[5] has shown further that the retentive effect of iron may be overcome either by heating the generator or by adding to the solution a salt of tin, cadmium, lead, or bismuth. Of these four metals stannous chloride was found to give the best results in all cases. The beneficial effect of stannous chloride and of the three other metals above considered in increasing the "activity" of the zinc is explained by Harkins[6] as due, in part at least, to the difference in excess potential between zinc and tin on the one hand and iron on the other. It is his belief[7] that the metals of high excess potential, such as zinc, tin, lead and cadmium, are all favorable to the reduction of arsenic compounds, while those with low excess—such as iron and platinum—are unfavorable.

RESULTS OF INVESTIGATION OF THE EFFECT OF IRON

Before the above explanation of the retarding effect of iron on the evolution of arsine had been brought to our attention, we had ascertained beyond question the very serious effect of iron—

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[1] J. S. C. I. 21, 94 (1902).
[2] Compt. rend. 137, 158–63. Bull. Soc. chim. 29, 859–863.
[3] Zeit. Angew. Chemie, 18, 416 (1905).
[4] Parsons & Stewart, J. Am. Chem. Soc. 24, 1005 (1902).
[5] W. D. Harkins, J. Am. Chem. Soc. 32, 518 (1910).
[6] loc. cit.
[7] See also Chapman & Law, Analyst, 31, 3 (1906).

especially ferric salts—on the evolution of arsine in the Gutzeit method. A thorough investigation of this whole subject has convinced us that correct results with the Gutzeit method can be obtained only by observing certain conditions.

Briefly stated—in order to obtain with zinc and acid a proper rate of evolution of hydrogen, and arsine, iron and tin salts must *both* be present, the former entirely in the *ferrous* condition at the time the test is started. We agree with Parsons and Stewart in acknowledging the very injurious effect of ferric salts, and with Harkins in requiring the addition of $SnCl_2$, and we claim further that iron is not to be looked upon as an objectionable impurity but that, in the ferrous form, it plays an indispensable part in Marsh or Gutzeit procedure.

The following method embodies the principles enumerated above; it has been found to give entire satisfaction in the laboratories of the General Chemical Company after several months of continual use.

METHOD FOR ESTIMATING TRACES OF ARSENIC BY THE GUTZEIT TEST

A. General Considerations. For a successful estimation of small amounts of arsenic by this method the following considerations must be carefully borne in mind:

1. The rate of evolution of arsine is of the greatest importance; this rate of evolution of arsine does *not* depend necessarily upon the rate of evolution of hydrogen. (For example, platinic chloride accelerates the evolution of hydrogen but the platinum prevents the reduction of arsenic compounds to arsine[1].)

2. Pure zinc and acid react slowly. For a proper reduction to arsine is required the presence of zinc, another metal of high excess potential (tin in the form of $SnCl_2$) and ferrous iron (a metal of very low excess potential). The stain produced when arsenic, tin, and ferrous iron are present is always *longer* than when ferrous salts are absent.

3. Ferrous iron should, moreover, always be present in about the same amount. It should be added to samples which contain no iron, and to known amounts of arsenic used in preparing stand-

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[1] Harkins—loc. cit.

ard stains. A good working amount is .05 =.10 gram FeO·

4. The amount of acid and zinc used should be so regulated as to give a uniform evolution in all cases. In the analysis of neutral salts, particularly, there is a certain amount of inhibition caused by the presence of a good deal of sodium or similar compounds; to counteract this inhibition the amount of acid and zinc used should be increased.

5. By observing these precautions all the arsenic is evolved in thirty minutes, and standards and samples are run under similar conditions.

B. Preparation of Sample for Analysis. The following observations must be borne in mind in preparing the sample for the arsenic determination:

1. Sulphides, sulphites, thiosulphates, and other compounds which liberate H_2S or SO_2 when treated with H_2SO_4 must be oxidized by some arsenic free oxidizing agent before introducing into the apparatus.

2. Nitric acid, free chlorine, bromine, or iodine must be removed by evaporation, boiling, or some other effective procedure, before the test is started. Iodic acid should also be reduced to iodine and removed by boiling.

3. Difficultly soluble compounds, i.e. ferric oxide, clays and other raw materials for making aluminum compounds, phosphate rock, ores, etc. must be decomposed by preliminary fusion with As-free $KESO_4$ or by solution in aqua regia as the case may require.

4. Starch should be converted to dextrose or maltose by gently boiling with dilute HCl.

5. When iron is absent an equivalent of .05 = 10. gram Fe_2O_3 should be added to the sample; for this purpose a solution of arsenic free ferric ammonium alum is advantageous.

After the required preliminary treatment, as above indicated, for the solution of the sample the ferric compounds must be next completely reduced to ferrous. For this purpose ½ cc. $SnCl_2$ (80%) is added[1] and the mixture boiled gently until colorless; as ferric compounds are reduced more rapidly in the presence of HCl than in H_2SO_4 alone, it is advisable to have present 1 gram

[1] $SnCl_2$ also reduces arsenic to arsenious compounds.

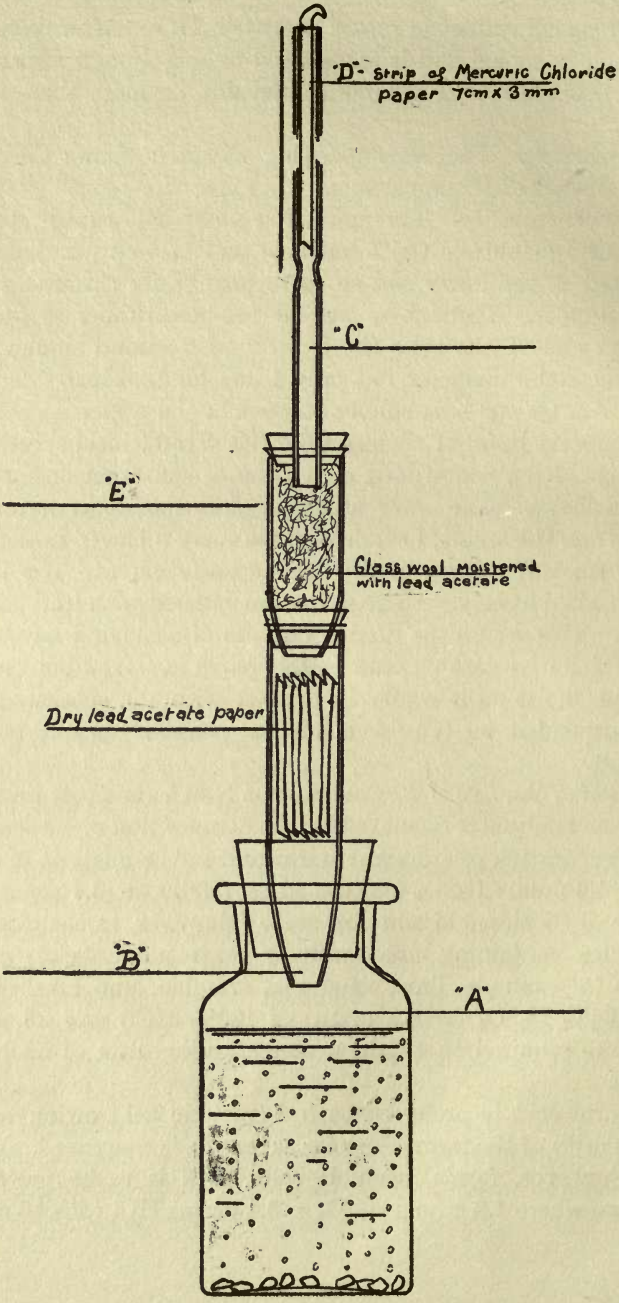
NaCl, or its equivalent in grams of As-free HCl. After reduction the sample is cooled and is transferred to the Gutzeit apparatus. At this point the total volume should not be more than 40 cc. or 50 cc.

C. Apparatus. The accompanying diagram shows the form and dimensions of the apparatus. (A) is a wide-mouth bottle of about 60 cc. capacity. Through a No. 4 one-hole rubber stopper is inserted a glass tube (B) 7 cm. long and 1.25 cm. in diameter, constricted at the lower end so as to pass easily through a hole in the stopper. Through a No. 00 one-hole rubber stopper in the upper end of the tube (B) is inserted a second similar tube (E) of the same diameter but only 4 cm. long. Finally through another No. 00 one-hole rubber stopper in the upper end of the second tube is inserted a glass tube (C) 4 mm. inside diameter, and 10 cm. long, constricted at a point 6 cm. from one end as shown in sketch. The lower tube is used as a scrubber to remove the H_2S from the arsine; for this purpose there is placed in the tube before each test a strip of dry lead acetate paper. The upper tube is packed loosely with glass wool moistened with lead acetate solution. This serves the double purpose of removing any traces of H_2S which may pass the lead acetate paper in (B) and of keeping the arsine moist as it comes in contact with the sensitized test paper suspended in (C)—a condition essential to the success of the test.

D. Making the Test. The amount of H_2SO_4 (or HCl) and zinc used in the analysis is regulated by the composition of the sample. In the preparation of standard stains and in the analysis of most samples 4.2 grams H_2SO_4 (calculated as 100%) or (3.1 gram HCl 100%) and 15 pieces of zinc are used. However, in the analyses of samples containing comparatively large amounts of certain salts, as for example, lime, magnesia, alumina, and alkalies, 6.3 grams 100% H_2SO_4 (or 4.3 grams of 100% HCl) and 25 pieces of zinc are required to obtain a corresponding rate of evolution of arsine.

Sulphuric acid is preferred to hydrochloric acid owing to the greater purity of the former—as far as arsenic is concerned. When H_2SO_4, however, forms insoluble salts, HCl is to be preferred.

In cases where 4.2 grams H_2SO_4 or 3.1 grams HCl with 15 pieces


"D"- strip of Mercuric Chloride paper 7cm x 3mm
"C"
"E"
Glass wool moistened with lead acetate
Dry lead acetate paper
"B"
"A"

of zinc are used and the evolution of arsine is found to be incomplete at the end of a half-hour run, the sample should be analysed using the larger amounts of zinc and acid.

After the sample has been transferred to bottle (A) and the required amounts of zinc and acid added the connections are inserted at once.

The contents of bottle (A) are well mixed by careful shaking after which the apparatus is placed in a water bath which is kept at a temperature within a few degrees of 75° F.[1] After thirty minutes the sensitized paper is withdrawn from the tube, dipped in melted paraffine, and compared with the standard stains.

E. Preparation of Standard Stains. (*a*) *Standard Arsenic Solutions.* One gram of resublimed As_2O_3 is dissolved in 25 cc. 20% NaOH (As-free), neutralized with H_2SO_4 and diluted to a liter with recently boiled distilled water to which has been added 10 cc. of 96% H_2SO_4. Ten cc. of this solution is diluted to a liter with recently boiled distilled water to which 10 cc. of 96% H_2SO_4 has been added. One cc. of this solution (A) = .01 mg. As_2O_3. By diluting 100 cc. of (A) to a liter with recently boiled distilled water to which 10 cc. of 96 % H_2SO_4 has been added (B) is obtained in which 1 cc.=.001 mg. As_2O_3. This solution (B) is the only one that is necessary in preparing standard stains. The solutions are made acid to prevent possible precipitation of arsenic and consequent change in value of solution. Glass stoppered flasks should be used as containers. It is advisable to prepare fresh solutions whenever new standard stains are to be prepared.

(*b*) *Preparation of Stains.* The set of standard stains should contain color strips produced by .001, .002, .004, .006, .01, .015, and .02 mgs. As_2O_3. As a preliminary precaution several "blank tests" should be run on all the reagents used; no appreciable stains should be formed in half an hour. The proper number of cc. of arsenic solution (B) are then added together with .05 gram Fe_2O_3 (as ferric ammonium alum) and ½ cc. $SnCl_2$ (80%). The iron must be entirely reduced by boiling before the test is

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[1] This temperature is carefully regulated in order to properly control the reaction, and that just the right amount of moisture may be carried along with the arsine.

started. After cooling, 15 pieces of zinc are added and the test run for thirty minutes in a constant temperature bath as described above. The test paper is then dipped in melted paraffine and kept in a dry, dark place until ready for mounting.

Light, heat, and moisture will produce rapid fading of the stians. They are best preserved by keeping them in a sealed tube over P_2O_5. They will last for many months if kept away from light.

F. Preparation of Reagents. (*a*) *Zinc.* C.P. shot zinc free from arsenic is used. The pieces should not be larger than will pass a screen three meshes to the inch, nor smaller than will remain on a screen six meshes to the inch[1]. The zinc is given a thorough cleaning in a casserole with dilute HCl (1—1) until a dull gray clean surface is obtained. The zinc is then washed free of acid and kept covered with distilled water; if allowed to dry out it will become less "active."

(*b*) "*Mixed Acid.*" Dilute 1 volume of As-free sulphuric acid with 4 volumes distilled water. Dissolve 10 grams of NaCl in each 100 cc. of the dilute acid.

(*c*) *Stannous Chloride Solution.* 80%. Dissolve 80 grams of $SnCl_2$ in 100 cc. distilled water, to which 5 cc. As-free HCl has been added.

(*d*) *Sensitized Test Paper.* Swedish filter paper No. 0 (20 x 20 in.) is most satisfactory. Cut large sheets into four equal squares and dip into a ½ % solution of $HgCl_2$ (.5 gram $HgCl_2$ in 100 cc. water); the excess of solution is removed by a "squeegee" roller and the paper dried rapidly by spreading it on a flat hot cloth in a drying oven at a temperature of 100° C; the paper should be turned over once during the drying to insure an even heating. The paper should be removed as soon as dry, as $HgCl_2$ is slowly volatile, and cut into strips 7 cm. long and 4 mm. wide. The large sheets should be trimmed on all four edges to a depth of ¼ inch or more as the outer edges are often more concentrated. All the paper should be cut the same width. As soon as cut the paper should be bottled and sealed with paraffine until ready for use. Each new lot of paper should be carefully standardized.

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[1] This zinc may be obtained from Baker & Adamson Chemical Company, Easton, Pa.

EFFECT OF H_2S, SBH_3, AND SO_2 ON STAINS

H_2S and SbH_3 in sufficient quantity change the character of the stain. H_2S should be oxidized with $KMnO_4$ before running the test. Sb if present in excess of .0002 gram Sb_2O_3 will affect the character of the stain, causing it to be longer and lighter in shade. Such a stain if subjected to fumes of HCl will fade distinctly while a pure arsenic stain will be intensified. The same holds for stains obtained with H_2S. SO_2, if present, reacts with hydrogen to form H_2S.

CONCLUSIONS

In the modification of the Gutzeit method given above, the estimation of small amounts of arsenic is shown to be accurate in the presence of iron compounds, provided the iron is entirely reduced to the ferrous condition by $SnCl_2$ before the test proper is begun. This preliminary reduction is essential as the arsenic is incompletely evolved in thirty minutes when ferric compounds are present. It has been found, further, that when a standard stain is prepared from a known amount of arsenic in the presence of reduced iron compounds this stain is about one third longer than when prepared in the absence of iron. In order to obtain correct comparative results, then, standard stains should be made with ferrous iron and $SnCl_2$ present in the solution in approximately the same amounts as are found in the samples analysed. Moreover, iron should be added to all samples which do not contain it.

It is only by observance of these precautions that reliable results are obtained with the Gutzeit method; with these precautions the method is exceedingly exact.

RATIONAL ANALYSIS OF NITRATE OF SODA. THE USE OF THE DEVARDA METHOD VS. THE MISLEADING "REFRACTION" METHOD

By Walter S Allen
Laurel Hill, N. Y.

The analysis of commercial nitrate of soda by the "Refraction" or "Difference" method—subtracting from 100% the sum of the percentages of H_2O, NaCl, Na_2SO_4, and water insoluble matter, and considering all the rest as $NaNO_3$—is not only irrational but misleading as well. For the calculation of yields in nitric acid manufacture it is absolutely worthless, and as a basis for purchase and sale is equally objectionable.

H. Fresenius[1] condemns the "Refraction" method and strongly recommends the universal adoption of a direct method for estimating the $NaNO_3$ content. We are heartily in agreement with this position.

In our choice of a direct method we may consider as most suitable either a gas volumetric method, of which Lunge's nitrometer is the most widely used, or a reduction method wherein the nitrate is reduced to ammonia and distilled into standard acid; of the several methods depending upon the last named principle, that of Devarda[2] is the most rapid[3]. Of the two methods the nitrometer is the quicker but in our opinion the Devarda method is more exact. Our reasons for this opinion are based upon about two years' experience with the modified Devarda method described below, in comparison with the nitrometer. Moreover, in a laboratory where nitrates are analysed only occasionally and the assistants employed are not thoroughly familiar with the very careful manipulation required for the nitrometer, the Devarda method will be found much simpler.

Devarda's procedure, as is well known, consists in a reduction

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[1] V. International Congress of Applied Chemistry 1903, Vol. 1, 214.

[2] Zeit. fur. Anal. Chem. XXXIII (1894) p. 113.

[3] cf. Wiley—Principles & Practice of Agricultural Anal. Vol. 1, p. 536 (1894).

of nitrate to ammonia in an alkaline solution, by an alloy of the following composition: Cu 50, Al 45, Zn 5. This heavy alloy is easily ground to the desired fineness, and gives off hydrogen in a mass of very fine bubbles which very quickly reduce all the nitrate. In dissolving, the copper is left in a finely divided state.

In Devarda's procedure[1] a .5 gram sample of nitrate is used; this is reduced to NH_3 in a strong alkaline solution with 2 grams alloy and the NH_3 distilled over into an excess standard H_2SO_4, using methyl orange as indicator in the final back titration. When using the apparatus described by Treadwell & Hall[2] several objections are encountered, as follows: (1) it is impossible with this apparatus to prevent the passing over mechanically of a little alkali mist into the standard acid; (2) for the most accurate results methyl orange is not an entirely satisfactory indicator; (3) the procedure of boiling over half the contents of the distilling flask is very objectionable, in that the strong alkali softens the rubber stopper quite rapidly and attacks the glass and shortens its life. Edward Cahen[3] suggests two improvements over Treadwell-Hall's method, viz. distillation of the NH_3 with steam instead of direct boiling, and the use of the new indicator, methyl red instead of methyl orange. The table of results given in his paper, while a vast improvement over those obtained by the Pozzi-Escot method[4], are not consistently accurate enough to warrant entire confidence in the method.

With the realization of the uselessness of the "Refraction" method and with the belief that the Devarda method[5] had within it the possibility of being made a very accurate quantitative method, a long series of experiments were carried out in the laboratories of the General Chemical Company, testing all the details of procedure. The result of this work has convinced us that the Devarda method under proper conditions and with suitable apparatus, is a very exact method, more exact in fact than the nitrometer unless unusual pains are taken with the latter method.

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[1] cf. Treadwell & Hall Anal. Chemistry II (1910) 414.

[2] loc. cit.

[3] A comparison of Pozzi-Escot's method and Devarda's method for the estimation of Nitrates, Analysts 35, 307.

[4] Reduction of Nitrate with Aluminum-Mercury couple.

[5] First called to our attention by Prof. E P. Harris, Amherst College.

In order to obtain the most accurate results it was considered necessary to use at least a gram sample and to improve the apparatus used by Treadwell and Hall so as to prevent any possible loss of NH_3 and to eliminate rubber stoppers. In fact our investigations clearly showed us that the successful use of the method is absolutely dependent upon proper apparatus.

The apparatus and method of analysis for nitrate of soda are herewith described in detail.

I—PREPARATION AND WEIGHING OUT OF SAMPLE

In order that the sample used may be representative and contained in a volume of about 10 cc., the following procedure is adopted.

All lumps in the sample are broken up to at least the size of small peas, 100 grams weighed out, transferred to a 500 cc. beaker, and dissolved in water; this is made up to one liter. (If a frothy scum persists it can be broken with a little alcohol.) 100 cc. of this is accurately weighed (in a bottle as described below) to determine the sp. gr., and analysis made on approximately 10 grams of this solution. The weighing bottle is made by cutting the top off a 100 cc. measuring flask about 1 inch above the 100 cc. mark. A dropping tube, whose bulb has a little over 10 cc. capacity, is inserted through the rubber stopper of the flask. In making an analysis after finding the weight of apparatus "Y" and solution, the latter is well shaken up, approximately 10 cc. run from the dropper into the Devarda apparatus, and the weight of "Y" again taken. By subtracting the second weight from the first and dividing by the sp. gr. there is found the number of cc. of solution used. Each cc. of solution is equal to .1 gram of sample. Dividing the cc. found by 10 gives the grams of sample used.

II—DESCRIPTION OF APPARATUS

The apparatus used is a modification of Knorre's apparatus for the distillation of arsenic. It consists of a "reduction" flask "A," a steam jacket and scrubber "C—F" and a condensing absorption apparatus "E—H—K." "G" is a flask for NaOH to remove CO_2 from the air drawn through during distillation,

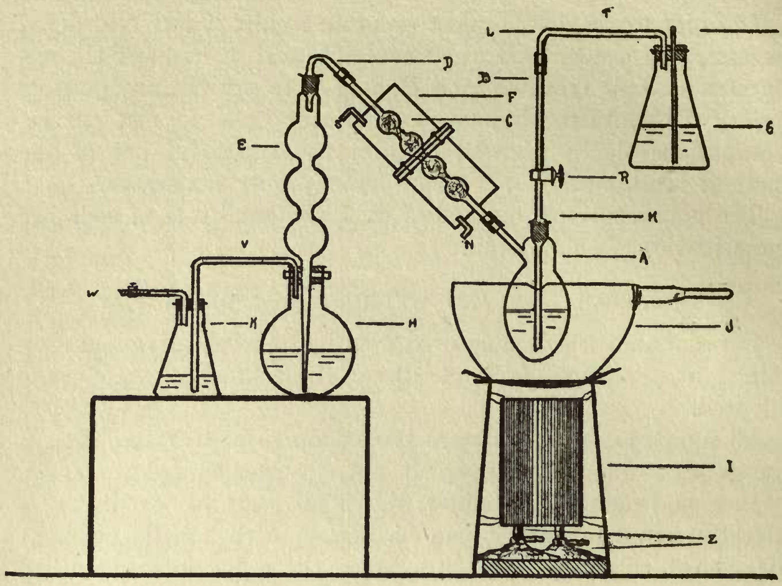

PLATE I - Fig 1

"J" a large size casserole, and "I—Z" burner stand and burners. "A, B, C, D, E, and F" are made of Jena glass.

The flask "A" holds 145 cc. "B" is a tube 11½ long, having a stop cock near the middle; it is enlarged and ground so as to fit tightly into the neck of flask "A" and reaches nearly to the bottom of "A." "G" is a flask of about 175 cc. capacity, fitted with a cork stopper, through which passes a straight tube "O" reaching to the bottom of "G," and a short bent connecting tube "T." This tube "T" connects with tube "B" at "L." The scrubber "C" is made of four bulbs about 1 inch in diameter, the whole scrubber being about 8½ inches long. The bulbs are loosely packed with glass wool and the whole is fitted into the steam jacket "F." This latter is made either of a piece of glass tubing about 2 inches in diameter and closed at the ends by rubber stoppers, or preferably of lead. Live steam enters through "S" and the condensed steam and water pass out through "N." The purpose of scrubber "C" is to retain on the glass

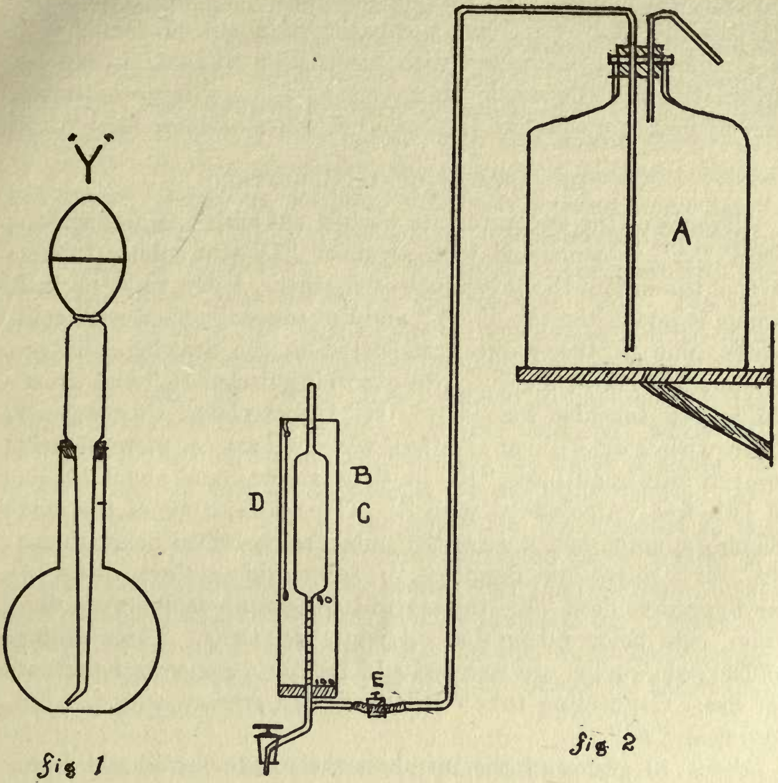

fig 1

fig 2

PLATE II

wool any NaOH mist; the steam jacket prevents condensation of H_2O in "C"; unless the jacket is used a large condensation takes place which is very objectionable. "E" is a series of bulbs about 1¼ inches in diameter and drawn out at its lower end into a tube which reaches nearly to the bottom of "H." "C" is connected with "E" by a bent tube "D" which fits tightly into "E" by means of a ground glass stopper. "H" is an ordinary flask of about 275 cc. capacity, fitted with a rubber stopper through which passes "E" and the bent tube "V" which connects "H" with "K." "K" has a capacity of about 175 cc. "W" is a rubber tube connected with the suction so that air can be drawn through the whole apparatus. "J" is a large casserole serving first as a cold and then as a hot water bath for flask "A."

III DETAILS OF MANIPULATION

All parts of the apparatus are washed out with CO_2 free water. Flask "A" is connected with scrubber "C" by rubber tubing so that the ends of the glass touch each other. A dry, short-necked funnel is put in the top of "A" and the casserole, filled with cold water, put in the position indicated in the drawing. 98 cc. of standard H_2SO_4 are run into absorbing flask "H," the tip of the burette touching the side of "H" and the latter then washed down with 2 or 3 cc. of CO_2 free water. Two cc. more of acid are run into small flask "K" in the same way and about 10 cc. of CO_2 free water added with it. The temperature of the acid should be noted and a correction made as described below under "A" of "Notes and Solutions." After adding three drops of methyl red to flask "K" the apparatus is set up as shown in diagram, care being taken that all joints are tight. Three grams of Devarda's alloy are weighed and put on a paper in readiness for use. Connecting tube "B" is slightly greased where it fits into flask "A."

About 10 grams of the nitrate solution are introduced from apparatus "Y" into flask "A" through the short funnel, washed in with 10 cc. CO_2 free water measured from a pipette and 25 cc. of 20% caustic soda (free from nitrogen compounds). The inside and outside of the funnel are washed into "A" with about 3 cc. more of CO_2 free water. The alloy is then put into "A" through a perfectly dry tube, so constricted at one end that it fits into the neck of "A." This is to prevent any of the alloy from adhering to the sides of the flask which would cause a sudden frothing during boiling. The alloy should be put in quickly, the tube removed and the tube "B" placed in position at once with the stop cock "R" closed. The action begins quickly and is aided by shaking a little to mix the sample, alloy, and caustic. The cold water in the casserole prevents too violent action at first and it is advisable to stir the water for the first few minutes after adding the alloy to "A." The casserole should be removed at the end of five minutes. The reduction is allowed to continue for twenty minutes. The steam should then be turned on in the jacket and the top of tube "B" connected with the caustic flask "G." When the reduction is complete the casserole is filled with boiling hot water, placed in position, and both burners immediately lighted. Boiling should begin at once, the casserole being kept full during the distillation. The rubber tube connected with the suction is then connected to the bent tube in "K." The stop cock "R" in tube "B" is then opened and the suction so regulated that a continuous stream of bubbles is seen coming out of "E" into flask "H." Care must be taken to have enough suction so that no ammonia escapes back into flask "G" when "R" is opened. The distillation is continued for thirty minutes, air being drawn through the apparatus for the whole period. The burners are then turned off, the apparatus disconnected at the upper end of tube "E," and the disconnected parts "D, E, H, and K" washed into an 800 cc. beaker with CO_2 free water. The total volume should not amount to more than 500 cc. Two cc. of methyl red are added to the solution and the excess acid titrated with standard caustic soda. The endpoint should be taken just as the pink changes to a straw color.

IV. CALCULATION OF RESULTS

The 100 cc. standard acid used is corrected for temperature and from this volume is deducted the standard NaOH titration (1 cc. of NaOH being equivalent to 1 cc. of H_2SO_4). The difference is calculated to % $NaNO_3$.

V. NOTES AND SOLUTIONS

A. *Standard H_2SO_4.* This should be of such a strength that 1 cc. equals about .0057 gram H_2SO_4 (equals about 1% equivalent $NaNO_3$). A useful arrangement for this standard H_2SO_4 and burette is shown in Plate II, figure 2. The standard acid is drawn from the reservoir "A" into burette "B" by opening pinch cock "E." Chamber burette "B" is graduated merely from 90 to 100 cc. in 1/10 cc. The difference between the 90 and 100 cc. marks is about 25 cm; the diameter of the stem above the chamber is about 3 mm. The outlet of the burette is so constricted that it will require about three minutes to deliver 100 cc. The burette is surrounded by a water jacket "C" in which is suspended thermometer "D." "C" should be kept filled with water at room temperature to a point opposite the zero mark of the burette. The acid in burette "B" should be allowed to stand five minutes before drawing out in order to equalize temperature. All temperature readings should be taken with thermometer "D" immersed in "C" as shown in sketch. No allowance for drain should be made as such a correction will be very small when three minutes are required for the burette to empty itself.

It is advisable to determine the value of 1 cc. of H_2SO_4 in terms of $NaNO_3$ by a procedure identical with that in analysis of nitrate samples. This corrects for the small "blank" test on the apparatus and also assures the analyst that his manipulation of the method is correct. For standardization purposes pure dry KNO_3 is used. The best KNO_3 obtainable is recrystallized in small crystals, dried first at 100° C. to remove most of the H_2O, then to constant weight at 210° C. to remove every trace of H_2O, after which it is preserved in a glass stoppered bottle. This KNO_3 should then be very carefully tested for all impurities, including nitrite, chloride, sulphate, carbonate, sodium compounds, lime, magnesium, etc. The impurities, if present, are allowed for in the standardization.

11.4 grams KNO_3 (= about 9.6 grams $NaNO_3$ in nitrogen equivalent) are dissolved in 50 cc. cold distilled water and carefully transferred to apparatus "Y," the volume diluted to 100 cc. and 10 cc. of this transferred to flask "A," reduced to NH_3 by the alloy and distilled into 100 cc. H_2SO_4, as in the procedure for nitrates outlined above. From the amount of H_2SO_4 neutralized is then calculated the value of H_2SO_4 in terms of $NaNO_3$. The temperature of the H_2SO_4 should be carefully noted at the time of standardization and a correction applied in all analyses where the temperature is different from that at standardization.

Temperature correction for 100 cc. H_2SO_4 of this strength = .029 cc. for each 1° C.

B. Standard NaOH. This standard alkali should be of a strength equivalent to the standard H_2SO_4. The NaOH is standardized as follows: In a beaker are placed 500 cc. cold distilled H_2O (free from CO_2) and 2 cc. methyl red; if the water is acid or alkaline it should be neutralized at this point. Ten cc. standard H_2SO_4 are then added and the NaOH run in from a 10 cc. burette until the pink just changes to a straw color. Ten cc. NaOH should equal 10 cc. H_2SO_4.

C. Methyl Red Solution. .25 gram methyl red are dissolved in 2,000 cc. 95% ethyl alcohol. Two cc. are used in each determination. As the indicator is sensitive to CO_2 all the water used must first be boiled to expel CO_2 present[1].

D. Devarda's Alloy. This consists of 45 parts aluminum, 50 parts copper, and 5 parts zinc. The Al, in sheet form, is cut into strips about 1 inch wide, rolled compactly together and heated in a Hessian crucible in a furnace until the Al begins to melt. The copper is then added in portions until all is liquefied, and finally the zinc, which should be in one or two pieces, is plunged beneath the surface of the molten mass. After heating very hot for a few moments the cover is removed, the mass mixed with an iron rod, and allowed to cool slowly with the cover on. The cold, crystallized mass is finally crushed to a 60-mesh powder.

E. NaOH (or KOH) sp. gr. 1.3. This is prepared from C. P. NaOH (or KOH) and distilled H_2O. Before use the alkali should be boiled in an open casserole with .5 gram Devarda's alloy to remove any ammonium compounds, cooled, and kept in a well stoppered bottle.

VI. ACCURACY OF THE METHOD

Duplicate analyses should agree within .15% $NaNO_3$. With the sharp endpoint afforded by methyl red there is no difficulty in obtaining duplicate results within the above limit. The experience of nearly two years with this method in the laboratories of this Company has thoroughly convinced us of its accuracy and reliability. We consider it indeed an exceedingly exact volumetric method. It has many times been our experience that two different laboratories of this Company will obtain results which

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[1] Methyl Red is now manufactured by Baker & Adamson Chemical Company Easton, Penn'a.

agree within .15% of each other, on the same H_2O basis. The use of a 1 gram sample in the analysis cuts down greatly on the chances of error—no other accurate method for this analysis, with which we are familiar, permits the use of so large a sample.

RESULTS WITH A KNOWN AMOUNT OF HNO_3

HNO_3 Taken—Calculated as $NaNO_3$	HNO_3 Found	Deviation from theoretical as per cent $NaNO_3$ on a 1 gram sample
.9097 gram	.9108 gram	.11% high
.8789	.8794	.05% high
1.0220	1.0216	.04% low
.9752	.9758	.06% high
.9759	.9765	.06% high
1.0194	1.0197	.03% high
1.0012	1.0018	.06% high

RESULTS WITH A SAMPLE OF N_aNO_3, RUN IN DUPLICATE BY TWO ANALYSTS

Moisture	$NaNO_3$ (Devarda)
1.62%	95.10%
	95.13%
1.65%	95.08%
	95.03%

COMPARISON OF RESULTS BY NITROMETER, DEVARDA'S METHOD, AND THE "REFRACTION TEST"

Twenty-three samples of commercial nitrate of soda were analysed by the above three methods, with the following results:

Agreement within	Devarda and Nitrometer	Devarda and Refraction
.1% $NaNO_3$	4 samples	2 samples
.3% $NaNO_3$	18 samples	5 samples
.5% $NaNO_3$	22 samples	6 samples
.6% $NaNO_3$	23 samples	7 samples

Sixty-nine samples of commercial nitrate of soda were analyzed by the Devarda Method and the "Refraction" method with the following differences in % $NaNO_3$:

	Out of 69 Samples
Agreement within .1%	5
Agreement within .3%	11
Agreement within .5%	19
Agreement within .8%	32

	Out of 69 Samples
Agreement within 1.0%	35
Agreement within 1.5%	54
Agreement within 2.0%	63
Agreement within 2.5%	67
Agreement within 3.0%	69

As will be noted from the above, one half the samples show a difference of more than 1% $NaNO_3$ between the two methods, 22% of the samples differ by more than 1.5% $NaNO_3$, and 9% of the samples by more than 2% $NaNO_3$. In every case the results by the "Refraction" method are *high*. These high results are, of course, accounted for by the fact that in the "Refraction" method no consideration is given to the potassium nitrate, sodium chlorate, perchlorate, and iodate, lime, magnesia, etc., which are almost invariably present.

The following four comparative complete analyses show the variation in impurities in different commercial nitrates:

	No. 1	No. 2	No. 3	No. 4
H_2O	2.15%	2.99%	2.74%	3.00%
Na_2SO_4	.20%	.38%	.34%	.28%
$NaCl$	1.28%	1.50%	1.16%	1.43%
(Insoluble)	.08%	.52%	.10%	.26%
SiO_2	.08%	.52%	.10%	.20%
Al_2O_3 Fe_2O_3	.13%	.35%	.11%	.10%
CaO	.06	.09	.09	.04
MgO	.08	.07	.14	.24
$NaIO_3$	.02	.04	.04	.04
$NaClO_3$	Trace	.01	.01	None
$NaClO_4$	Not determ.	Not determ.	Not determ.	.90
KNO_3	1.31	1.92	4.82	8.09
$NaNO_3$	94.54	92.53	90.43	85.34
Total N as $NaNO_3$ by Devarda method	95.64	94.14	94.48	92.15
$NaNO_3$ by "Refraction" test	96.29	94.61	95.66	95.03
$NaNO_3$ deducting from 100% all the impurities found (calculating $K_2O=Na_2O$)	95.79	93.74	94.50	92.49

These analyses show considerable variation in impurities, especially in KNO_3. Samples No. 3 and 4 show the very marked effect of high potash salt on the "Refraction" test, and all the samples show that the latter test can only be relied upon when *all* the impurities present are deducted from 100%.

CONCLUSION

The inaccuracy and uselessness of the so-called "Refraction" test for commercial nitrate of soda is shown both by a series of complete analyses of this material, and by the analysis of 69 samples by both a direct and indirect (refraction) method. The "Refraction" test takes into account only the H_2O, NaCl, Na_2SO_4, and water insoluble matter present and takes no account whatever of potassium salts, chlorate, perchlorate, iodate, lime, magnesia, etc. The complete analyses show that it is only by taking into account *all* these impurities that a reliable value for $NaNO_3$ can be obtained.

Obviously it is much simpler to estimate the total nitrogen by a direct method. For this purpose the modified Devarda procedure is recommended. This method, using the modified Knorre apparatus, is shown to be very accurate. A one gram sample is used and results are reliable within .15% $NaNO_3$. This method, while not as rapid as the nitrometer, is believed to be more accurate; it is, moreover, simple and easy of manipulation.

As the results obtained by the "Refraction" test are almost without exception *high*—sometimes nearly 3% high—the purchaser is at an obvious disadvantage when compelled to pay for this material on the "Refraction" test basis. He is not only getting *lower* nitrate content than the "Refraction" test shows, but he can have no definite idea how much too low these results are, and for works control, calculation of yields, etc. he is compelled to re-analyze the samples by a direct method which will reveal the actual nitrogen value.

The only rational procedure is to discard entirely the misleading "Refraction" method, and substitute therefor a direct method—the same to be used as a basis of valuation in all contracts.

The importance of a proper method of analysis for Sodium

Nitrate, to determine its valuation accurately, must be obvious to all, and it is hoped that the presentation of this subject to the Eighth International Congress will result in sufficient discussion of this important matter to warrant the recommendation and adoption of the Direct method of analysis.

AN EXACT METHOD FOR THE DETERMINATION OF SULPHUR IN PYRITES ORES

By Walter S. Allen and Howard B. Bishop
Laurel Hill, Long Island, N. Y.

I. Outline of the Problem and the Results Obtained by Investigation

That the accurate determination of sulphur in pyrites ore is of very great importance is universally recognized by technical chemists, as well as by the purchasers and sellers of such ore. Any improvement, therefore, in the accuracy of the analytical method for determining sulphur is worthy of very serious consideration.

The General Chemical Company several years ago became dissatisfied with the well known methods for determining sulphur, and under the inspiration and direction of Mr. W. C. Ferguson, consulting chemist of this Company, the new method herein presented was worked out. The main features of this method were worked out by Mr. H. B. Bishop and Mr. W. S. Allen and the very thorough and painstaking work necessary to establish the proof of the accuracy of the method was carried out by Mr. Joseph L. Coon, assistant chemist. Acknowledgment is also heartily given to other members of the research and analytical staff of this Company who, by their interest and suggestions, aided in the final solution of the problem.

The methods generally in use for the estimation of sulphur in ores are usually modifications of Lunge's well known method. Recently E. T. Allen and J. Johnston[1] published a very valuable and illuminating series of experiments on the exact determination of sulphur in soluble sulphates. They showed convincingly the errors occurring as a result of the solubility of $BaSO_4$, the occlusion of alkali sulphates and acid sulphates (especially in the presence of alkali chlorides), and the loss of SO_3 (or ammonium sul-

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[1] J. Am. Chem. Soc., *32*, 588 (1910).

phate) when the $BaSO_4$ precipitate is ignited; they recommend a correction for these errors in each determination of sulphur. In another paper[1] the same authors apply the results of their researches to the analysis of pyrites and marcasite. They employ the oxidation method of Carius (heating the ore in a sealed tube with fuming nitric acid), separate the iron with Na_2CO_3 and correct the final precipitate of $BaSO_4$ for the errors above mentioned. This method, while it undoubtedly yields very accurate results, in skilled hands, lays no claim to rapidity, as the authors admit, and is not applicable to the demands of a technical laboratory.

More than two years before the appearance of these articles[2] we realized the difficulties inherent in the usual methods for sulphur determination and by a long series of experiments established clearly the facts that low results are inevitably obtained when alkali salts (especially ammonium salts) are present. Our efforts were then directed toward an improved method, wherein, if possible, all alkali salts should be eliminated. Throughout all our investigation work it was kept clearly in mind that the method toward which we were concentrating our attention *must* give theoretical results, not only with a known amount of H_2SO_4 corresponding to the sulphur percentage in average ores, but also with a "theoretical ore," made by adding to a known amount of H_2SO_4, iron, zinc, copper, lead, etc., in such proportions as are present in average ores. It is possible to obtain the strength of H_2SO_4 by titration to a very high degree of accuracy.[3] The acid thus standardized gave us a material of whose sulphur content we were absolutely certain. The ideal procedure would have been, of course, to work entirely with a standard pyrites ore whose sulphur content had been established beyond any doubt; this material, however, was not and is not available.

In order to eliminate alkali salts entirely during a determination of sulphur in pyrites the sulphate must either be precipitated by $BaCl_2$ in the presence of iron salts, or some other method of separating the iron than by the use of NH_4OH or Na_2CO_3 must be

[1] J. Ind. & Eng. Chem., *2*, 196 (1910).
[2] loc. cit.
[3] W. C. Ferguson, J. S. C. I., *24*, 781 (1905).

found. Precipitation with $BaCl_2$ in the presence of ferric salts is not to be considered where accuracy is required on account of the well known precipitation of a part of the SO_3 as $Fe_2(SO_4)_3$[1] which loses SO_3 on heating and gives low results. As there seemed to be no practical way of separating the iron except by precipitation with an alkali, attention was turned to precipitation of the sulphate in the presence of *reduced* iron salts.

It has been known for some time that it is possible to precipitate $BaSO_4$ in the presence of *reduced* iron salts and obtain an iron free $BaSO_4$[2]. Hydroxylamine hydrochloride has been successfully used as a reducing agent but is fairly expensive. Sodium thiosulphate and hydrogen sulphide have been suggested for the same purpose but their use is at least open to obvious objection, notwithstanding the favorable results obtained with H_2S by G. v Knorre[3].

W. H. Seaman[4] calls attention to the value of aluminum as a reducing agent for ferric iron and it occurred to us at once that here was the ideal reducing agent for the method. It was found that the finest aluminum powder obtainable[5] is exceedingly well suited to this purpose; this powder is sulphur free and works with great rapidity. It has, moreover, a further value aside from its reduction of ferric salts, in that all Cu and Pb[6] are thrown out as metals and can be removed with the excess of aluminum powder by filtration before the barium sulphate is precipitated; this is an obvious advantage. The $BaSO_4$ precipitated from a sulphate solution containing as much as .7 gram of iron in the ferrous condition is pure white, even after ignition, and has been found by repeated tests to actually contain only a trace of iron—less than enough to effect the determination of sulphur by .01%.

Attention was next turned to the manner of precipitating the $BaSO_4$, and conditions under which this precipitation should take place. In consulting the literature on this very important part of the determination, it is evident that a great deal of time

[1] Anal. Chem. Treadwell-Hall, II, 368 (1908).
[2] cf. Gyzander, Chem. News, 93, 213.
[3] Chem. Ind. *28*, 2.
[4] Chem. Eng. (1908).
[5] Baker & Adamson Chem. Co., Easton, Pa.
[6] $PbSO_4$ is completely converted to metallic lead and a soluble sulphate by powdered aluminum.

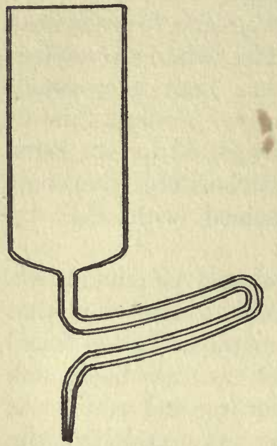

fig. 1

Precipitating Cup

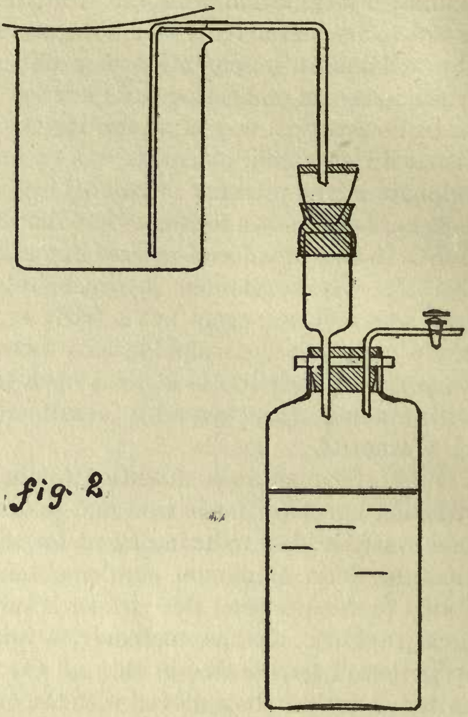

fig. 2

Filtering Arrangement

and care have been expended in examining the effects of free acid, volume of solution, rate of addition of $BaCl_2$, etc. The method usually prescribed is to precipitate slowly with constant stirring, in a boiling hot, slightly acid solution. Hintz & Weber[1] recommend a very rapid precipitation, pouring the hot $BaCl_2$ all at once into the sulphate solution. According to Allen and Johnston[2] the precipitate obtained by rapid precipitation, while often giving results very close to the theoretical, is not always reliable, due to a variable compensation of errors. Otto Folin[3] points out that when both the sulphate solution and the $BaCl_2$ are cold and dilute and the latter adding to the former *without stirring*, at a rate not

[1] Z. Anal. Chem., *45*, 31 (1906).
[2] loc. cit. p. 617.
[3] J. Biol. Chem., *1*, 131–159.

exceeding 5 cc. per minute, large crystals of $BaSO_4$ are obtained which settle rapidly. This method of precipitation was given a thorough trial, and after considerable experimental work in determining the proper dilution and necessary amount of free HCl it was found to give theoretical results with known amounts of H_2SO_4.

To insure uniformity in rate of precipitation a form of "precipitating cup" was devised which should automatically deliver the $BaCl_2$ at the required rate — 5 cc. per minute. This consists of a cup holding 130 cc. attached to a capillary tube which is bent around a watch glass, over a beaker. (See Plate, Fig. 1.) The $BaCl_2$ is delivered in small drops. The $BaSO_4$ is completely precipitated without stirring, although as a precaution it is advisable to gently stir the supernatant liquor after the $BaCl_2$ has all run out of the cup.

The $BaSO_4$ formed under these conditions of precipitation has the appearance under the microscope of beautiful, large, well defined crystals, in contradistinction to the very fine powder formed by precipitation from a hot slightly acid solution. These crystals are easily retained and washed on a Gooch asbestos filter. The use of a Gooch crucible does away with the possible reduction of the $BaSO_4$ when using filter paper and also mechanical loss during ignition; these crucibles have been used altogether and with entire satisfaction in all work with this method.

Having thus proved the way for a rigorous testing out of the method, a long series of experiments were carried out using a known amount of H_2SO_4 and adding thereto iron and such impurities as are present in different kinds of pyrites ore, to determine their effect, if any, on the accuracy of the method. In addition to this the method of oxidation with Br, CCl_4, and HNO_3 was thoroughly tested to insure completeness of oxidation, and to make certain that no sulphur compounds escape by volatilization during oxidation. A part of the results of this experimental work is given in part III of this paper. These results may be briefly summarized as follows: (1) the method gives theoretical results with sulphuric acid in amounts ranging from 35% to 50% S; (2) the addition of iron, zinc, copper, lead, arsenic, silica, etc., in such amounts as may be present in pyrites ores, does not affect at all the accuracy of the method; (3) a theoretical ore of the following composition gave results within .03% of calculated sulphur content: S 49.80%, Fe 44.00%, Pb 2.00%, As .50%, Cu .50%, CaO 1.00%, Zn 1.00%, SiO_2 1.20%; (4) the ignited $BaSO_4$ contains only a faint trace of iron; (5) the oxidizing mixture ($Br + CCl_4$ followed by HNO_3) completely oxidizes the ore without loss of volatile sulphur compounds; (6) the use of aluminum powder for the reduction of the iron and the consequent presence of small amounts of aluminum salts does *not* detract from the accuracy of the sulphur determination; (7) in comparison with other methods our method tends always to give a little higher results.

II. DETAILS OF METHOD OF ANALYSIS

Preparation of Sample

The ore sample is ground merely enough to pass an 80-mesh sieve, screening occasionally and grinding only those particles coarser than 80 mesh.

About 10 grams are dried for one hour at 100°C. in a 1-oz. wide-mouth glass bottle, and the bottle is stoppered as soon as removed from the oven.

Oxidation of the Sulphur

1.3736 grams of the dried ore are put in a dry 300 cc. Jena beaker (4½ in. high, and 2½ in. diam.), 10 cc. of a mixture of 2 parts by volume liquid bromine and 3 parts CCl_4[1] are added and the beaker is covered with a watch glass. After standing fifteen minutes at room temperature with occasional gentle shaking, 15 cc. HNO_3 (sp. gr. 1.4) are added and the mixture is allowed to stand fifteen minutes longer at room temperature with occasional shaking. The beaker is then placed on an asbestos board on top of the steam bath and allowed to remain there until all action has ceased and most of the bromine has been volatilized. It is then placed within the rings of the bath and the solution evaporated to dryness, the cover glass being raised above the rim of the beaker by means of riders made of bent glass rods. Ten cc. HCl (sp. gr. 1.2) are next added and, after shaking to mix

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[1] It is very important to use CCl_4 which is free from sulphur compounds. The CCl_4 made by Baker & Adamson, Easton, Pa. is very satisfactory.

thoroughly, the solution is again evaporated to dryness, still keeping the beaker covered as in the former evaporation. When completely dry the SiO_2 is dehydrated by heating in an air bath at 100°C for several hours (preferably overnight).

Reduction of Iron and Precipitation of Sulphate

4 cc. of HCl (sp. gr. 1.2) are now added to the dehydrated mass, followed after five minutes by 100 cc. of hot water. The cover, sides of beaker, and riders are carefully washed down with hot water and after the removal of the riders the cover is replaced. The mixture is gently boiled for five minutes to insure complete solution of all sulphate. After the solution has partially cooled by standing for about five minutes, .2 to .3 gram of powdered aluminum is added and the beaker gently shaken until the iron color has disappeared, showing complete reduction. It is now advisable to cool the solution to prevent possible mechanical loss of mist when filtering, due to the action of warm HCl on the excess of aluminum powder. After cooling, the cover glass and sides of the beaker are washed down and the solution is filtered through a 12½ cm. filter paper (B & A grade "A") (S & S No. 590) into a No. 9 beaker (capacity about 2500 cc.) and the residue washed nine times with hot water. To the filtrate are added 6 cc. more of HCl (sp. gr. 1.2) and sufficient cold water to dilute to 1600 cc. After stirring to mix well, the beaker is covered with a large clock glass and the sulphate precipitated by adding through a special form of "precipitating cup" (discharging at the rate of 5 cc. per minute) 125 cc. 5% $BaCl_2$ solution. The solution is *not* stirred while the $BaCl_2$ is being added but after all is in, the supernatant liquor is well mixed by gentle stirring.

Filtration and Ignition of the Precipitate

After the $BaSO_4$ has settled[1] it is filtered through a tared Gooch crucible, using suction. The Gooch crucible used has a capacity of 35 cc., with perforated bottom attached, and with a moderately thick asbestos mat[2]. The filtering arrangement is shown in sketch (see Fig. 2).

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[1] Preferably after standing 12 hours.

[2] Long fibred Italian asbestos, scraped into "lint" and digested with strong HCl until all soluble impurities have been removed.

The crucible *C* is nearly filled with water before the syphon and cork are placed in position. Then by exhausting the air in *A* the supernatant liquor in the beaker rapidly syphons over. The syphon tube and cork are then removed and well washed. The precipitate is transferred to the Gooch filter by a stream from a wash bottle, the beaker "copped out" and the precipitate washed six times with cold water. The Gooch is then ignited slowly, placing it first on an asbestos board over a flame for 25 minutes so as to expel the water gradually, or it may be given this preliminary drying by placing it in the steam oven for a few hours if more convenient. The Gooch crucible is then heated with the full flame of a Fletcher burner[1] for thirty minutes, cooled in a desiccator, and weighed.

$$\text{Weight } BaSO_4 \times 10 = \% \text{ S in Ore.}$$

Duplicates should agree within .05%. Tested sulphur free reagents should always be used.

III. EXPERIMENTAL PROOF OF THE ACCURACY OF THIS METHOD

In the analysis of pyrites we have always used a larger sample than is usually recommended, viz. 1.3736 grams. This weight is ten times the factor from $BaSO_4$ to S—hence the final weight of $BaSO_4 \times 10 = \%$ S. in sample. There is no trouble whatever in handling a sample of this size and any errors which may creep in are divided by 1.3 instead of being multiplied by 2, as is the case when using a .5 gram sample of ore. In all our experimental work, therefore, the $BaSO_4$ precipitated was in amount equivalent to the sulphur in 1.3736 grams ore.

The following conditions were, with few exceptions, those under which the experimental proof of the accuracy of the method was carried out.

Volume at the time of precipitation 1600 cc.

HCl present 10 cc. (sp. gr. 1.2).

$BaCl_2$ solution (125 cc. 5% $BaCl_2$) added through special "precipitating cup," which requires 25 minutes for this amount to run out.

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[1] (or preferably in an electric oven kept at about 1600°F.).

After the precipitation the supernatant liquor was stirred, without disturbing the precipitate, to insure thorough mixing.

The $BaSO_4$, after settling, was filtered through a tared Gooch crucible with an asbestos mat, dried, and heated for thirty minutes over a Fletcher burner, using full heat, cooled, and weighed.

I. Results with a Known Amount of H_2SO_4 Alone

Very carefully standardized H_2SO_4[1] (about 52%) was diluted to volume and aliquot 100 cc. portions were taken by a dividing pipette.

(A) H_2SO_4 used corresponding to 5.000 grams $BaSO_4$ (= 50.00% sulphur on factor weight of ore).

Vol. at Precip.	HCl Added	No. of Runs.	Average Wt. in Grams of $BaSO_4$ Found	As % S.	Extreme Variation in Tests	Mean Variation in Tests
1600 cc.	10 cc.	12	5.0000	50.00	.13%	.07%
1600 cc.	10 cc.	3	4.9993	49.99	.02%	.02%
1600 cc.	10 cc.	3	4.9972	49.97	.04%	.03%
1600 cc.	10 cc.	3	4.9993	49.99	.07%	.06%

(B) H_2SO_4 used corresponding to 3.5000 grams $BaSO_4$ (=35.00 % S on factor weight sample).

Vol. at Precip.	HCl Added	No. of Runs.	Average Wt. in Grams of $BaSO_4$ Found	As % S.	Extreme Variation in Tests	Mean Variation in Tests
1600 cc.	10 cc.	6	3.4990	34.99	.03%	.01%

Conclusions

Theoretical results are obtained with both 50% and 35% S, the volume and concentration of HCl being the same in each case.

II. Results with H_2SO_4 and Iron in the Ferrous Condition

Samples prepared as in I. Iron added in the form of $FeCl_3$ (sulphur free), reduced with Al and filtered.

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[1] cf. W. C. Ferguson, J. S. C. I., *24*, 781 (1905).

H_2SO_4 Taken as % S	Iron Added as % Fe	No. of Runs	Average Wt. $BaSO_4$ Found as % S	Extreme Variation in Tests	Mean Variation in Tests
50.00	50.00	4	50.00	.05%	.03%
50.00	50.00	5	50.02	.09%	.06%
35.00	65.00	3	35.04	.11%	.08%
50.00	44.00	3	49.94	.02%	.02%

The ignited precipitates were all pure white.

Conclusions

Iron in the ferrous condition does not affect the accuracy of the results.

III. Results with H_2SO_4 and Iron in the Ferric Condition

Samples prepared as in I. Iron added in the form of $FeCl_3$ (sulphur free) and not reduced.

H_2SO_4 Taken as % S	Iron Added as % Fe	No. of Runs	Average Wt. $BaSO_4$ Found as % S	Extreme Variation in Tests	Difference between Theory and Determinat'n
50.00	44.00	2	49.65	.07	.35%
50.00	44.00	3	49.46	.11	.54%

Conclusions

Low results are obtained with iron present in oxidized condition. During the ignition SO_3 could be seen passing off. Ignited $BaSO_4$ was red.

IV. Effect on the $BaSO_4$ Precipitate of Standing for Varying Lengths of Time before Filtration

Samples prepared and precipitated as in II.

Time of Standing	Grams $BaSO_4$	% Sulphur
2 hours	4.9998	50.00
4 hours	4.9969	49.97
6 hours	4.9950	49.95
18 hours	5.0005	50.01
24 hours	4.9985	49.99
48 hours	5.0013	50.01

Conclusions

As indicated by these experiments, there is no difference between the results obtained after standing for varying lengths of time, viz. from 2 to 48 hours.

V. *Purity of the $BaSO_4$*

Samples prepared and precipitated as in II.

(A) Iron (and $BaCl_2$) in Ignited $BaSO_4$:

$BaSO_4$ Weight in Grams.	Iron in the Solution when $BaSO_4$ was Precipitated. Weight in gms.	Condition of Iron at Precipitation	Iron in Precipitate	Chlorine as $BaCl_2$
5.000	.6868	Reduced	.00018 gms.	.0140 grams
5.000	.6044	Reduced	.00021 gms.	.0150 grams
3.500	.8918	Reduced	.00013 gms.	.0137 grams
5.000	.6044	Oxidized	.0135 gms.	.0046 grams
3.500	.8918	Oxidized	.0210 gms.	.0023 grams

Conclusions

Iron in the ferrous form does not contaminate $BaSO_4$ in any appreciable amount, while if present in the ferric condition it does contaminate the $BaSO_4$ considerably. $BaCl_2$ is occluded in all precipitates of $BaSO_4$, and in larger amount in reduced iron solutions.

VI. *Analysis of the Vapors Given off During Ignition of the $BaSO_4$*

Samples prepared as in II and III. Weight of $BaSO_4 = 4.4$ grams.

Ratio S to Fe at Precipitation	Volume at Precipitation	Iron	Found in Vapors Chlorine (calc. as HCl)	Sulphur (calc. as $BaSO_4$)
44%: 50%	1600 cc.	Reduced	.0011 gm.	.0007 gm.
44%: 50%	1600 cc.	Oxidized	.0044 gm.	.0051 gm.
44%: 50%	250 cc.	Oxidized	.0104 gm.	.0201 gm.

The precipitates were heated in a combustion tube with the full heat of a Fletcher burner. The vapors evolved were caught in KOH and determined gravimetrically as $BaSO_4$ and AgCl. It was assumed that the Cl and S found passed off as HCl and SO_3.

Conclusions

The HCl and SO_3 lost on ignition of the $BaSO_4$ precipitated from reduced solution are negligible. Allen and Johnston[1] have shown that when $BaSO_4$ is precipitated from solutions containing *alkali salts*, the acid remaining constant, the loss by volatilization is greatly increased.

VII. *Effect of an Excess of HCl*

Samples prepared as in I except for amount of HCl added.

HCl Added	No. of Runs	$BaSO_4$ Found (As % S)
10 cc.	6	34.99
20 cc.	1	34.97
30 cc.	1	34.98
40 cc.	1	35.04
50 cc.	1	34.96

The theoretical amount of $BaSO_4$ as % Sulphur was 35.00.

Conclusions

The presence of HCl in amounts greater than 10 cc. does not seriously affect the results, but there is obviously no advantage to be gained by using more than 10 cc.

VIII. *Effect of the Presence of $AlCl_3$ in Varying Amounts*

As the powdered aluminum added to reduce the iron must itself dissolve in the HCl present, a series of tests were made to determine the effect of varying amounts of Al on the barium sulphate precipitate.

Samples prepared as in II, except the first which was prepared as in I.

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[1] loc. cit.

Amount of Al Present	No. of Tests	Average Wt of $BaSO_4$		Extreme Variation between Tests	Al_2O_3 in $BaSO_4$ after Ignition
None	3	4.408 gms.	44.08%	.02%	None
.1 gm.	3	4.4076 gms.	44.08%	.04%	.0016 gms.
.3 gm.	3	4.411 gms.	44.11%	.02%	.0020 gms.
.5 gm.	3	4.4157 gms.	44.16%	.03%	.0048 gms.

Conclusions

As much as .5 gram Al appears to raise the results but the amount used in the method produces no effect. This conclusion is diametrically opposed to that of Huybrechts (Chem. Abs., *4* 2247): "The method of reduction of Fe by a metal or a metallic salt is impossible when $BaSO_4$ is to be precipitated subsequently."

IX. *Effect of Alkali Salts*

Samples prepared as in I except for the addition of the alkali chloride.

Salt	Added	No. of Runs	$BaSO_4$ Found	Difference between Theory and Determination.
NaCl	5 gm.	1	34.82	.18%
NaCl	10 gm.	1	34.76	.24%
NaCl	15 gm.	1	34.71	.29%
KCl	5 gm.	1	34.96	.04%
KCl	10 gm.	1	34.93	.07%
KCl	15 gm.	1	34.85	.15%
NH_4Cl	5 gm.	1	34.51	.49%
NH_4Cl	10 gm.	1	34.44	.57%
NH_4Cl	15 gm.	1	34.35	.65%

The theoretical amount of $BaSO_4$ as % Sulphur was 35.00.

Conclusions

The very pronounced effect of alkali salts is shown clearly. KCl produces the least effect and NH_4Cl the most.

X. *Effect of Other Metals*

To samples prepared as in II were added other metals (as S-free chlorides). These mixtures were evaporated to dryness and given the entire treatment according to the method for ores.

TAKEN						
H_2SO_4	Fe	Metal Added		No. of Runs	Average $BaSO_4$ Found	Extreme Variation in Tests
Equivalent to:					as % S	
50.00% S	50.00%	Pb	1%	3	50.01	.05%
50.00% S	50.00%	Cu	1%	3	50.00	.04%
50.00% S	50.00%	Cu	5%	3	50.04	.06%
50.00% S	50.00%	Ca	1%	3	49.96	.05%
50.00% S	50.00%	Pb,Cu Ca	1% each	3	49.96	.02%
35.00% S	65.00%	Zn	10%	2	35.06	.04%
35.00% S	65.00%	As	.5%	3	35.05	.02%
35.00% S	65.00%	SiO_2	5%	3	34.98	.07%

Conclusions

Practically theoretical results are obtained with the extremes of metallic impurities usually to be found in pyrites.

XI. Theoretical Ore

The sulphur was added as H_2SO_4 and the metals as S-free chlorides in amounts corresponding to those in 1.3736 grams of an ore of the following composition:

S	49.80%
Fe	44.00%
Pb	2.00%
As	.50%
Cu	.50%
CaO	1.00%
Zn	1.00%
SiO_2	1.20%
	100.00%

This mixture was evaporated to dryness and given the entire treatment according to the method for ores.

No. of Runs	Average $BaSO_4$ Found	Extreme Variation in Tests	Mean Variation in Tests
	as % S	as % S	as % S
6	49.77	.05	.03

Conclusions

With the theoretical ore the results were within .03% of the calculated sulphur content.

The experimental work thus far described shows that the method gives accurate results with an amount of H_2SO_4 equivalent to 35% and 50% sulphur ores, and that ferrous iron, zinc, lime, copper, lead, arsenic, etc., do not interfere with the accuracy of the results. It is established, then, that with a properly oxidized ore the results obtained will be accurate within .05% to .10% of theory. The barium sulphate precipitated from reduced iron solution loses only a negligible amount of HCl and SO_3 on ignition and the ignited $BaSO_4$ contains only a trace of iron. It does contain some $BaCl_2$ but this amount is constant and apparently compensates for the slight solubility in the large amount of water used.

XII. Oxidation of the Ore Sample

In our choice of the most suitable oxidizing agent we were limited to those which do not contain alkali salts. The two mixtures used in our experimental work were: (1) "reversed" aqua regia[1] (with or without bromine), and (2), a mixture of CCl_4 and bromine, followed by nitric acid.

It has been pointed out by many investigators that with certain ores a part of the sulphur may separate out on treating with "reversed" aqua regia. This free sulphur may be oxidized by continued digestion with $KClO_3$ but this is a disagreeable and lengthy process and, moreover, introduces alkali salts. Liquid bromine itself is too violent and its water solution too weak. CCl_4 mixes in all proportions with bromine, is a solvent for free sulphur in case any separates, and volatilizes with the excess bromine upon evaporation. A mixture of 2 parts by volume liquid bromine +3 parts CCl_4 was found to give excellent results. An ore treated with this mixture followed after 10 minutes by HNO_3 is oxidized completely, and evaporates to dryness more quickly than when "reversed" aqua regia is used.

The CCl_4 should be entirely free from all sulphur compounds; very erratic results are obtained if such volatile sulphur compounds

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[1] 3 vols. HNO_3 sp. gr. 1.4, and 1 vol. of HCl sp. gr. 1.2.

(CS_2 etc.) are present. The CCl_4 supplied by Baker & Adamson[1] is entirely satisfactory.

In order to prove that oxidation is complete when using the above proposed method, the silicious residues left after oxidation have been repeatedly filtered and re-oxidized. The amount of sulphur so obtained has never amounted to more than .04%.

To further prove that there is no loss of volatile sulphur compounds during oxidation the vapors given off were drawn through bulb scrubbing tubes containing NaOH and the latter tested for S. None was found.

From the above we have shown that $Br-CCl_4$, followed by HNO_3, gives a complete oxidation of the sulphur without loss of volatile sulphur compounds. It is to be preferred to aqua regia in that it evaporates more quickly and there is never any separation of free sulphur. Both methods of oxidation have been shown to give identical results, however, on the same ore sample, as is shown in the following:

Oxidation with $Br+CCl_4+HNO_3$	Oxidation with $HNO_3+HCl+Br$
43.83% S	43.83% S
43.82% S	43.84% S
43.84% S	43.87% S

XIII. The Effect of Fine Grinding on the Sulphur Content

As pointed out by Allen and Johnston[2] the sulphides of iron gradually oxidize on grinding. In order to show clearly the amount of this oxidation and also the amount of oxidation due to oven drying of samples of varying degrees of fineness, a large sample of dry ore was ground to pass 60 mesh; a portion of this was reserved and the remainder ground to pass 80 mesh. This operation was repeated, withdrawing samples left on the 80, 100, and 120 mesh screens. The material passing 120 mesh was further ground for half an hour, a portion reserved, and the remainder ground for another half hour. In the accompanying table are shown the % sulphur found in each reserved portion, analysed (1) without drying, (2) after drying 1 hour, (3) after drying 16 hours.

[1] Easton, Pennsylvania.

[2] loc. cit.

Ground to Mesh	Total Time Ground	Dried at 212°	Loss of Wt. on Drying	No. of Runs	Average per cent Sulphur	Extreme Variation in % S.
60	2 hrs. 20 min.	Not dried	....	2	46.66	.04
	2 hrs. 20 min.	1 hour	.07%	3	46.61	.10
	2 hrs. 20 min.	16 hours	.06%	3	46.65	.06
80	2 hrs. 45 min.	Not dried	....	3	46.63	.07
	2 hrs. 45 min.	1 hour	.07%	3	46.64	.06
	2 hrs. 45 min.	16 hours	.06%	3	46.69	05
100	3 hrs. 15 min.	Not dried	....	3	46.63	.06
	3 hrs. 15 min.	1 hour	.08%	3	46.65	.07
	3 hrs. 15 min.	16 hours	.04%	3	46.69	.04
120	3 hrs. 35 min.	Not dried	....	3	46.32	.01
	3 hrs. 35 min.	1 hour	.08%	3	46.29	.02
	3 hrs. 35 min.	16 hours	.04%	3	46.29	.06
Further than120	4 hours	Not dried	....	3	45.98	.03
	4 hours	1 hour	.10%	2	45.98	.06
	4 hours	16 hours	.05%	3	46.00	.03
Further than120	4 hrs. 30 min.	Not dried		3	45.61	.03
	4 hrs. 30 min.	1 hour		2	45.60	.03
	4 hrs. 30 min.	16 hours		3	45.61	.01

Conclusions

After the ore was ground finer than 100 mesh the oxidation due to grinding was quite rapid. After the final grinding the ore contained 1% less sulphur than the original sample. The oxidation taking place in an oven at 212° even in 16 hours was inappreciable.

XIV. Comparative Results Between Different Methods Used for Determination of Sulphur in Ores

A sample of ore was analyzed in our laboratory by several different methods with results as follows:

	% Sulphur	Average
New Method	46.32	
	46.31	
	46.33	46.32
Fresenius Method (Quan. Anal., II, P. 561 1904)	46.22	
	46.16	
	46.31	46.23
Lunge's Method (Sulphuric Acid and Alkali Edn. 2, Vol. 1, p. 56)	45.84	
	46.01	
	45.93	45.93
Lunge-Gladding Method	46.03	
	46.18	
	46.13	46.11

These results were obtained by an analyst skilled in the new method, who interpreted and followed the directions given for the other methods to the best of his ability, but who had had little previous experience in their manipulation.

The method has also been investigated independently by the Nichols Copper Company and its accuracy proved with known amounts of H_2SO_4.

Moreover, as shown by comparative results between our laboratory and commercial analysts of New York—the latter using some form of the Modified Lunge method—it has been found that our method tends to give about .15% higher results than the latter.

At a meeting of representatives of Stillwell & Gladding, Ricketts & Banks, Ledoux & Company, and Dr. Lucius Pitkin, commercial analysts of New York, held June 25th 1912, the following resolution was unanimously adopted:

Whereas certain differences exist between the results reported on sulphur in pyrites, between different chemists, and

Whereas the necessity of uniform results on this basic material of chemical manufacture is to be highly desired, we recommend the adoption of a standard method for the determination of sulphur in pyrites, and state that in our experience the method as described in the paper by Mr. W. S. Allen and Mr. H. B. Bishop to be read before the Eighth International Congress of Applied Chemistry, gives the true sulphur contents of the material, and we endorse it as an accurate and satisfactory method.

IV. Final Summary

The method for the determination of sulphur in pyrites ore as now offered consists essentially of the complete oxidation and solution of a comparatively large sample by means of a solution of Br and CCl_4, followed by HNO_3; the reduction of the iron present by means of aluminum powder; and the cold precipitation of the $BaSO_4$ in a large volume by the slow addition of a dilute $BaCl_2$ solution.

In order not to greatly increase the length of this paper, a portion only from a large mass of data covering every detail of the method has been presented. This portion, however, demonstrates fully the accuracy of the method and presents evidence as to the soundness of the principles involved and necessity for the observation of certain details.

A number of experienced analysts and inexperienced men fresh from college have by the method accurately analysed samples of pyrites ore, their duplicates almost invariably agreeing within a few hundredths of a per cent. Men who used the method for the first time obtained results agreeing closely with those by analysts of long experience with the method, evidencing its ease and simplicity.

Commercial chemists of New York have analysed samples both by their regular methods and by this new method. The results obtained are in accord with our experience, viz., that the new method tends to give results, about .1 to .15% higher, and that check determinations agree within a few hundredths of a % S. In view of the clear proof by Allen and Johnston[1] of the necessity for various calculations in the presence of alkali salts, the higher results obtained by this method—where alkali salts are absent—are to be expected. We believe that the method gives accurate results without the addition of any corrective factor whatever, and we submit it to the Eighth International Congress in the hope that the Congress will recommend its general adoption and thus assist in obtaining uniformity of standards in analytical methods.

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[1] loc. cit.

THE RELATIVE STABILITY OF PRIMARY CADMIUM POTASSIUM IODIDE AND ITS APPLICATION IN THE DETERMINATION OF OZONE

By Charles Baskerville and W. J. Crozier
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Of the several methods which have been proposed for the determination of ozone, that of Schönbein, which consists in estimating the iodine liberated from metallic iodides, has been quite generally employed, although it is open to a number of serious objections. It is well known that when acid potassium iodide solution is employed, the potassium iodide-starch reaction is neither a qualitative nor a quantitative indication of the presence or amount of ozone; and that various agencies influence the liberation of iodine from the acidified potassium iodide solution, while chlorine, bromine and nitrites (frequently found in the air) also give the reaction. These influences, of an order of magnitude safely disregarded in other analytical work, must be dealt with. With regard to the reliability of neutral metallic iodide solutions, Lechner[1] maintained that unsatisfactory results were obtained when determining ozone with the aid of neutral potassium iodide solutions, as large quantities of iodine vapor were liberated. This is directly contrary to the results obtained by Ladenburg and Quasig[2], who found that neutral solutions only give correct results, and that acid solutions give no sharp end-point and the results are too high[3]. They obtain good results, but used, apparently, only ozone of a high state of purity.

Baskerville and Hamor[4] have pointed out the objections to which potassium iodide is open as a reagent for hydrogen dioxide, and the authors have found that as a test for ozone, potassium iodide is subject to the same limitations, and, generally, even to a greater degree. Baskerville and Hamor found that since primary

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[1] Z. Elektrochem., *17*, 412.
[2] Ber., *34*, 1184 (1901).
[3] Our experiments would tend to confirm these findings.
[4] J. Ind. Eng. Chem., *3*, No. 6 (1911.)

cadmium potassium iodide ($CdKI_3.H_2O$) is unaffected by the presence of any likely amounts of acids in ethyl ether, and is much more stable in light than potassium iodide in solutions of comparable strength, its use is preferable for the detection of peroxidized compounds in ether. The authors have extended the observations on the stability of cadmium potassium iodide and have employed it as a reagent for the quantitative determination of ozone.

I.

THE COMPARATIVE STABILITY OF POTASSIUM IODIDE AND CADMIUM POTASSIUM IODIDE

The cadmium potassium iodide used in the experiments which follow was found to possess the following composition:

	Water.	Cadmium.
Calculated for $CdKI_3.H_2O$	3.27%	21.17%
Found	3.36	20.98

It was free from foreign metals, sulphuric acid, and hydriodic acid, and was soluble in about 0.95 parts of water at 15 deg. C. The potassium iodide used was also found to be pure.

The statement is made in the literature[1] that solid cadmium potassium iodide assumes a slight yellow color on standing. In the experiments made by the authors on this point, the salt was from two different lots: (*a*) Some which, after purification, had been standing for five years in a museum case, freely exposed to diffused light during most of every day. This sample possessed no yellowish tinge whatsoever, nor was there present any detectable free iodine. (*b*) Samples of a fresh lot of "Cadmium & Potassium Iodide Merck." These were exposed to direct sunlight for periods ranging up to 25 days, and analysis showed that no decomposition occurred. We are therefore inclined to believe that pure primary cadmium potassium iodide uncontaminated with cadmium iodide, potassium iodide or water in excess will not become colored upon storage.

The next experiments were made on the rate of the decomposition of stock solutions of potassium iodide and cadmium potassium iodide under laboratory conditions. N/10 solutions were

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[1] E. g. by Abegg and by Merck (*1907 Index*, p. 110).

kept in the ordinary diffused light of the laboratory for two months, at the end of which time the following comparative results were obtained in g. of iodine:

Potassium iodide.	Cadmium potassium iodide.
0.00053	0.00046

A series of experiments was then made on the relative stability of cadmium potassium iodide toward various reagents[1]. A 10 per cent solution was prepared and the following tests were made with 2 cc. quantities, the exposures being to diffused daylight during the daytime:

1. With 2 cc. of hydrochloric acid (density, 1.20), no perceptible reaction occurred until after 30 hours.
2. With 2 cc. of sulphuric acid (density, 1.84) a yellow coloration resulted at once.
3. With 2 cc. of 10 per cent sulphuric acid, after two days, the reaction was as strong as in 6.
4. With 2 cc. of concentrated nitric acid, the reaction was immediate.
5. With 2 cc. of 1:10 nitric acid, a reaction resulted.
6. With 2 cc. of 1:50 nitric acid, a reaction occurred after 40 hours.
7. Nitrogen tetroxide was found to give a prompt reaction, being apparently the same as in the case of potassium iodide.
8. An equal volume of 99.5 per cent acetic acid gave no separation of iodine even after 5 days.
9. With 10 cc. of dilute hydrochloric acid, a slight reduction was noted after three days. A 10 per cent potassium iodide solution treated in the same way gave a strong reaction over night.
10. Two small flasks were 1/3 filled with (A_1) 10 per cent potassium iodide and (B_1) 10 per cent cadmium potassium iodide, and then exposed to diffused sunlight. After three days, there was a faint yellow coloration in A_1, but no separation of iodine in B_1. Titration gave the following results:

		A_1	B_1
After 3 days	Cc. N/100 $Na_2S_2O_3$ per 10 cc. sol.	0.16	None.
After 7 days	2	0.70	0.15

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[1] The results recorded are at least the result of duplicate experiments.

11. As in No. 10 except that to each 0.10 cc. hydrochloric acid (density 1.20) was added. After two days, the liquids were withdrawn and the free iodine determined.

	A_2 (10 per cent KI)	B_2 (10 per cent $CdKI_3$)
Cc. N/100 $Na_2S_2O_3$ per 10 cc. sol.	1.25	0.19

12. 1 cc. of N/4 hydrochloric acid was added to 10 cc. each of potassium iodide and cadmium potassium iodide in 10 per cent solution, and the solutions were then placed in the sunlight. After four days' exposure, the results were:

	A_3 (10 per cent KI)	B_3 (10 per cent $CdKI_3$)
Cc. N/100 $Na_2 S_2O_3$ per 10 cc. sol.	19.91	1.88

13. Replacing the hydrochloric acid with 99.5 per cent acetic acid, the following results were obtained after four days' exposure:

	A_4 (10 per cent KI)	B_4 (10 per cent $CdKI_3$)
Cc. N/100 $Na_2S_2O_3$ per 10 cc. sol.	9.63	2.12

14. Following the same procedure, except that an equal volume of N/8 hydrochloric acid was added in each case, the results were after five days:

	A_5 (10 per cent KI)	B_5 (10 per cent $CdKI_3$)
Cc. N/100 $Na_2S_2O_3$ per 10 cc. sol.	33.22	14.20

The above experimental results demonstrate the comparatively high stability of cadmium potassium iodide,— a fact which would seem to be of importance in the selection of a reagent for the determination of ozone, especially since we have found that the compound is a sufficiently sensitive reagent for the detection of nascent oxygen. It has been shown that in diffused sunlight the action of mineral acids on cadmium potassium iodide is of the following order: nitric acid reacts rapidly, while sulphuric and hydrochloric acids react much more slowly, although sulphuric acid reacts with greater velocity. No attempt was made to maintain the oxygen concentration constant, but all the experiments were run under identical conditions, and thus the relative stability of the solutions experimented with are on a comparative basis. Since Schwezoff[1] has shown that equivalent quantities of sodium, potassium and cadmium iodides under similar conditions evolve equal quantities of iodine, this point was not determined.

Some experiments were also made on the chemical action of ultra-violet light upon cadmium potassium iodide and potassium iodide solutions. One hundred cc. portions of the solutions and 10 cc. of starch solutions were exposed to the rays from a Cooper-Hewitt quartz lamp in porcelain vessels, with the following results:

Concentration of solutions run side by side.	Results with Potassium Iodide.	Results with Cadmium Potassium Iodide.
Saturated	After an exposure of 5 minutes, 1.0 cc. N/10 $Na_2S_2O_3$ required.	Negative even after 40 minutes.
N/10	Traces of iodine in 20 to 30 seconds. In 5 minutes, 0.05 cc. N/10 $Na_2S_2O_3$ required.	Traces of iodine in 3 minutes when the lamp was started with the experiment; titratable amount of iodine in 10 minutes, 0.03 cc. $Na_2S_2O_3$. When the experiment was started after the lamp had been running 30 minutes, a faint reaction was noted in 30 seconds and 0.04 cc. $Na_2S_2O_3$ were required after 5 minutes.
N/100	Traces of iodine in 30 seconds.	Traces of iodine in 30 seconds. No difference from KI.
N/1000	No coloration with starch solution even after 25 minutes.	No coloration even after 1½ hours.

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[1] J. Russ. Phys. Chem. Soc., *42*, 219 (1910).

These results showed that N/10 and N/100 cadmium potassium iodide is fully as delicate a reagent for hydrogen dioxide and ozone as are solutions of the same strength of potassium iodide. Our results on potassium iodide solutions present differences with those of Ross[1], but this is probably to be ascribed to the difference in the form of lamp and to the natural variability of such results. Ross found that ultra-violet light alone probably liberated a very small amount of iodine from potassium iodide; his observations are, in our opinion, to be ascribed to the formation of hydrogen dioxide.

II.

THE EMPLOYMENT OF CADMIUM POTASSIUM IODIDE AS A REAGENT IN THE ESTIMATION OF OZONE.

In the first experiments the air to be ozonized was taken from a water gasometer and passed through the system including an ozonizer and a Meyer bulb apparatus, the latter being connected with the ozonizing apparatus by means of a ground glass joint. The type of ozonizer employed was not very efficient, as is shown by the results obtained[2]:

With neutral N/10 KI	With neutral N/10 $CdKI_3$
Mg. ozone per liter.....0.36	......................0.33
With acid (HCl) N/10 KI	With acid N/10 $CdKI_3$
Mg. ozone per liter.....0.42	......................0.34

It will be seen that the results with acid potassium iodide were high, while those obtained in using cadmium potassium iodide, although slightly lower than those found by using neutral potassium iodide, were about the same whether neutral or acid N/10 solutions were used. Alkaline solutions were found to be unreliable, as the end-point is difficult to determine and a precipitate results in the case of cadmium potassium iodide.

In further experiments, a different type of "silent discharge"

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[1] J. Am. Chem. Soc., *28*, No. 6; Chem. News, *94*, 245.

[2] All analytical results are the average of a series of runs; in no case were other than duplicate analyses made, and these invariably checked satisfactorily.

ozonizer was used; this, operated on a storage battery circuit at 22-23 volts, gave much more satisfactory yields of ozone. In the runs which were made, the ozone was absorbed, except where noted to the contrary, and the iodine liberated by agitation of the absorbent with the iodide solution was then determined by titration with standard sodium thiosulphate solution.

1. One-half liter of air was ozonized and turpentine (157° to 165° C.) was used as the absorbent. The amount of iodine liberated from neutral N/10 potassium iodide was then determined. Cc. of N/10 $Na_2S_2O_3$ required $=29.48=140.1$ mg. ozone.

2. Run under the same conditions. Cc. of N/10 $Na_2S_2O_3 = 29.70 = 143.2$ mg. ozone.

3. Run under the same conditions. Cc. of N/10 $Na_2S_2O_3 = 29.71 = 143.2$ mg. ozone. In Nos. 2 and 3, 20 minutes were found to be sufficient.

4. Run under the same conditions, but using neutral N/10 cadmium potassium iodide solution. Cc. of N/10 $Na_2S_2O_3 = 25.5$.

5. As in No. 4. Cc. of N/10 $Na_2S_2O_3 = 25.5$.

6. As in No. 4. Cc. of N/10 $Na_2S_2O_3 = 25.6$.

7. As in No. 1, but adding 10 per cent of N/20 hydrochloric acid to the potassium iodide solution. Cc. of N/10 $Na_2S_2O_3 = 34.8$ and 34.75.

8. As in No. 4, but adding 10 per cent of N/20 hydrochloric acid to the cadmium potassium iodide solution. Cc. of N/10 $Na_2S_2O_3 = 27.21$ and 27.20.

In other experiments, alkaline iodide solutions were found to be totally unsatisfactory; vegetable oils were found to be unsuitable for the absorption of ozone; and the use of anesthetic ethyl ether gave low results (20.00 and 18.5 cc. N/10 $Na_2S_2O_3$ when used as in No. 4) and a slow evolution of iodine from acid or neutral solutions. A higher turpentine fraction (165° to 185°) than that used before gave accurate results, but a longer time was required to complete a run.

It is shown that acid potassium iodide solutions always give high results, and that the results obtained by the use of both neutral and acid N/10 cadmium potassium iodide solutions are lower than those by means of neutral potassium iodide solutions, a result attributable to the greater stability of the cadmium potassium iodide towards light and certain likely contaminants of ozonized air. We believe that cadmium potassium iodide solution acidified with hydrochloric acid is a more reliable reagent than potassium iodide in neutral solution; its employment is only necessary, however, when absorption of the ozone in turpentine is the method followed. In the method of Schönbein, as used by Ladenburg and Quasig, either neutral or acid solutions of cadmium potassium iodide may be used; sharp end-points are obtained and the results are not too high.

DETERMINATION OF MANGANESE AS SULPHATE AND BY THE SODIUM BISMUTHATE METHOD[1]

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Contents

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[1] Published by permission of the Director of the Bureau of Standards.

I. INTRODUCTION

1. IMPORTANCE OF ACCURATE MANGANESE DETERMINATIONS

In spite of the large number of methods in use for the determination of this important element, results by different methods and different chemists seldom show satisfactory agreement. While differences of as much as a few per cent of the manganese present have little commercial significance in iron and steel containing one per cent or less of manganese, the highest possible accuracy is demanded in the analysis of high-grade materials such as manganese ore and ferro-manganese, of which large amounts enter into commerce, at prices dependent upon the results of analysis. For example, imports of manganese ore by this country in 1911 amounted to 176,852 long tons, valued at $1,186,791. It can readily be seen that a constant error of one per cent in the analyses of such material may cause a considerable difference in the total amount paid for the ores. That constant errors of such magnitude are possible with our present methods will be shown in this paper.

2. SOURCES OF ERROR IN GRAVIMETRIC METHODS

Even with the greatest care, the gravimetric results are not necessarily accurate, due not alone to the possibilities of losses by solubility of precipitates, and of too high weight due to contamination from vessels or reagents; but also to uncertainty in the composition of the precipitates as weighed. The three forms in which manganese is most commonly determined gravimetrically are Mn_3O_4, $Mn_2P_2O_7$ and $MnSO_4$. It is generally admitted that the first of these is unsatisfactory, as the composition depends directly upon the temperature of the ignition and the nature of the atmosphere surrounding the precipitate. Even under carefully regulated conditions Raikow and Tischkow[1] could not obtain results which agreed to better than one part in two hundred. Gooch and Austin[2] have shown that the composition of manganese "pyrophosphate" depends upon the content of ammonium salts and ammonia and the temperature, volume, and method of pre-

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[1] Chem. Ztg., *35*, 1013 (1911).
[2] Am. J. Sci., *6*, 233 (1898).

cipitation of the manganese ammonium phosphate. Even under the conditions which they recommend, their errors amounted in some cases to one per cent of the manganese present, and were in general too high. The method cannot therefore be considered satisfactory for highly accurate work; and certainly not for obtaining a known amount of manganese to serve as a primary standard. Experiments described in this paper have led to the conclusion that manganous sulphate, obtained under proper conditions, is the most accurate form in which this element can be weighed, both in gravimetric analysis and in securing a known amount of manganese.

3. SOURCES OF ERROR IN VOLUMETRIC METHODS

The difficulty of securing a known amount of manganese to serve as a primary standard has hindered the accurate investigation of the great number of volumetric methods which have been proposed. In most cases they have been tested by comparison with other methods, gravimetric or volumetric, which had not been shown to be intrinsically accurate. This fact, together with the usual dependence of the results of such methods upon the precise conditions of operation, has led to the publication of a large number of contradictory papers upon these methods. For example, the Volhard method and its various modifications have been the subject of over fifty investigations since its publication in 1879. It is generally admitted that the results by this method are low unless an empirical factor dependent upon the conditions of operation is employed, though some investigators have obtained theoretical results under certain conditions. In view of the above situation, it is highly desirable to find some method which will yield results of known accuracy, which are not closely dependent upon the exact conditions of operation, and which may serve to test other methods.

II. THE BISMUTHATE METHOD

1. OUTLINE OF METHOD

Of various methods considered, the bismuthate appeared most promising, and has been found to entirely fulfill the above requirements. In this method the manganese in nitric acid solution is oxidized with sodium bismuthate, of which the excess is removed by filtration through asbestos. To the resulting permanganic acid is added a measured excess of ferrous sulphate solution, which is then titrated with permanganate of known strength and of known ratio to the ferrous solution. The investigation therefore resolved itself into a study of the methods of standardizing the permanganate employed in the final titration and the influence of the various conditions of operation upon the results obtained by the bismuthate method.

2. HISTORY OF METHOD

The method as originally prepared by Schneider[1] depended upon the use of bismuth tetroxide as the oxidizing agent and titration of the permanganic acid with hydrogen peroxide. In this form the method was employed by Campredon,[2] Mignot[3] and Jaboulay.[4] Reddrop and Ramage[5] modified it by employing sodium bismuthate, which was more readily obtained free from chlorine, and suggested filtration of the permanganic acid directly into the hydrogen peroxide. On account of the instability of the latter reagent Ibbotson and Brearley[6] replaced it by ferrous ammonium sulphate, in which form the method has been since used, being described in detail by Blair[7], whose directions for this method are generally followed in this country.

3. STANDARDIZATION OF SOLUTION

(*a*) *Discussion of Methods.*—As above stated, the accuracy of any such volumetric method depends principally upon the method of standardization employed. Blair[8] mentions in his book three

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[1] Ding. Poly. Jour. *269*, 224.
[2] Rev. Chim. Indust., *9*, 306 (1898).
[3] Ann. Chim. anal. *5*, 172 (1900).
[4] Rev. gen. chim., *6*, 119 (1903).
[5] Jour. Chem. Soc. *67*, 268 (1895).
[6] Chem. News, *84*, 247 (1901).
[7] Jour. Am. Chem. Soc. *26*, 793 (1904) and "Chemical Analysis of Iron." 6th and 7th ed.
[8] In the appendix of the 1912 edition, p. 330, Blair recommends the standardization with sodium oxalate, under approximately the conditions given by McBride, as the most accurate method; a conclusion based upon the work described in this paper.

methods, viz.: (a) calculation from the iron value, (b) use of a steel of known content, and (c) use of a known amount of manganous sulphate; without expressing any preference, or opinions as to their relative accuracy. Standardization by means of sodium oxalate may be included under (a) since values found with this standard under proper conditions[1] have been found at this Bureau to agree with iron values within one part in a thousand[2]. Method (b) is a secondary method and is evidently unsuitable for work of high accuracy. As will be shown later, the standardization of manganous sulphate is a tedious operation and subject to considerable errors. For this reason sodium oxalate was considered at this Bureau to be the most convenient and accurate standard for this method. Brinton[3] however stated that there was a difference of one per cent (at first stated as over three per cent) between the values based upon sodium oxalate and manganese sulphate respectively. In a paper from this Bureau by Dr. W. F. Hillebrand and the author[4] the reasons for our belief in the accuracy of the sodium oxalate standard were expressed in the form of a preliminary paper, the conclusions of which have been verified by subsequent investigations described in this paper.

(*b*) *Evidence based on Reduction and Reoxidation.*—The original basis of our use of the sodium oxalate standard for this method was the fact that if a definite amount of a permanganate solution be reduced and then reoxidized by means of the bismuthate method it is exactly equivalent in oxidizing power to the original permanganate. This experiment was based upon a similar one suggested by Wolff[5] and employed by de Koninck[6] for testing the accuracy of the Volhard method for manganese. Its significance as applied to the bismuthate method is that the manganese is oxidized to the same state of oxidation as was originally present in the permanganate, theoretically Mn^{VII}. In the absence of evidence to the contrary it seems highly improbable that any appreciable manganese can be present in a filtered permanganate solution in a form

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[1] McBride: Jour. Am. Chem. Soc., *34*, 415 (1912).

[2] See Bureau of Standards Certificate for Sibley Iron Ore, Standard Sample 27.

[3] Jour. Ind. Eng. Chem., *3*, 237 and 376 (1911).

[4] Jour. Ind. Eng. Chem., *3*, 374 (1911).

[5] Stahl u Eisen, *11*, 373 (1891).

[6] Bull. Soc. Chim. Belg., *118*, 56 (1904).

other than Mn^{VII}, and still less probable that in an entirely different medium the manganese should be oxidized by bismuthate to the same state of oxidation, other than Mn^{VII}. Since, however, at least two persons in addition to Brinton had observed a discrepancy of the order of one per cent between the sodium oxalate and manganese sulphate values, the subject deserved further investigation; not alone from the standpoint of the manganese determination, but also as possibly throwing light upon the composition of permanganate solutions and their action as oxidizing agents. At this point it may be mentioned that the original observations regarding the reduction and reoxidation of the permanganate have been confirmed entirely, with solutions A_1, B, E and G, prepared as shown on p. 67.

4. PREPARATION OF MATERIALS AND SOLUTIONS

(*a*) *Water.*—Water used in the purification of permanganate and in the preparation of all the permanganate solutions except I and K was distilled three times, the last two being from alkaline permanganate. Water used for the rest of the work was ordinary distilled water of good grade.

(*b*) *Air.*—The air used to deliver the solutions from the stock bottles was washed with acid bichromate solution and alkaline permanganate followed by a column of glass wool.

(*c*) *Asbestos.*—The asbestos used in the filtration of the permanganate solutions and in the bismuthate method was digested for several days with hydrochloric acid, which was finally removed by thorough washing with hot water. It was then suspended in water and the finest portions separated and used in this work. For a few of the experiments this asbestos was ignited, without making, however, any appreciable difference in the results. A two-inch platinum cone, arranged as suggested by Blair[1], was used for preparing the filter.

(*d*) *Potassium Permanganate.*—Two commercial samples of potassium permanganate were employed, Baker & Adamson's C. P. salt, and Kahlbaum's "K" grade. A portion of the former was purified by two recrystallizations in Jena glass flasks, the solutions being electrically heated, and filtered through ignited asbestos just before being allowed to crystallize. The fine crystals

[1] "Chemical Analysis of Iron." 7th ed. p. 123.

so obtained were sucked dry on a platinum cone and were then exposed in a thin layer in the dark for four weeks in a vacuum desiccator over concentrated sulphuric acid, the vacuum being maintained at approximately two centimeters. In spite of this long drying, the material was found to contain 0.38% water as determined by heating to decomposition and collecting the water in a weighed calcium chloride tube. When dissolved in pure water and immediately filtered through asbestos, the solution left a slight stain upon the filter. After thorough washing this stain was dissolved off with sulphurous acid, and its manganese content determined colorimetrically, being equal to about 0.01%, i.e., a negligible quantity. Numerous attempts to prepare a permanganate solution which would leave absolutely no stain upon asbestos proved unsuccessful. Whether such stains were due to the action of the asbestos itself as claimed by Tscheishvili[1], or to reduction of the permanganate by traces of dust or other reducing substances, could not be determined. The amount of such reduction was however negligible, and far less than that observed by Tscheishvili.

(*e*) *Permanganate Solutions* were prepared by dissolving a weighed amount of the salt in water; and in the case of the commercial samples, filtering through asbestos to remove manganese peroxide, etc. They were then made up to a definite weight of solution, since the subsequent analyses were conducted entirely with weight burettes.

The following solutions were employed in the investigation:

TABLE I. PERMANGANATE SOLUTIONS USED

Solution	Approximate Strength	$KMnO_4$	H_2O	Preserved
A_1	0.03N	Purified	Purified	Dark
A_2	0.03N	Purified	Purified	Dark
B	0+1% KOH	Purified	Purified	Dark
E	0.1N	Purified	Purified	Dark
G	0.1N	B & A	Purified	Dark
I	0.1N	B & A	Ordinary	Light
K	0.1N	Kahlbaum	Ordinary	Light

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[1] J. Russ.: Phys. Chem., Soc., *42*, 856 (1910).

These solutions were preserved in stock bottles provided with an inlet and exit tube with ground glass joint as in an ordinary gas wash bottle. To the inlet tube was sealed a U-tube containing some of the same solution as was in the bottle, thereby preventing changes in concentration of the latter. The exit tube was provided with a three-way stop cock and a tip by which the solution could be delivered to the weight burette by means of purified compressed air.

(*f*) *Stability of Permanganate Solutions.*—At first it was thought necessary to protect these solutions with black paper, but later experiments showed that in the course of several months no appreciable decomposition took place in the solutions exposed to diffused daylight, provided they were first freed from peroxide and were protected from dust and other reducing substances, and that only purified air entered the bottles. Solution I, for example, prepared from ordinary distilled water, and permanganate containing appreciable peroxide, which was removed by a single filtration through asbestos, did not suffer decomposition within the limits of observation (one part in two thousand), on standing for two months without protection from the light; even though it was intentionally exposed to bright sunlight for several hours soon after it was prepared. In connection with this observation, which simply confirms previous work of others[1], it is desirable to call attention to another point in connection with the stability of permanganate solutions, which so far as I know has not been previously noted, or published. Under conditions which rapidly reduce neutral permanganate solutions, e.g., the presence of dust, reducing gases, or precipitated peroxide, decomposition is greatly retarded by the addition of a small amount of alkali. It was upon the basis of this observation, first noted qualitatively, that solution B was prepared with one per cent. of potassium hydroxide. Results with this solution were entirely satisfactory, but since the other solutions, when protected from reducing substances, were perfectly stable, the use of alkaline solutions for this work was found unnecessary. Under commercial

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[1] Morse, Hopkins & Walker: Am. Chem. J., *18*, 401 (1896). Gardner and North: J. Soc. Chem. Ind., *23*, 599 (1904). Warynski & Tscheishvili-Jour. Chim. phys., *6*, 567 (1908).

conditions, however, where it is not always practicable to protect the solutions, the addition of a small amount of alkali will add to their stability.

(*g*) *Manganese Sulphate.*—Pure material was prepared from 300 grams of Kahlbaum's crystallized manganese sulphate ("Zur analyse"), the operations being conducted entirely in platinum. It was dissolved in water and filtered to remove a small amount of insoluble matter. It was next saturated with hydrogen sulphide, producing a small amount of a black precipitate which was found to contain copper. Additional hydrogen sulphide and a small amount of ammonia produced a precipitate entirely pink, which was filtered out. The hydrogen sulphide was expelled, a few drops of sodium hydroxide were added and the solution was boiled and filtered; the precipitate being found to contain iron. This last operation was twice repeated, the third precipitate being free from iron. An excess of pure, freshly prepared ammonium carbonate was then added and the precipitate of $MnCO_3$ washed with hot water, by decantation and suction, till free from sulphate. It was dissolved in a slight excess of hydrochloric acid and crystallized twice as $MnCl_2, 4H_2O$ (at $-5°$). The latter crystals were treated with an excess of sulphuric acid, and heated in a double-walled platinum dish till almost all the excess sulphuric acid was expelled. The product was entirely soluble in water, and contained a slight excess of sulphuric acid as determined in subsequent tests (Table II A, p. 74).

(*h*) *Sodium Oxalate.*—Two samples were employed, one which had been especially purified by the author for a previous investigation[1], and a larger sample prepared especially for this Bureau, and which was found to have a reducing value equal to the former, within the limits of one part in two thousand.

(*i*) *Ferrous Sulphate* and ferrous ammonium sulphate were employed indiscriminately after it was found that the solutions possessed about the same stability. The C.P. salts as purchased were employed, since their exact composition was not important. For use with 0.03N permanganate, the solution was prepared according to Blair, with 12.4g ferrous ammonium sulphate (or 8.8g crystallized ferrous sulphate) and 50 cc. concentrated sul-

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[1] Blum: Jour. Am. Chem. Soc., *34*, 123 (1912).

phuric acid per kilogram of solution. For use with 0.1N permanganate, a solution containing 39.2g ferrous ammonium sulphate (or 27.8g ferrous sulphate) and 50 cc. concentrated sulphuric acid per kilogram was prepared. If phosphoric acid was employed, as recommended by Dudley[1], it replaced half of the sulphuric acid in the 0.03N solutions; but was added in addition to the regular amount of sulphuric acid in the 0.1N solutions.

Stability of the Ferrous Sulphate Solution. Incidental observations upon the change in strength of 0.03N ferrous ammonium sulphate indicated that the rate of oxidation, though slow, was erratic, due no doubt to variation in the extent of its exposure to air. With 0.1N ferrous sulphate and ferrous ammonium sulphate, the daily rate of oxidation under the conditions used was approximately one part in five hundred, i.e., about one per cent in five days, over considerable periods. This rate will depend no doubt upon the conditions of its preservation, and is of interest only as indicating how often its strength should be checked up for work of any desired degree of accuracy. Ratios obtained at the beginning and end of various series of determinations showed that no appreciable change took place in a period of a few hours, thus confirming the observation of Baskerville and Stevenson[2].

(*j*) *Nitric Acid* of regular C.P. grade was employed; in the concentrated form, and diluted to twenty-five per cent and three per cent by volume. The former two solutions were preserved in the dark, since it has been recently shown by Reynolds and Taylor[3] that nitric acid as weak as ten per cent is decomposed by light, but that recombination takes place in the dark.

(*k*) *Bismuthate.*—Two samples of C.P. sodium bismuthate were employed, one from Baker & Adamson and one from Eimer and Amend. These two samples differed very markedly in appearance, the former being dark brown and the other yellow. In spite of this fact, no difference could be detected between them as regards their suitability for this oxidation. It is well to mention however that this compound, of more or less indefinite composition, is somewhat unstable, and if preserved for over six months should be tested for its efficiency of oxidation.

[1] Blair: "Chemical Analysis of Iron," 7th ed., p. 125.

[2] Jour. Am. Chem. Soc., *33*, 1104 (1911).

[3] Jour. Chem. Soc., *101*, 131 (1912).

(l) *Ferric Nitrate.*—In order to test the effect of ferric salts upon this method, it was necessary to obtain iron, or some salt of iron which was free or practically free from manganese. This proved to be a difficult task, and after testing American ingot iron, and a large number of ferrous and ferric salts, the only one found satisfactory was a sample of Merck's crystallized ferric chloride, which contained less than 0.001% manganese. To convert this to nitrate, it was first converted to sulphate by evaporation to the appearance of fumes with an excess of sulphuric acid, and the sulphate was precipitated with ammonia, washed and dissolved in nitric acid. The resulting salt was free from chloride (of which traces interfere in the bismuthate method) and contained only a small amount of sulphate (which is without effect on this method).

(*m*) *Use of Weight Burettes.*—Simple weight burettes were made by drawing down the tips of cylindrical graduated separatory funnels (50 and 100 cc.). The increased accuracy gained by the use of weight burettes is especially desirable in an operation involving a back titration, and also the ratio of the two solutions used. Weighings were usually made to 0.01g, except in the case of the smaller amounts of manganese sulphate solutions, which were weighed to 0.005g or in some cases 0.001g. The titrations were usually made in Erlenmeyer flasks of convenient size.

5. STANDARDIZATION OF PERMANGANATE WITH SODIUM OXALATE

Nothing is to be added to the conclusions of McBride,[1] except to emphasize their relation to the present problem. The conditions recommended by him for the standardization of 0.1N permanganate are briefly as follows: Volume of 250 cc. acidity 2% sulphuric acid by volume, initial temperature, 80°–90°; slow addition of permanganate, especially at beginning and end; final temperature not less than 60°, and endpoint correction by comparison with a blank containing a known amount of the permanganate. His statement that the variation in results over a wide range of conditions does not exceed one part in a thousand, applies to titrations involving the use of about 50 cc. of 0.1N permanganate. If, however, 0.03N permanganate, commonly used in the bismuth-

[1] Jour. Am. Chem. Soc., *34*, 415 (1912).

ate method, is standardized with sodium oxalate, slight variations in the conditions may cause a relatively much larger error, especially if, as is not uncommon, only about 25 cc. of permanganate is employed. For standardization of 0.03N permanganate, the conditions of McBride were employed, except that the initial volume was 75 cc., instead of 250 cc., i.e., the oxalate concentration was about the same as for 0.1N permanganate. In this way the uncertainty in the endpoint caused by titrating in a large volume with weak permanganate, can be reduced to a minimum. For accurate work, however, the endpoint correction should be made since the object of this titration is to determine the absolute oxidizing power of the permanganate. With so small a volume of solution it is usually necessary to reheat it to 60°–70° before completing the titration. These conditions, as shown by McBride, represent a minimum consumption of permanganate, i.e., the iron or manganese values are a maximum. Any deviation from these conditions will tend to lower the iron or manganese values, which it is believed accounts in part for the discrepancy noted by Brinton and others between values derived from sodium oxalate and from manganese sulphate. For calculation of the manganese value from the sodium oxalate, the factor 0.16397 was employed.

6. STANDARDIZATION ON PERMANGANATE WITH MANGANOUS SULPHATE

(*a*) *Standardization of Manganous Sulphate Solutions.*—The two methods commonly used for determining the strength of a manganous sulphate solution are (a) precipitation as manganese ammonium phosphate and ignition to pyrophosphate, and (b) evaporation of the solution and heating the residue to a certain temperature. Unfortunately both of these will yield high results if the solution contains substances other than manganese sulphate; whether in the original salt or derived from the glass in which the solution is preserved. But even with pure solutions the results are of uncertain accuracy, especially in the case of the pyrophosphate as above mentioned (p. 3). Weighing as sulphate was therefore adopted as the means of securing a known amount of manganese. The chief source of uncertainty here is the temperature of the final heating, a point upon which the evidence is rather uncertain and contradictory. Volhard[1] was able to obtain constant weight with a special burner, but not with a Bunsen burner. Marignac[2] determined the atomic weight of manganese by heating the sulphate "nearly to red heat." Meineke[3] determined this element as the sulphate, which, after being heated to a temperature not stated, was completely soluble in water. Friedheim[4] heated the salt to 360°–400°, while Gooch and Austin[5] obtained constant weight by heating in double crucibles, one centimeter apart, the outer one being at red heat, a procedure since recommended by Treadwell.[6] In determining the water of crystallization of the various hydrates of manganous sulphate, Thorpe and Watts[7] heated the salt to 280°, Linebarger[8] to 170°–180° and Cottrell[9] to 270°–280°, though the latter found that no decomposition took place at 350°. Richards and Fraprie[10] showed, however, that as much as 0.1% H_2O remained in the salt after heating for one half hour at 350°, but that five minutes' heating at 450° produced complete dehydration without decomposition. Classen[11] and Blair[12] recommend heating to dull red; while Fresenius[13] declares that accurate results can be obtained only by chance, as it is impossible to expel all excess sulphuric acid without decomposing the salt.

The following experiments were conducted to determine the temperature to which manganous sulphate may and must be heated, to expel all the water or excess sulphuric acid and to obtain the normal anhydrous salt. About two grams of the salt was heated in an open platinum crucible in a small electrically heated muffle, temperatures of which up to 400° were measured with a 450° nitrogen-filled thermometer, and above 400° with a platinum-rhodium thermocouple calibrated at this Bureau. The crucible

[1] Ann. Chem., *198*, 318-64 (1879).
[2] Arch. Sci. phys. et Nat. 3, *10*, 25 (1883).
[3] Chem. Ztg., *9*, 1478, 1787 (1885).
[4] Z. anal. Chem., *38*, 687 (1899).
[5] Am. Jour. Sci., *5*, 209 (1898).
[6] Treadwell & Hall: Quant. Analysis II, 104.
[7] Jour. Chem. Soc., *37*, 113 (1880).
[8] Am. Chem. Jour., *15*, 225 (1893).
[9] Jour. Phys. Chem., *4*, 637 (1900).
[10] Am. Chem. Jour., *26*, 75 (1901).
[11] "Ausgew. Meth. Analytische Chem." I, p. 363.
[12] "Chem. Analysis of Iron," 7th ed., p. 126.
[13] Fresenius-Cohn: "Quant. Analysis." I, p. 297.

was kept covered in the desiccator and upon the balance, where it was weighed against a similar crucible as a tare. The results of three series of heatings are shown in Table II, the figures in the last column being calculated from the weight which remained practically constant from 450° to 500°.

TABLE II

TEMPERATURE OF DECOMPOSITION OF MANGANOUS SULPHATE

A

MANGANOUS SULPHATE PREPARED AS ON P. 69

Temp.	Time Hours	Weight of $MnSO_4$, g	Per cent of Constant Weight	Remarks
300°	1	2.3655	100.10	
350°	16	49	100.07	
420°	2	42	100.04	
420°	2	40	100.03	
420°	17	37	100.02	
480°	4	33	100.00	
480°	17	32	100.00	
540°	4	31	100.00	
550°	18	29	99.99	
620°	4	25	99.97	Slight darkening

The final product was dissolved in water and the insoluble residue filtered out, washed and ignited, yielding 0.0006g Mn_3O_4, equivalent to 0.0004g Mn, or 0.0011g $MnSO_4$. The filtrate was evaporated for series B.

B

Temp.	Time Hours	Weight $MnSO_4$ g	Per cent of Constant Weight	Remarks
300°	3	2.3659	100.15	
340°	18	44	100.10	
400°	4	28	100.03	
440°	18	23	100.00	
480°	5	22	100.00	
480°	18	22	100.00	
570°	5	17	99.98	Slight darkening
570°	18	09	99.95	Decided darkening

A few drops $H_2SO_3+H_2SO_4$ were added to the final product, which was then reheated for series C.

C

Temp.	Time Hours	Weight $MnSO_4$ g	Per cent of Constant Weight	Remarks
300°	4	2.3717	100.40	
320°	17	690	100.28	
400°	5	41	100.08	
400°	17	34	100.05	
460°	5	23	100.00	
460°	17	23	100.00	
525°	5	21	99.99	
525°	17	19	99.98	
580°	5	17	99.97	Slight darkening
580°	17	08	99.94	Decided darkening

From Table II the following conclusions may be drawn: 1—Manganous sulphate does not undergo any appreciable decomposition upon prolonged heating to temperatures up to 550°. 2—At temperatures from 550°–600° (from incipient to dull redness) this salt decomposes slowly. 3—The anhydrous normal salt can be obtained only by heating, for considerable periods at 450°–500°, especially if an excess of sulphuric acid be originally present. 4 — Attempts to obtain the pure salt by heating directly over a flame, or even in a double crucible, without temperature regulation or measurement, must be subject to considerable uncertainty.

Having now a means for obtaining a known weight of manganous sulphate, solutions of known strength (from 0.002 to 0.005 gram manganese per gram of solution) were prepared by dissolving a known weight of the pure salt, heated to constant weight at 450°–500°, and making up to a definite weight of solution, the manganese content of which was calculated by the use of the factor $MnSO_4$—$Mn = 0.3638$. In one case, for example, 5.749 grams pure anhydrous $MnSO_4$ was dissolved in water and the solution made up to exactly 1000 grams; producing a solution one gram of which contained 0.002091g Mn, which value was confirmed by evaporation of a weighed portion of the solution and heating to 475° to constant weight. Determinations made by another chemist upon this solution, by evaporation and heating for a short time to "dull redness," yielded the values 0.002100, 2092, 2103, and 2101; the mean value 0.002099 being therefore 0.38% too high, i.e., an error of about one part in two hundred and fifty. Upon another solution prepared in the above manner, and containing 0.002000g Mn per solution, the same chemist obtained by direct heating to dull redness 0.002004, 2006 and 2005; i.e., the results were high, in spite of the fact that in the latter series at least, very slight decomposition had evidently taken place in the bottom of the crucible. Apparently therefore those parts of the salt on the sides of the crucible had not been heated to the necessary temperature for a sufficient length of time to expel all water or excess acid. In view of these facts, the desirability of substituting for the manganous sulphate, some other standard, such as sodium oxalate, is very evident.

(*b*) *Effect of Conditions upon Standardization with Manganous Sulphate.*—(1) Ferrous sulphate-permanganate ratio. This ratio, which is fundamental for the accuracy of the method, is usually determined by means of a blank experiment, that is, a determination is run through in the absence of manganese, under the conditions to be used in the regular analyses. This procedure, which was evidently devised for the purpose of eliminating errors due to impurities in the reagents, has been found to be unnecessary, i.e., the ratio so obtained is the same as that obtained by direct titration of the ferrous sulphate in the same volume. This is due to the fact that on the one hand the bismuthate oxidizes readily any traces of nitrous acid which may be present in the nitric acid; and that on the other hand nitric acid of the strength present in the final solution does not have any effect upon the ferrous salt in the short time necessary for a titration. If, however, the ferrous salt be titrated in the presence of nitric acid containing small amounts of nitrous acid, which has not been treated with bismuthate, an excessive amount of permanganate will be consumed, due to the reducing action of the nitrous acid upon the permanganate, which takes place more rapidly in the presence of ferrous salt than in its absence. It must be clearly understood that conducting the blank experiment in the usual way does not obviate the necessity of avoiding the presence of nitrous acid in the solutions of manganese used in the standardizations or analyses; since as indicated by Blair[1], nitrous acid will reduce part of

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[1] Seventh Ed. p. 128.

the permanganic acid, precipitating manganese peroxide, which is not reoxidized by the bismuthate.

While not strictly necessary, the determination of this ratio by means of a blank affords a convenient means of testing the efficacy of the filter, and has therefore been followed in all this work. The conditions found most satisfactory are as follows. To 50 cc. of nitric acid (25% by volume), add a small amount of bismuthate. Shake and allow to stand a few minutes, dilute with 50 cc. of 3% nitric acid; filter through the asbestos filter and wash with 100 cc. of 3 % nitric acid. To the filtrate, which should be perfectly clear, add a volume of ferrous sulphate approximately equal to that to be used in the subsequent determinations (25 to 50 cc.) and titrate at once to the first visible pink. Even for the most accurate work, no endpoint correction is required for this titration, provided only that the solutions are always titrated to the same color, and that about the same volumes are used in the standardization and analyses.

(2) *Amount of manganese present in a determination.*—One of the serious limitations of this method is the small amount of manganese generally determined, making it somewhat unreliable for high-grade materials. Blair recommends the presence of from 0.01 to 0.02g Mn, involving the use of a sample of manganese ore of only 0.02g, obtained by taking an aliquot of the solution of a gram of the ore, Ibbotson and Brearley[1] state that the method is equally applicable for large or small amounts of manganese without however giving the evidence for this conclusion. Since with 0.03N permanganate, 0.015 Mn is the largest amount that can be conveniently determined, the following experiments were conducted with approximately 0.1N $KMnO_4$ and $FeSO_4$. The results are expressed in terms of the manganese value of one gram of the permanganate solution. It should be noted that a high result indicates incomplete oxidation of the manganese by the bismuthate. In these and the following series the following conditions were tentatively employed, and the variation produced by a change of one condition was noted in each series of experiments. The manganese sulphate was oxidized at room temperature in a volume of about 50 cc., containing 25% nitric acid by volume. An excess of bismuthate (about 0.5g) was added, the

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[1] Chem. News, *82*, 269 (1900).

solution was agitated for one minute, the sides of the flask were rinsed down with 50 cc. of 3% nitric acid, and the solution at once filtered with suction through the asbestos filter, previously coated with bismuthate. The flask and filter were washed several times with 3% nitric acid of which about 100 cc. was used. The filtration and washing required from 1 to 3 minutes. To the filtrate ferrous sulphate was added immediately in slight excess which was at once titrated with permanganate.

TABLE III. Effect of Amount of Manganese in the Presence of Variable Amounts of Iron

Manganese Values calculated from			
Sodium Oxalate	Manganous Sulphate		
Values Determined Over a Period of Three Weeks	Grams Manganese Present	Grams Iron Present	1 g. $KMnO_4$ Solution= g. Mn.
0.001090	0.03	...	0.001088
91	0.03	...	88
92	0.03	1.0	89
92	0.03	1.0	89
91	0.03	1.0	91
91	0.03	1.0	92
		B	
91	0.05	...	90
92	0.05	...	92
91	0.05	...	90
92	0.05	...	87
90	0.05	...	90
90	0.05	1.0	89
89	0.05	2.0	90
92	0.05	3.0	89
		C	
91	0.10	...	89
91	0.10	...	89
90	0.10	...	1161
90	0.10	...	1089
	0.10	...	97
	0.10	...	96
	0.10	...	1107
	0.10	...	1088
av. 0.001091	av. of A & B.		0.001089

From Table III it is evident that for amounts of manganese up to 0.05g the method is accurate within the limits of error, i.e. about one part in five hundred, while results obtained with as much as 0.10g Mn are decidedly erratic, only one half approaching the correct values. It is apparent therefore that about 0.05g Mn is the practical limit under these conditions. This amount is however far more satisfactory than only 0.01–0.02g, and permits the use of 0.10g of high-grade manganese ore, a decided advantage. As seen in series A and B, the results with as much as 3g iron present, are entirely satisfactory. The agreement of the sodium oxalate and manganese sulphate values will be discussed later.

(3) *Acidity, volume, time of standing, etc.* — The results of several series of experiments to determine the effect of various conditions upon the bismuthate method are summarized in the following table.

TABLE IV

EFFECT OF CONDITIONS UPON BISMUTHATE STANDARDIZATION

$KMnO_4$ Solution K

Series	Method	Modification	No. of Detns.	1 g $KMnO_4$ Solution=g Mn.
A 1	$Na_2C_2O_4$	Standard—p	6	0.001098
B 1	$MnSO_4$	Standard—p	9	1098
C 1	$MnSO_4$	Initial conc. HNO_3—10%	3	1114
2	$MnSO_4$	Initial conc. HNO_3—40%	3	1098
D 1	$MnSO_4$	Initial volume—150 cc.	3	1098
E 1	$MnSO_4$	Shaken with bismuthate 15 sec	3	1097
F 1	$MnSO_4$	Stood before filtration 10 min.	3	1097
2	$MnSO_4$	Stood before filtration 30 min.	1	1097
G 1	$MnSO_4$	Stood after filtration 10 min.	1	1097
2	$MnSO_4$	Stood after filtration 20 min.	1	1097
3	$MnSO_4$	Stood after filtration 30 min.	1	1098
H 1	$MnSO_4$	Stood after addition of $FeSO_4$ 10 min.	1	1096
2	$MnSO_4$	Stood after addition of $FeSO_4$ 30 min.	1	1084
I 1	$MnSO_4$	Addition of H_3PO_4—5 cc.	3	1099
		Mean of all $MnSO_4$ values except C_1&H_2		1098

Of the $MnSO_4$ values given in Table IV, the individual determinations of all except those in C_1 and H_2, varied less than one part in five hundred from the mean, showing that accurate results can be obtained over a very wide range of conditions. The only conditions found to produce appreciable errors were (a) deficiency of nitric acid, and (b) allowing the solution to stand more than ten minutes after the addition of the ferrous sulphate, of which about 10 cc. excess was present. Since there is no occasion for either of these conditions to arise in good practice, the method may be considered accurate under all ordinary conditions of procedure, an important criterion for a standard method of analysis.

Use of phosphoric acid.—The addition of this reagent as recommended by Dudley, was found convenient though not necessary; since with 0.1N solutions, there was no difficulty in obtaining a sharp endpoint within 0.03 cc. of permanganate, without its use. If used, it should be added to the ferrous sulphate solution beforehand, rather than during the titration, since in the latter case a white precipitate, probably consisting of basic bismuth phosphate, separates, rendering the endpoint slightly less distinct. With very large amounts of iron, e.g. 3–5g, such as would have to be used if Mn in steel were determined with 0.1N permanganate, it was found that addition of phosphoric acid possesses no advantage, since it tends to produce a pink color, due probably to the formation of an acid ferric phosphate[1], which obscures the endpoint as much as does the ferric nitrate. The use of 0.1N solutions is therefore recommended only for manganese ores and similar high-grade products, in which the highest accuracy is desired.

(c) *Probable course of reactions.*—From Table IV, some light may be thrown upon the probable course of the reactions when manganese is oxidized by bismuthate. At least two reactions are probable: (a) direct oxidation to Mn^{VII} and (b) interaction of unoxidized Mn^{II} with the Mn^{VII}, precipitating Mn^{IV}, which is then removed from the oxidizing influence of the bismuthate. If these two reactions may take place, the problem resolves itself into a determination of the conditions under which reaction (a) will be accelerated and (b) will be retarded, so that (a) goes practically to completion before (b) can take place to an appreciable extent. The favorable conditions for (b) as conducted in the Volhard method, for example, are slight acidity and high temperature; which should therefore be avoided in the bismuthate oxidation. That this explanation is plausible is shown by a comparison of C_1 and C_2. That complete oxidation may be effected in a short

[1] Erlenmeyer and Heinrich: Ann. Chem., 190, 191, (1877.)

time is indicated in E_1; in which connection the necessity for thorough agitation must be emphasized. Other experiments, not recorded here, showed that with 0.05g or more of Mn, complete oxidation could not be effected if the solution was not thoroughly agitated. In the earlier experiments in this investigation, the solutions were artificially cooled to about 5°; but after it was found that results at room temperature, 20°–25°, were entirely satisfactory, artificial cooling was dispensed with.

(*d*) *Conditions recommended.*—Correct results can be obtained under the following conditions. To the manganese solution containing 20–40% nitric acid (free from nitrous acid), in a volume of 50–150cc., add a slight excess of bismuthate (usually 0.5 to 1.0 gram), agitate thoroughly for about one half minute; wash down the sides of the flask with 3% nitric acid, add a slight excess of ferrous sulphate, and titrate at once with permanganate. For iron and steel,0.03N solutions as described by Blair are satisfactory.

For ores and ferro manganese 0.1N permanganate solution may be employed, and an amount of material containing about 0.05 gram manganese. For the rapid solution of ores, a method recommended by Blair[1] has been found convenient. One gram of the ore is fused in a large platinum crucible with 10 grams potassium bisulphate, one gram of sodium sulphite and 0.5 gram sodium fluoride. The heating should be very slow till effervescence ceases. After complete fusion the product is cooled, then heated carefully with 10 cc. concentrated sulphuric acid, cooled, dissolved in water, and made up to a definite volume. The slight precipitate of barium sulphate usually present will not influence the manganese determination.

7—AGREEMENT OF VALUES DERIVED FROM SODIUM OXALATE AND MANGANOUS SULPHATE

Consideration of the values in Table V shows plainly that no greater difference than one part in five hundred exists between the results derived from sodium oxalate and manganese sulphate respectively, instead of the former values being one per cent lower, as claimed by Brinton and others. In fact in the case of the 0.1N solutions, the only ones in which an accuracy of more

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[1] Private communication.

than one part in five hundred is realizable, the manganous sulphate values show a tendency to be from one to two parts per thousand lower than the sodium oxalate results. It is at least interesting, though perhaps not significant, that if the value 55.00 instead of 54.93 be used for the atomic weight of manganese, the results with the 0.1N solutions agree in every case to within one part in a thousand.

TABLE V

COMPARISON OF $Na_2C_2O_4$ AND $MnSO_4$ VALUES

Permanganate Solution	MANGANESE VALUES DERIVED FROM			
	Sodium Oxalate		Manganese Sulphate	
	No. of Detns.	1g $KMnO_4$=g Mn.	No. of Detns.	1g $KMnO_4$=g Mn.
A_1	3	0.0003465	3	0.0003469
A_2	4	0.0003462	3	0.0003462
B	6	0.0003454	5	0.0003458
E	9	0.001096	4	0.001094
G	7	0.001091	5	0.001090
I	18	0.001091	28	0.001089
K	6	0.001098	29	0.001098

8—ANALYSIS OF PURE PERMANGANATE CRYSTALS

Additional evidence of the correctness of the above values was found in the analysis of the pure permanganate prepared as described on p. 10, which contained 0.38% water. The salt should therefore contain 34.63% manganese, instead of 34.76%, the theoretical content for pure anhydrous $KMnO_4$. This difference with specially purified permanganate indicates clearly the probable presence of water as well as manganese peroxide in C. P. permanganate, rendering it unsuitable as a primary standard. Manganese was determined gravimetrically by precipitation with ammonium sulphide; the manganese sulphide being washed with dilute ammonium sulphide, ignited in a weighed crucible, treated with sulphurous and sulphuric acids, evaporated, heated to 450° to constant weight, and weighed as $MnSO_4$. The manganese in the filtrates was determined colorimetrically. Results of duplicate analyses were 34.70% and 34.66%, the mean 34.68% agreeing closely with the theoretical value 34.63%. The oxidizing value of this permanganate was determined by means of solutions A_1, A_2, and E (Table V) which were prepared by the solution of an exact weight of the salt in a definite weight of solution. In A_1 and A_2, exactly one gram $KMnO_4$ was dissolved and diluted to one kilogram; yielding solutions having an oxidizing value equivalent to 34.65% Mn (average of all sodium oxalate and manganous sulphate values for A_1 and A_2). Solution E contained 3.1606g of the salt per kilogram, and possessed an oxidizing power equivlent to 34.65% Mn, (derived from the average of all sodium oxalate and manganous sulphate values for solution E). Solutions B, G, I, and K were prepared of only approximately the desired strength, and the results have no relation to the composition of the solid permanganate employed.

9—ANALYSIS OF MANGANESE ORES

TABLE VI

ANALYSES OF MANGANESE ORES

Analsyt	Method	Ore I	Ore II	Ore III
A	Bismuthate	52.47	52.53	50.50
B	Modified Acetate	52.40	52.29	50.52
Author	Bismuthate	51.93	52.03	50.12

Analyses of the Bureau of Standards Manganese Ore (Standard Sample No. 25) by means of permanganate I, gave as the average of nine determinations, 56.30% Mn upon the basis of the sodium oxalate standardization, and 56.20% if calculated from the manganous sulphate. These results are in good agreement with the mean value 56.36% derived from all determinations upon the certificate; and with the value 56.33 formerly found by the author with the bismuthate method, using sodium oxalate as the standard. Unfortunately comparisons based upon this sample are not necessarily conclusive, since the mean value 56.36% is derived from results ranging from 56.15 to 56.63, obtained by eight chemists using a variety of methods, the lack of agreement of which is illustrated. If the bismuthate results by the author are correct, a conclusion made highly probable by the work here described, the value of the ore lies between 56.20 and 56.30% manganese; and many of the values found by other methods, by the author and others, are too high. That the tendency of many commercial methods is to yield results higher than those by the method here recommended, is shown in the results of analyses of three manganese ores by the author and two well known commercial chemists. The differences here shown, amounting to 0.8 to 1.0% of the manganese present, are by no means insignificant. The discrepancy between the results by A and the author, both using the bismuthate method, was found to be due mainly to differences in the method of standardizing the manganous sulphate solution (see p. 75). These results show clearly the necessity for a thorough investigation of other methods for determining manganese, in order that accurate results may be uniformly obtained.

10—SUMMARY

1—To obtain normal, anhydrous manganous sulphate, the salt may and must be heated for a considerable time at 450°–500°, i.e., just below red heat.

2—Standardizations of permanganate solutions (both 0.03N and 0.1N) by means of sodium oxalate, manganous sulphate, and solid permanganate agree within the experimental error, which in the bismuthate method could not be reduced much below one part in five hundred. Taken together with the agreement of sodium oxalate and iron values, and the experiments upon the reduction and reoxidation of permanganate, the absolute accuracy of the above results, within the experimental limits, is rendered almost certain.

3—In view of the difficulties attending the use of manganous sulphate, standardization by means of sodium oxalate, under definite but easily realizable conditions is recommended.

4—Results by the bismuthate method, are accurate over a very wide range of conditions, for amounts of manganese up to 0.05 gram.

5—For accurate determinations on rich ores, etc., the use of 0.1N permanganate is recommended, while for iron and steel the method described by Blair is entirely satisfactory.

6—The statement of Blair that "this method for materials containing small amounts of manganese, say up to 2 per cent, is more accurate than any other method, volumetric or gravimetric" may be extended to include materials containing large amounts of manganese.

7—Filtered permanganate solutions preserve their strength when exposed to diffused light, if protected from dust and reducing substances. In the presence of the latter, alkaline permanganate solutions decompose less rapidly than do neutral solutions.

The author desires to express his thanks to Dr. W. F. Hillebrand for valuable suggestions and advice during the course of this investigation.

ON THE DETECTION AND SEPARATION OF ALUMINUM AND BERYLLIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES

By Philip E. Browning and Simon B. Kuzirian
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PRELIMINARY

The work to be described is a study of the process of dehydration with amyl alcohol, as applied to the separation of aluminum and beryllium.

Aluminum nitrate was dissolved in a few drops of water in a test-tube, about 10 $\overline{\text{cm}}.^3$ of amyl alcohol was added, and the whole was brought to the boiling point, 128°–130°. Apparently the aluminum salt separated completely; and after filtration on a dry paper the filtrate, upon treatment with ammonium hydroxide, showed no evidence of aluminum in solution. Beryllium nitrate, similarly treated, remained in solution; 5 $\overline{\text{cm}}.^3$ of a saturated solution made in this way proved to contain from 0.10 grm. to 0.13 grm., calculated as BeO.

QUALITATIVE METHOD

Table I shows the results of a number of experiments upon the application of this method to the qualitative separation and detection of aluminum and beryllium. The aqueous solution of the salts was in each case evaporated to a few drops, and about 10 $\overline{\text{cm}}.^3$ of amyl alcohol was added. The whole was then brought to the boiling point, and the complete dehydration was indicated when the fumes of the alcohol burned quietly at the mouth of the test-tube. The separation of a solid residue in the liquid or upon the side of the tube indicated aluminum. The alcohol was then allowed to stand until cool, and was filtered on a dry paper. Upon the addition of a drop of ammonium hydroxide to the filtrate, a precipitate [$Be(OH)_2$] showed the presence of beryllium. Care was taken to treat not more than 0.1 grm. of material with

10 cm.^{3} of alcohol, in order to be well within the limit of solubility of the beryllium salt in amyl alcohol.

The solutions used were prepared by one of the experimenters, and the tests were made by the other, without knowledge of the content of the solution under examination. The method was thus given an unprejudiced trial.

QUANTITATIVE METHOD

The first experiments on the quantitative side of the problem were made upon the salts separately.

Solutions were prepared and standardized in the usual manner, by precipitation as the hydroxides, ignition, and weighing of the oxides. Portions of these solutions were drawn from burettes into small counterpoised beakers and weighed, as a check on the burette readings. In each case the solution was then evaporated to dryness and the residue dissolved in a few drops of dilute nitric acid. About 15 cm.^{3} of amyl alcohol was added, and boiling was continued until a thermometer placed in the liquid registered from 125° to 130°. After cooling, the alcohol was decanted through asbestos felt in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

In the case of aluminum, the residue in the beaker was dissolved in dilute nitric acid, and the dehydration was repeated with another 15 cm.^{3} of alcohol. This double treatment was employed because of the tendency of a separating salt to include some of the soluble salt, when the two are present together. After the second dehydration, the aluminum nitrate was filtered on the felt previously used, having been washed from the beaker with amyl alcohol contained in a wash bottle. The salt that adhered to the beaker was dissolved in water and dilute nitric acid, and the aluminum was precipitated as the hydroxide by ammonium hydroxide. The aluminum nitrate on the felt was then ignited to the condition of the oxide, and the aluminum hydroxide belonging to the same determination was added, and filtered on the same felt, and the whole was ignited to constant weight. Table II gives the results when aluminum was present alone.

The results when beryllium was present alone are to be found in Table III. In these determinations two boilings were made, the clear liquid obtained was poured upon the weighed felts, and the felts were washed with alcohol. In a number of cases the felts were ignited and weighed, and were shown to be free from beryllium by their unchanged weight. Several methods were tried for estimating the beryllium in the amyl alcohol filtrate, such as burning the alcohol and weighing the residue, precipitating directly with ammonium hydroxide with or without mixture with ethyl or methyl alcohol, and extracting from the alcohol by shaking with water in a separating funnel and precipitating from the water extract by means of ammonium hydroxide. The last proved to be the most convenient method. Two shakings with about four times the volume of water gave satisfactory results. By this procedure the alcohol may be recovered for repeated use.

When aluminum and beryllium were present together some difficulty was encountered, due, apparently, to the tendency of the aluminum to include the beryllium, even after two treatments. However, the results given in Table IV show a rough separation, and the authors feel confident that further study of the method will make better results possible.

As a qualitative method the results are entirely satisfactory, and the process can be recommended for the preparation of beryllium salts free from aluminum.

TABLE I

Al taken Calculated as Al_2O_3	Be taken Calculated as BeO	Al result	Be result
0.1000	0.0000	Decided test	No test
0.1000	0.0010	Decided test	Fair test
0.0080	0.0020	Decided test	Distinct test
0.0040	0.1000	Decided test	Decided test
0.0008	0.0000	Faint test	No test
0.0008	0.0020	Faint test	Distinct test
0.0002	0.0000	Very faint test	No test
0.0000	0.0040	No test	Distinct test
0.0000	0.0002	No test	Faint test
0.0000	0.0000	No test	No test

TABLE II

Al calculated as Al_2O_3

Taken grm.	Found grm.	Error grm.
0.0652	0.0654	0.0002+
0.1042	0.1040	0.0002−
0.1039	0.1024	0.0015−
0.1042	0.1050	0.0008+
0.0429	0.0442	0.0014+
0.0421	0.0427	0.0006+

Average error 0.0002+

TABLE III

Be calculated as BeO

Taken grm.	Found grm.	Error grm.
0.1087	0.1074	0.0013−
0.0313	0.0312	0.0001−
0.1022	0.1025	0.0003+
0.1020	0.1027	0.0007+
0.1021	0.0034	0.0013+

Average error 0.0002+

In the last three cases Be was extracted from the alcohol by shaking with water.

TABLE IV

Al calculated as Al_2O_3			Be calculated as BeO		
Taken grm.	Found grm.	Error grm.	Taken grm.	Found grm.	Error grm.
0.1048	0.1060	0.0012+	0.0364	0.0340	0.0024−
0.0653	0.0675	0.0022+	0.0316	0.0320	0.0004+
0.0456	0.0474	0.0018+	0.0316	0.0316	0.0000
0.0625	0.0615	0.0010−	0.0407	0.0395	0.0012−
0.0639	0.0644	0.0005+	0.0410	0.0440	0.0030+

Average error, Al, 0.0012+ Average error, Be, 0.00004−

THE METHODS OF THE UNITED STATES STEEL CORPORATION FOR THE COMMERCIAL SAMPLING AND ANALYSIS OF PIG IRON[1]

THE CHEMISTS' COMMITTEE OF THE U. S. STEEL CORPORATION

PREFACE

In conformity with the design of the Officials of the United States Steel Corporation for the standardization of the methods employed in the sampling and analysis of all materials encountered in their various lines of manufacture, the Chemists' Committee presents this compilation of standard methods for the sampling and subsequent analysis of molten pig iron.

In selecting the methods, the Committee employed the same line of procedure as in former cases, viz., the careful consideration of all the methods employed in each laboratory of the Corporation, evolving therefrom the several methods herein described, the immediate adoption of which is desired.

The services of Messrs. W. B. N. Hawk, Wm. Brady and C. H. Rich, a sub-committee appointed for the preparation of this pamphlet, are gratefully acknowledged.

INTRODUCTION

A quite obvious cause of nonconformity of results of comparative analyses in the various laboratories of the Corporation has been an apparent lack of uniformity of method in the sampling and analysis of molten iron.

This condition is particularly apparent with regard to the determination of the sulphur, numerous discrepancies in which would appear to indicate the absence of, and the necessity for, some uniform method of procedure. The estimation of the sulphur by the gravimetric method and the determination of the remaining constituent elements of the iron, are susceptible of a most satisfactory degree of accuracy. The successful issue of the volumetric

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determination of the sulphur, however, is largely dependent upon the grade of the iron and the conditions under which the test is taken. A disturbing factor in establishing a satisfactory standard of comparative values in such analyses is the loss of uncertain and varying proportions of the sulphur, due to the formation of volatile and difficultly oxidizable organic sulphides, upon solution of white or chilled iron in hydrochloric acid. Comparative tests by a number of chemists of the Corporation having shown quite satisfactory agreement in sulphur values as obtained by the evolution method in sand cast and properly taken so-called chilled test samples, it has been decided to adopt for all purposes the more convenient chilled test, which, it is believed, will tend to conserve the desired comparative accuracy. True values may be obtained in the crushed shot sample by annealing the powder in a current of natural gas or under any convenient non-oxidizing conditions, but the exigencies of the routine of the works laboratory, as demanded by the conditions necessarily involved in the manufacture of iron and steel, would in most cases prohibit this metallurgical refinement.

The methods of analysis herein described represent the best present day practice and it is hoped that their adoption will go far toward reconciling those too often variant conditions, convenience of manipulation and accuracy of result.

The solutions as prescribed are indicated in their various proportions on a one litre basis. It will be found convenient, however, in most cases to employ in actual practice corresponding multiples of a greater volume.

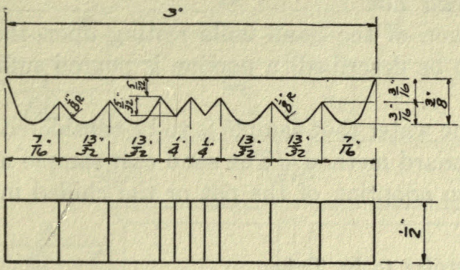
SAMPLING

Character of the Sample

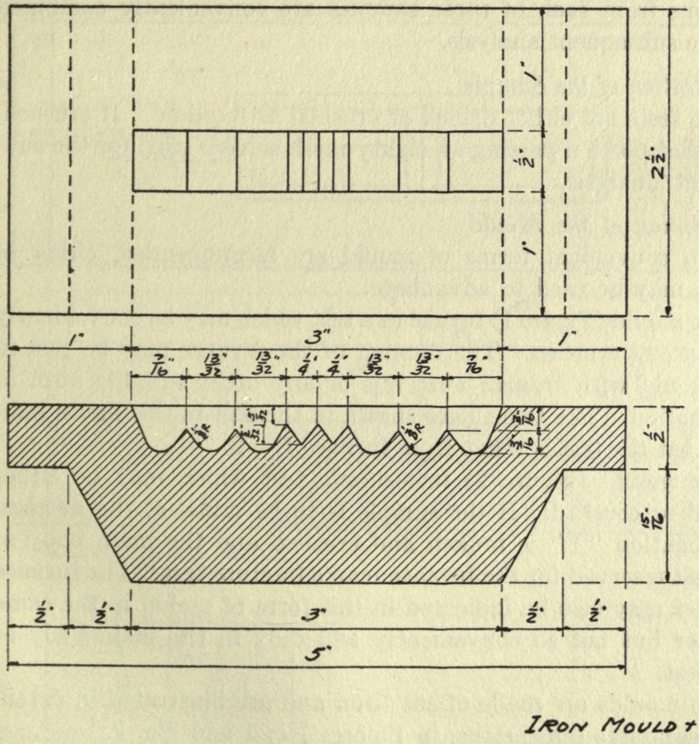
Two optional methods are prescribed for taking the test:

1. *Plate or Pat Test*

With a suitable hand ladle a portion is dipped from the stream of molten iron and, with the spoon of the ladle resting upon a clean dry iron plate, a pat of such size as may be desired is poured thereon.



SAMPLE.



IRON MOULD + TEST

FIG. 1

2. Chilled Mould Test

With the spoon of the hand ladle resting upon the dry clean mould (later to be described) a portion is poured sufficient to fill the mould.

The use of the water shot sample is to be considered as in violation of the standard method. The sand cast sample may be used but the uniform adoption of the pat or the chilled mould test is urged.

Number of Samples to be Taken

As tending to a reasonable degree of accuracy, it is recommended that a portion be secured, timed as nearly as may be practicable for the middle of each ladle of iron representing the cast. Equal portions from each of these samples are conveniently combined for the subsequent analysis.

Preparation of the Sample

The tests are either drilled or crushed as required. If crushed, only that portion passing an eighty-mesh sieve is used for the subsequent analysis.

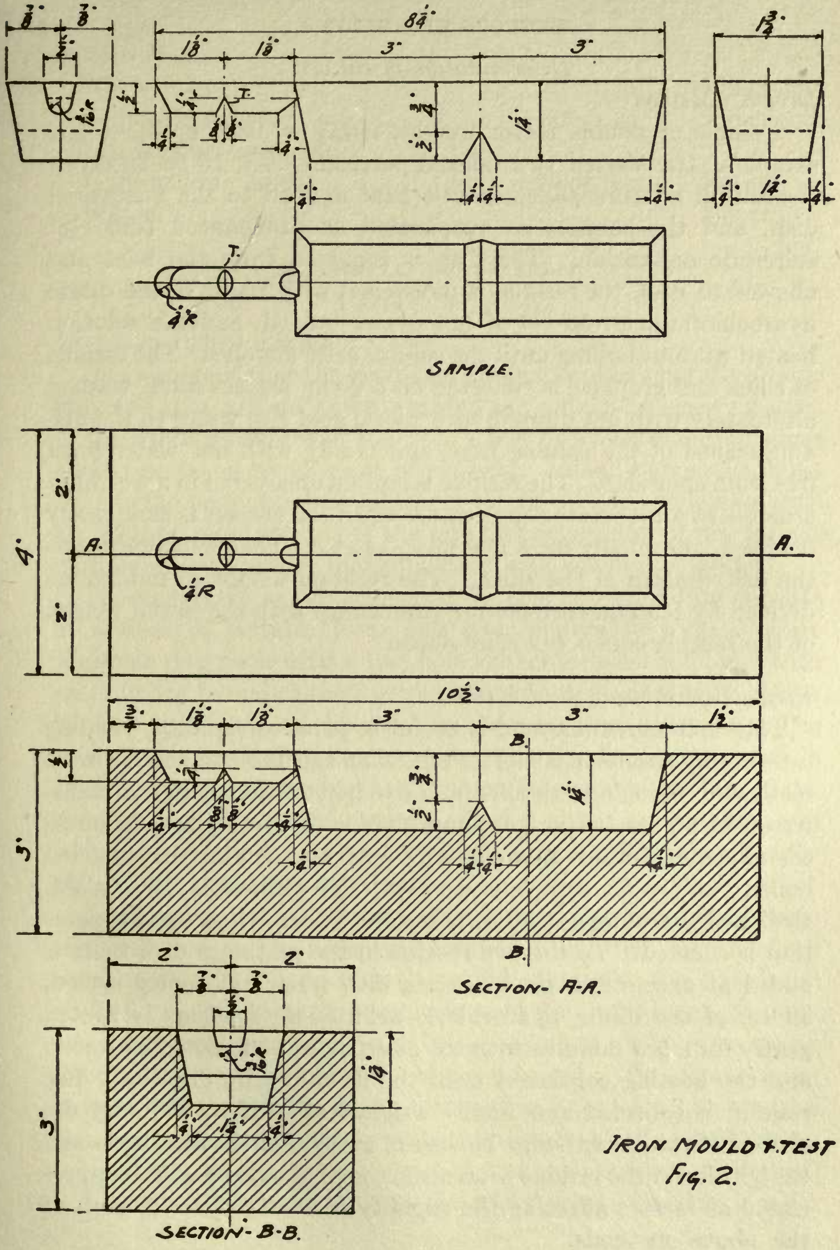
Description of the Mould

Two convenient forms of mould are recommended, either of which may be used to advantage.

The mould (Figure 1) furnishes a test which may be conveniently broken and crushed. The number of the furnace may be cast in the mould with Roman numerals or any other suitable form of designation. The two ridges shown in the test in this figure indicate that the test is taken from furnace No. 2.

The mould (Figure 2) furnishes a test which may be either drilled or crushed. If the sample is to be crushed, the notched prolongation "T" is broken and crushed and the main body of the test reserved for the furnace man's fracture test. The furnace number may also be indicated in this form of mould in the same manner but not so conveniently and only in the main body of the test.

The moulds are made of cast iron and are illustrated in detail, with complete dimensions, in Figures No. 1 and No. 2.



SAMPLE.

SECTION- A-A.

SECTION- B-B.

IRON MOULD & TEST

FIG. 2.

METHODS OF ANALYSIS

Determination of Silicon

Drown's Method

A single or double factor weight, .4693 or .9386 gram, of the sample is transferred to a glazed porcelain dish, 15 to 25 cc. of the silicon mixture added, gentle heat applied to the uncovered dish, and the solution is evaporated to pronounced fumes of sulphuric anhydride. The dish is removed from the heat and allowed to cool, the residue is moistened with 10 cc. of the dilute hydrochloric acid, 50 cc. of hot water added and the solution heated without boiling until the soluble salts dissolve. The residue of silica and graphite is collected on a 9 cm. ashless filter, washed alternately with hot dilute hydrochloric acid and water to the disappearance of the soluble iron, and finally with hot water until free from chlorides. The residue is ignited uncovered in a weighted crucible at a moderate temperature until the carbon is completely oxidized, and finally for a few minutes at a higher temperature to the dehydration of the silica. The residual weight in milligrams divided by ten and corrected in conformity with the initial weight of the sample equals per cent silicon.

Ford's Hydrochloric Acid Method

This well known method is useful in point of rapidity, yielding satisfactory results in a shorter time than the more refined Drown's method. A single or double factor weight of the sample is transferred to a porcelain or platinum dish with cover glass, 20 or 30 cc. of concentrated hydrochloric acid added and the solution boiled rapidly to complete dryness; the residue is not baked. Ordinarily, decomposition is complete by the time the evaporation is effected. To the dry residue in the platinum dish there is added at once, or in the porcelain dish when sufficiently cooled, 20 cc. of the dilute hydrochloric acid. The solution is heated gently for a few minutes with the addition of 50 to 60 cc. of water, and the heating continued until the soluble salts dissolve. The residue is collected and finally weighed as in the previously described Drown's method. The use of suction in the filtrations and the ignition of the residue in an atmosphere of oxygen will be appreciated as factors affecting the rapidity of the analyses in both of the above methods.

SOLUTIONS REQUIRED

Silicon Mixture		
Nitric Acid	1.20 sp. gr.	750 cc.
Sulphuric Acid	1.50 sp. gr.	250 cc.
Dilute Hydrochloric Acid		
Hydrochloric Acid	1.20 sp. gr.	500 cc.
Water		500 cc.

DETERMINATION OF SULPHUR

Volumetric Method

Evolution Iodine Titration

It is apparent that the evolution method is of comparative value only and is in no sense to be regarded as yielding the exact measure of the sulphur content of the iron, a fact of which due cognizance should be taken by all users of pig iron. Equally apparent, however, is the undoubted usefulness of the method in connection with the routine requirements of the iron laboratory and of the various metallurgical processes in conjunction with which it is used.

The apparatus as recommended for this determination consists of a flask of suitable form and size, preferably sixteen ounce Florence ring neck with a two hole rubber stopper equipped with an ordinary funnel or thistle tube and a short piece of glass tubing bent at right angles (exit tube) in the respective apertures. The exit or delivery tube is connected with the absorption vessel in such manner as to conduct the evolved gases to the bottom of the vessel. The absorption may be effected either in the beaker in which the titration is to be conducted, or in a test tube, preferably 10″ by 1″, suitably supported.

A minimum of 2.5 grams or a maximum of 5 grams of the sample is transferred to the flask, the stopper is inserted and the flask conveniently connected with the vessel containing the absorbent; 40 to 60 cc. of dilute hydrochloric acid are introduced through the funnel and heat applied, a brisk evolution of the gases being maintained until the powder is decomposed. The temperature is then raised until the steam formed has forced the last trace of the hydrogen sulphide gas into the absorbent. The heat is removed, the apparatus disconnected and the titration conducted.

Ten cc. of the starch solution are added to the titrating beaker and the contents of the absorption tube transferred thereto. Both the absorption and delivery tube are rinsed with cold water and any adhering precipitate is dissolved by means of a fine jet of the dilute hydrochloric acid. Care is exercised that the acid solution be not unduly agitated before the introduction of the iodine solution. If the absorption is effected in the beaker, the delivery tube is removed first, cleansed with the acid and water and, with the precaution suggested above, an excess of the dilute acid is added. The final volume of the solution should approximate 400 cc. The solution is stirred gently in order to neutralize the alkali of the absorbent, which, if left undisturbed, reacts with the iodine with formation of a substitution product from which the iodine is but partially liberated upon acidifying the solution. The iodine solution is then added in successive portions, while the solution is stirred as the color fades, until the addition of a final drop yields the permanent blue color of the adopted endpoint. The number of cubic centimeters of the iodine required multiplied by .01 is equivalent to per cent sulphur.

The volume of the solution in the absorption vessel is so adjusted as to insure a sufficient body for the absorption of all of the gas, and a sufficient excess of the stock absorbent is maintained in proportion to the total volume of the solution. The proportions as used in the 10 in. by 1 in. test tube (15 cc. of any of the stock absorbents diluted to 60 cc.) may be taken as a basis therefor. If desired, the starch indicator solution may be added to any of the stock absorbent solutions in such proportions as to furnish the equivalent of 10 cc. of the indicator in the titration.

SOLUTIONS REQUIRED

Starch Indicator. To one litre of boiling water in a suitable flask, a cold emulsion of six grams of starch suspended in 100 cc. of cold water is cautiously added, and the boiling continued five minutes after the final addition. The solution is cooled to room temperature, and, with the addition of six grams of zinc chloride in 50 cc. of cold water, mixed thoroughly and set aside for a day or two with occasional shaking. After the final subsidence of the heavier residue, the starch solution is siphoned into the container and the settlings rejected. The zinc chloride is added as a preservative. Preliminary boiling of the water tends to les e the fronting or formation of large bubbles on the addition of the starch.

Standard Iodine. Ten grams of potassium iodide crystals, followed by 4.5 grams of resublimed iodine, are transferred to a glass stoppered graduated flask; 25 cc. of cold water are added and the flask is shaken until the iodine is completely dissolved. The solution is diluted to volume of one litre and set aside for not less than twenty-four hours before standardizing. The known sulphur of a standard steel, as determined both by the evolution and oxidation methods, is used as the basis of standardization with final adjustment so that 1 cc. is equivalent to .01 per cent sulphur on the basis of the weight of sample used

Dilute Hydrochloric Acid

Concentrated Acid	500 cc.
Water	500 cc.

ABSORBENTS

Ammoniacal Solution of Cadmium Chloride

Cadmium Chloride	5 grams
Water	375 cc.
Ammonia	625 cc.

Caustic Alkali

Caustic Potash or Soda	5 grams
Water	1,000 cc.

Ammoniacal Solution of Zinc Sulphate

Zinc Sulphate	10 grams
Strong Ammonia	625 cc.
Water	375 cc.

Gravimetric Method

Five grams of the sample are transferred to a clean No. 4 beaker or twelve ounce Erlenmeyer flask, and with the addition of 100 cc. of concentrated nitric acid, gentle heat applied until solution is complete. It is sometimes necessary to check a too violent action of the acid, which might result in loss of unoxidized sulphur, by placing the beaker or flask in cold water. The solution is boiled briskly to low bulk, and after cooling somewhat, 30 cc. of strong hydrochloric acid added, the solution is again concentrated, and following the precautionary addition of one gram of pure sodium carbonate, transferred to a clean porcelain dish and evaporated to complete dryness and the residue baked a short time at a moderate temperature.

The dish is allowed to cool, 35 cc. of concentrated hydrochloric acid added and heat applied until the soluble salts dissolve; the solution is again evaporated to complete dryness and the residue baked as before. This procedure insures the elimination of the nitric acid. The dish is cooled, 35 cc. of concentrated hydrochloric acid are added and heat is applied until the soluble salts are again dissolved. The cover is removed, and with the dish placed upon a suitable asbestos ring in order to prevent the formation of a crust of the metallic salts upon the sides, the solution is evaporated to the first appearance of the separation of the chlorides, which are then dissolved by the addition of a few drops of concentrated hydrochloric acid; three drops should suffice. Cold water is added to volume of about 75 cc., the residue is collected upon an 11 cm. filter and the filtrate received in a No. 2 beaker. The residue and filter are washed with the least possible amount of the hot dilute hydrochloric acid, alternated with cold water, to the disappearance of the iron stains and finally with hot water to volume of about 200 cc. To this cold solution 10 cc. of a ten per cent solution of barium chloride are added and the solution is allowed to stand with occasional stirring not less than twelve hours.

When the precipitate of barium sulphate has subsided, it is collected upon a 9 cm. close ashless filter, washed with dilute hydrochloric acid (five per cent) to the disappearance of the iron and finally with hot water until free from chlorides. The filter and residue are ignited uncovered in a weighed crucible at a moderate temperature to the disappearance of the carbon of the paper and finally at a somewhat increased temperature for ten minutes. The residual weight multiplied by 13.74 and divided by 5 equals per cent sulphur. The filtrate is set aside until satisfied that no further precipitation ensues.

The carbonaceous siliceous residue of the original solution usually retains some sulphur and is ignited in platinum under cover of pure sodium carbonate and decomposed by fusion with further addition of the carbonate and two-tenths gram of nitre; the subsequent hydrochloric acid solution is freed from its silica and added to the original filtrate, or examined separately for sulphur.

It is apparent that absolute purity of reagents and cleanliness of utensils and the final weighing of the barium sulphate effected under the most exact conditions, are determining factors in the successful issue of analyses by this method.

DETERMINATION OF PHOSPHORUS

Volumetric Method

Acid Alkali Titration

One to two grams of the sample are transferred to a flask, preferably twelve ounce Erlenmeyer, 40 cc. of nitric acid (1.13 sp. gr) added and heat applied until the sample is decomposed. The sides of the flask are washed down, one gram of ammonium persulphate is added and the solution boiled until the combined carbon is completely oxidized. The residue is caught on an 11 cm. filter and washed with dilute nitric acid (two per cent) and hot water to the disappearance of the soluble iron. The filtrate is heated to boiling in a suitable flask, a slight excess of a solution of potassium permanganate added and the boiling is continued until the excess of the permanganate is decomposed. The resultant precipitate of manganese dioxide is reduced to its soluble nitrate by means of the chosen reducing agent and the boiling continued until the excess thereof is decomposed.

With the solution at a temperature of 80° C., 40 to 60 cc. of ammonium molybdate solution are introduced and the flask is shaken for five minutes. The precipitate quickly subsides and is at once collected upon a 9 cm. filter, washed with dilute nitric acid (two per cent) until free from iron, and then with solution of potassium nitrate (one per cent) to the removal of the last trace of free acid.

The titration may be conducted in a beaker or in the flask in which the precipitation was effected. Care is exercised in the latter case to wash the flask thoroughly with the neutral wash, as any acid present of course reacts with the standard alkali. The filter and precipitate are transferred to the beaker or flask and the standard alkali is added in excess sufficient to render easy the subsequent maceration of the filter, which is accomplished by breaking up with a clean glass rod, or, if in a flask, by shaking the flask closed by a clean rubber stopper. When the precipitate has dissolved and the paper is thoroughly disintegrated, the solution is diluted and three drops of the indicator are added. The standard acid is then added to the disappearance of the pink tint, the sides of the titrating vessel washed down with cold water and, with a final volume of about 150 cc., the standard alkali is added to the adopted pink endpoint. The number of cubic centimeters of the alkali used in excess of the acid, multiplied by .01 or .02, is the equivalent of phosphorus in hundredths per cent.

SOLUTIONS REQUIRED

Standard Caustic Soda. Six and six-tenths grams of pure sodium hydroxide are dissolved in 100 cc. of boiled water. The solution is freed from any carbonic acid introduced by the caustic alkali, by the addition of about 1 cc. of a saturated solution of barium hydroxide with subsequent filtration, and the solution finally diluted to volume of one litre. If desired, a stock solution may be carried, a convenient aliquot portion of which is diluted for the working solution.

Standard Nitric Acid. Ten cc. of concentrated acid diluted to one litre. The acid and alkali solutions are standardized against the known phosphorus of a standard steel with final correction so that they are exactly agreeing and 1 cc. is equivalent to .01 per cent phosphorus on the basis of two grams of the sample.

Ammonium Molybdate. To 65 grams of molybdic acid (85 per cent) suspended in 142 cc. of cold water in a suitable flask, 143 cc. of strong ammonia are added and the flask is rotated until the molybdic acid is completely dissolved. The solution is cooled and added slowly to 715 cc. of nitric acid of 1.20 sp. gr. while the acid solution is vigorously stirred.

Molybdic acid is at times encountered which fails to yield a permanently clear solution of the ammonium molybdate; the addition of one or more drops of a 10 per cent solution of ammonium phosphate assists in clarifying the solution. The solution is allowed to stand over night, when it is filtered into the container, preferably through purified asbestos and with the aid of suction.

Phenolphthalein. One gram dissolved in one litre of ethyl alcohol.

Nitric Acid (1.13 sp. gr.)

Nitric Acid—Concentrated	240 cc.
Water	760 cc.

Potassium Permanganate Oxidant. Twenty-five grams to one litre.

REDUCING AGENTS

Ammonium Bisulphite. Five per cent solution.

Ferrous Sulphate

Ferrous Sulphate	50 grams
Water	1,000 cc.

Potassium Nitrite

Potassium Nitrite	50 grams
Water	1,000 cc.

Sugar. Saturated solution.

POTASSIUM PERMANGANATE TITRATION

The yellow precipitate as above obtained is washed with ammonium sulphate solution, or if desired, dilute sulphuric acid (2 per cent.) until free from iron and molybdenum salts. Dilute ammonia (1 part ammonia and 3 parts water) is poured over the precipitate and the filter is washed with hot water, and the solution caught in the flask in which the precipitation was effected. The volume of the solution should not exceed 25 cc. Eight grams of granulated zinc, 20 mesh, followed by 75 cc. of dilute sulphuric acid are added and the solution is gently boiled until reduction is complete. The undissolved zinc is then collected upon a glass wool filter and both flask and filter are washed with cold water. To the cold filtrate, standard potassium permanganate solution is added until a slight permanent pink tint is obtained. The measure of the permanganate solution required multiplied by its value in terms of phosphorus and divided by the initial weight of the sample equals per cent phosphorus.

SOLUTIONS REQUIRED

Acid Ammonium Sulphate

Strong Ammonia	15 cc.
Sulphuric Acid (1 part acid to 1 part water)	50 cc.

Diluted to one litre.

Standard Potassium Permanganate. Two grams potassium permanganate dissolved in one litre of water. One cc. equals approximately .0056 per cent phosphorus on a one gram basis. The known phosphorus of a standard steel is used as the basis of standardization.

Gravimetric Method

Weighing as Ammonium Phosphomolybdate

One to five grams of the sample are transferred to a No. 5 glazed porcelain dish with cover glass, 25 to 60 cc. of nitric acid (1.13 sp. gr.) are cautiously added, gentle heat is applied until the sample is completely decomposed, and the solution is then rapidly boiled to dryness. The temperature is raised gradually with final heating of the uncovered dish over the full flame of an Argand or Bunsen burner to the complete expulsion of the acid. After cooling sufficiently to avoid danger of breaking the dish, 30 cc. of concentrated hydrochloric acid are added, heat is applied until the soluble salts are dissolved, and the solution rapidly boiled to the first appearance of the separation of the chlorides. This evaporation is conducted with the same regard to the prevention of the formation of a crust upon the sides of the dish as in the previously described method for the determination of sulphur. The dish is removed from the heat, 10 cc. of strong nitric acid added and heat again applied for about one minute. Cold water is added to volume of about 60 cc., the solution stirred with a clean glass rod and filtered into a suitable flask; the residue, collected upon an 11 cm. filter, is washed with two per cent nitric acid and hot water alternately until free from iron, which insures also the complete removal of the soluble phosphate.

When the iron contains titanium in amount sufficient to interfere with the precipitation of the phosphorus and an exact determination is required, the residue of silica and graphitic carbon is ignited in a platinum crucible, the silica volatilized with hydrofluoric acid in the presence of a few drops of sulphuric acid and the resultant residue ignited and fused with sodium carbonate. The melt is boiled with hot water until disintegrated, the insoluble titanate is collected upon a filter and the soluble phosphate added to the main solution.

To the clear filtrate with a volume of about 150 cc., 25 cc. of strong ammonia are added at once and the flask is shaken until the resultant precipitate has coagulated. The addition now of 25 cc. of strong nitric acid renders the solution clear and furnishes an excess of about 10 cc. of strong nitric acid — which, it is found, yields a pure crystalline precipitate of the phosphomolybdate with no tendency to creep. The relatively large amounts of ammonia and nitric acid added are prescribed in the case of 5 gram samples and are essential in that they insure a sufficient proportion of ammonium nitrate in the solution. It is evident that these additions may be decreased with smaller initial weights of the sample, but it will be found advantageous to maintain approximately the excess of 10 cc. of the nitric acid.

With the solution at a temperature of 80° C., 50 to 75 cc. of the molybdate solution are introduced and the solution agitated for about five minutes. When the yellow precipitate has finally subsided, it is collected upon a previously dried and weighed 9 cm. filter, the filter and contents are washed thoroughly with two per cent. nitric acid, dried for one hour in an air bath at a temperature of about 115° C. and weighed between watch glasses with ground edges and enclosed in a suitable clip. It is of course essential that the light weight of the previously dried paper shall have been obtained under the same conditions. The increase in weight multiplied by 1.63 and divided by the initial weight taken is equivalent to per cent phosphorus.

Weighing as Magnesium Pyrophosphate

The yellow precipitate as above obtained is dissolved on the filter with hot ammonium citrate solution and the filter thoroughly washed with hot water, and the solution retained in a No. 0 beaker. To this cold solution, 5 to 10 cc. of the magnesia mixture are added, the solution is well stirred and allowed to stand in the cold not less than three hours. The precipitate of magnesium phosphate is collected upon a 9 cm. close ashless filter, washed with dilute ammonia, ignited at a low temperature to the disappearance of the carbon of the filter and finally for ten minutes at the full temperature of the blast. The weight of the magnesium pyrophosphate multiplied by 27.87 and divided by the initial weight taken is equivalent to per cent phosphorus.

SOLUTIONS REQUIRED

Ammonium Citrate

Citric Acid	50 grams
Strong Ammonia	350 cc.
Water	650 cc.

Magnesia Mixture

Magnesium Sulphate	84 grams
Ammonium Chloride	250 grams
Water	665 cc.
Ammonia	335 cc.

Dilute Ammonia

Strong Ammonia	200 cc.
Water	800 cc.

DETERMINATION OF MANGANESE

Walters' Color Comparison Method

Fifty to two hundred mg. of the sample are transferred to a suitable tube or flask, preferably an 8 inch by 1 inch test tube or a two ounce Erlenmeyer flask, 10 cc. of nitric acid (1.20 sp. gr.) added and heat applied either in a water bath or on a hot plate until the sample is decomposed. About one-half gram of moist ammonium persulphate, or its equivalent solution, is added and the heating continued until the combined carbon is completely oxidized. If silica or graphitic carbon separate in amount sufficient to render it necessary, the solution is filtered into a similar vessel and the residue retained on a small filter. The filter and residue are washed with the minimum of water, or the 15 cc. of silver nitrate solution required for the subsequent oxidation. The silver nitrate is introduced either through the filter or into the unfiltered solution, one gram of moist persulphate is added and the heating continued until the characteristic pink tint of the permanganic acid is well defined. The solution is cooled, transferred to the comparison tube and the color matched against a suitable standard which has been treated in exactly the same manner and with the same relative initial weight. The relative volume of the solution as required to match the color of the standard is equivalent to hundredths per cent. manganese.

Volumetric Method

The solution of permanganic acid is transferred to a beaker or flask, and following the addition of 10 cc. of sodium chloride solution, the standard sodium arsenite is added to the definite end point of the disappearance of the pink tint. The volume of the solution should not exceed 75 cc. If the silver is not precipitated, the reaction of the persulphate with the silver nitrate renders the endpoint somewhat fleeting and recurring. If conducted without delay, however, the titration may be accomplished with perfect satisfaction. The end point in this case while not so permanent is perhaps somewhat sharper than in the presence of the chloride.

When desired, a greater initial weight of the sample may be taken, the solution thereof diluted to a definite volume, the graphite and silica allowed to subside and aliquot portions withdrawn with a pipette.

SOLUTIONS REQUIRED

Sodium Chloride. Two and one-half grams sodium chloride to one litre of water.

Silver Nitrate. About 66.5 grams of silver nitrate are dissolved in one litre of water. Twenty cc. of this diluted to one litre affords a solution of which 15 cc. is equivalent to approximately .02 gram of silver nitrate.

Sodium Arsenite. A stock solution is prepared by dissolving 10 grams of C. P. arsenious acid in a boiling aqueous solution of sodium carbonate (30 grams dissolved in 250 cc. of water), with final dilution of the cold solution to volume of one litre. Sixty-two and one-half cc. of this solution are diluted to volume of one litre for the working solution of which each cc. is equivalent to approximately one-tenth per cent manganese, with an initial weight of two-tenths gram of the sample. The known manganese of a standard steel or iron is used as the basis of standardization.

Ford's Gravimetric Method

Five grams of the sample are transferred to a No. 5 glazed porcelain dish with cover glass, 75 cc. of nitric acid (1.20 sp. gr.) cautiously added and gentle heat applied until the sample is decomposed, and the solution then rapidly boiled to complete dryness. The residue is baked a short time at a moderate temperature. The dish is cooled, 35 cc. of strong hydrochloric acid are added and heat is applied until the soluble salts dissolve. Cold water is added to approximately 60 cc., the solution is filtered into a No. 5 beaker and the residue caught on an 11 cm. filter and washed with the least amount necessary of hot dilute hydrochloric acid and cold water alternately, to the disappearance of the soluble metallic salts. The filtrate is boiled to low bulk, cooled, 50 cc. of strong nitric acid are added and the solution is again boiled down to low bulk. The evaporation is repeated with successive portions of nitric acid to the complete expulsion of the hydrochloric acid and with conversion of the chlorides to their corresponding nitrates; the evaporation at this point is carried to the first indication of the separation of the nitrates as observed in the formation of a small nucleus of scum floating on the surface of the solution. After the solution has cooled somewhat, 75 cc. of strong nitric acid are added and the solution is again brought to the boiling point. To the boiling solution, crystals of potassium chlorate (five grams will be found sufficient) are cautiously added in small portions from a glass spoon, and the solution is boiled for five minutes.

The solution is allowed to cool before filtering. Filtration is effected through the medium of an asbestos plug held in a carbon filtering tube. The asbestos is prepared for use by heating with aqua regia to remove soluble lime salts and the plug is washed with strong nitric acid before using. The precipitated manganese dioxide on the filter is then washed with successive additions of strong nitric acid (free from nitrous fumes) to the practical elimination of the iron; the acid is added first to the beaker and transferred from thence to the filter. After the final washing, suction is continued until the plug is practically dry, when the rubber stopper carrying the filter is transferred to a clean flask. The filtering tube is filled with one per cent solution of ammonium bisulphite and allowed to stand about one minute, suction is then applied, successive portions of the bisulphite solution being added until the last trace of manganese dioxide is dissolved; the soluble manganese salt is finally washed from the asbestos filter with hot water. The solution is transferred to a No. 4 beaker or, if preferred, retained in the flask, 10 cc. of strong nitric acid added and the excess of the bisulphite decomposed by boiling. The manganese dioxide could be dissolved perhaps more conveniently by means of hot hydrochloric acid, but the use of the bisulphite solution obviates the possible danger of contamination by traces of soluble lime or magnesia, which in some grades of asbestos seem to be in evidence notwithstanding numerous successive treatments with the hot acid.

The solution is cooled somewhat and ammonia is added to the point of a faint permanent precipitate, followed by the addition of 15 cc. of a twenty per cent solution of ammonium acetate. The solution is boiled two minutes, filtered into a No. 5 beaker and the precipitate of the basic acetate of iron collected on an 11 cm. filter. The beaker or flask and the filter are washed twice with hot water, the precipitate is dissolved with hot dilute nitric acid and the solution returned to the vessel in which the precipitation was effected. The filter is washed with hot water until free from iron and the basic acetate precipitation and subsequent filtration repeated.

To the combined filtrates 5 cc. of glacial acetic acid are added and the solution is again brought to the boiling point; the cover glass is removed, 10 cc. of a ten per cent solution of ammonium or sodium phosphate added, and with the solution still at the boiling point and with constant stirring, strong ammonia is added to the first appearance of an incipient opalescence. The stirring is continued until the opalescence has developed into the characteristic crystalline precipitate, at which point the addition of the ammonia is continued, drop by drop and with constant stirring, until the total of 25 cc. has been added.

The precipitate is filtered at once upon an 11 cm. ashless filter and washed with dilute ammonia water (two per cent) until free from soluble salts. The filter and residue are ignited in a weighed porcelain or alundum crucible at a low temperature until the paper is burned off, and finally at a somewhat higher but still moderate temperature for ten minutes.

$$\frac{\text{Residual weight x 38.69}}{5} = \text{Per Cent Manganese.}$$

DETERMINATION OF TOTAL CARBON

Direct Combustion Method

The direct combustion of the carbon of iron or steel and their various alloys is fast coming to supersede the more tedious wet method. Certain limitations of this most excellent method, however, are to be noted. The inherent difficulty of successfully burning particles of steel of too great mass is apparent. Certain samples of both iron and steel or their alloys have been encountered of such a character as to necessitate the intimate admixture therewith of a finely divided metallic oxide, or, in the case of certain irons, fine drillings of low carbon steel to assist in the oxidation. The powder of the crushed test of white iron requires a somewhat longer time for complete combustion than the drillings from the test of gray iron but with proper care may be burned with perfect satisfaction. An essential requirement in the conditions of the method is the close control of the temperature which should approximate a constant of 1000° C. and should not fall below 960 C. A pyrometer couple will be found convenient in controlling the temperature.

The combustion is conducted preferably in a fused quartz tube in either an electric or suitable gas-fired furnace. A platinum tube may be used but is subject to damage from possible splashing of the oxidized metal and is, moreover, much more expensive than the quartz. The use of litharge or other volatile and easily reducible oxides is, of course, prohibited in the platinum tube. The quartz tube is 24 inches long by three-quarters inch or seven-eighths inch inside diameter, free from seams and selected of uniform diameter. Platinized asbestos, which may be secured at either end by short plugs of platinum gauze, is inserted for a space of five or six inches in the tube immediately following the position to be occupied by the boat. The rubber stopper at the end of the tube may be protected by the insertion of a removable plug of asbestos conveniently enclosed in a thin roll of platinum gauze. Platinum, nickel, alundum, porcelain or clay boats may be used. The dimensions, three to three and one-half inches long, by one-quarter inch deep, one-half inch wide at the bottom, flaring to five-eighths inch at the top, all inside measurements, will be found convenient. Suitable furnaces for either direct or alternating current, with transformers, rheostats, etc., to suit the individual requirements may be obtained of the trade.

The oxygen from the high pressure cylinder under control of the reducing valve is purified by passing through caustic potash solution of 1.27 sp gr. contained in washing bottles, preferably two arranged in tandem. A glass tube of convenient form and size, filled with granulated zinc, may be connected to the exit end of the combustion tube to retain possible fumes of sulphuric anhydride formed in the combustion of high sulphur irons. When the potash absorbent is used, a calcium chloride drying tube preceding the bulb or bottle is necessary.

Factor weights may conveniently be used in the direct combustion as follows: For the potash absorption and weighing of the bulb, .2727 gram or .5454 gram, where each one-tenth mg. gain in weight of the bulb is equivalent to .01 per cent or .005 per cent carbon respectively. For the barium hydrate absorption, with ignition of the barium carbonate, .304 gram or .608 gram, where each one-tenth mg. of the weight of barium carbonate is equivalent to .002 per cent and .001 per cent carbon respectively. For the titration methods it is convenient to employ for the initial weight even gram multiples, preferably 250 mg. to 500 mg.

One-quarter or one-half gram or the suitable factor weight of the sample is transferred to the boat. The boat is partially filled with ignited alundum depressed in the center in the form of a V about one inch in length, and in which the sample is spread in a compact mass. This intimate contact of the particles of iron conserves the heat for the continuous combustion of the carbon. The weighed potash container or the Meyer bulb tube, to which has been added 80–100 cc. of the barium hydroxide solution or 50 cc. of the standard potash solution, is connected with the tube and the boat is carefully pushed to its position in the center of the heat zone. The stopper of the tube is replaced and, with all connections tight, the current of oxygen is started at a rate approximating a continuous bubbling, as observed in the purifying solutions. It is essential that the tube should have acquired the maximum temperature before the introduction of the boat, a condition which will naturally obtain in the case of a continuous routine of combustion.

The first indication of the oxidation is observed in the sudden decrease of the bubbling of the oxygen through the absorption vessel. As the rate decreases the flow of oxygen is somewhat accelerated until the conclusion of the oxidation process as indicated by the recurrence of the rapid flow through the exit; the flow of oxygen is then reduced to the normal rate which is maintained for ten minutes to insure the complete oxidation of all the carbon and the final absorption of the resultant carbondioxide. The absorption vessel is disconnected, the current of oxygen discontinued and the analysis concluded by either weighing the potash bulb; titrating the standard solution of caustic potash; filtering, igniting and weighing the precipitated barium carbonate; or titrating the excess of the barium hydrate solution with a weak solution of hydrochloric acid and without preliminary filtration.

BY INCREASE OF THE WEIGHT OF THE POTASH BULB OR BOTTLE

The perfectly clean and dry bulb or bottle is at once weighed. The increase in weight as noted in connection with the initial weight of the sample is corrected to per cent carbon.

The potash container is prepared for use by carefully introducing the required volume of the solution, connecting with the apparatus and passing a current of oxygen through the hot combustion tube to the complete displacement of the air in the container. The vessel is disconnected and at once weighed. The weight so obtained furnishes the light weight for the succeeding combustion.

TITRATION OF THE CAUSTIC ALKALI

The absorption in this case is effected in a Meyer bulb tube containing 50 cc. of the potash solution, accurately measured. he contents of the tube are transferred to a flask, the tube is cleansed with freshly boiled water, three drops of the phenolphthalein solution are introduced and dilute hydrochloric acid (one part acid to one part water) carefully added until the color begins to fade. The more dilute standard acid is then added until the addition of one drop just discharges the pink tint. The excess alkali which has not entered into combination with the carbon dioxide has now been neutralized and the solution is ready for the actual titration. One drop of the methyl orange or methyl red solution is added and the standard acid added in successive portions until the addition of one drop causes the characteristic change from the yellow to the rose tint in the solution. The measure of the acid required for this titration minus the equivalent required in the blank titration and multiplied by the carbon value of the solution equals per cent carbon.

If preferred, the titration may be conducted with the phenolphthalein indicator, the measure of the standard acid required to discharge the pink tint being deducted from the blank equivalent and calculated to per cent carbon as above. This method, however, would not appear to offer any advantage over the other and obviously requires more of the standard acid.

The blank equivalent is established by passing the oxygen through the hot combustion tube and into the measured volume of the absorbent solution with final titration as outlined above. The carbon value of the acid solution is established by titration of the measured volume of the potash solution following the combustion of a standard steel. Additional confirmation may be had by titrating against a standard solution of sodium carbonate. The use of sodium oxalate in this connection is recommended.

SOLUTIONS REQUIRED

Standard Acid, one-sixth normal. Fifteen cc. hydrochloric acid (1.20 sp. gr.) diluted to one litre.

Caustic Potash, one-sixth normal. Nine and one-half grams diluted to one litre. This solution need not of necessity be absolutely one-sixth normal.

Phenolphthalein. One gram dissolved in one litre of ethyl alcohol.

Methyl Orange. One gram dissolved in one litre of water.

Methyl Red. One gram dissolved in one litre of ethyl alcohol.

FILTRATION AND IGNITION OF THE BARIUM CARBONATE

The bulb tube is detached from the train, the index finger of the left hand being simultaneously placed over the exit end in order to prevent the solution from flowing back in the tube. The solution is filtered through an 11 cm. ashless filter, the filter and precipitate are washed with freshly boiled water (six good washings will be found sufficient), ignited in a weighed platinum crucible at a moderate temperature to the disappearance of the carbon of the filter and finally at a good full heat for five minutes. The weight of the barium carbonate multiplied by 6.08 and divided by the weight taken, or with correction in agreement with the initial factor weight, is equivalent to per cent carbon. The solution and precipitate are transferred to the filter either by way of the bulb entrance with control of the flow by the index finger upon the open exit end of the tube or by control with the thumb placed over the bulb entrance with the solution poured through the exit end. The precipitate may be readily removed by shaking the tube after successive additions of the water. The washing is conducted as thoroughly and expeditiously as possible and care is exercised to avoid the passage of air unduly through the filter.

TITRATION OF THE EXCESS BARIUM HYDROXIDE

The bulb tube is detached as before, the solution and precipitate are transferred to a twelve ounce Erlenmeyer flask, and the tube thoroughly washed with freshly boiled water. Three drops of the indicator solution are introduced and the standard hydrochloric acid is added in successive small portions, while the flask is shaken, to the disappearance of the pink tint. The agitation of the solution insures the recovery of any carbon dioxide liberated upon the addition of the acid. The equivalent of the acid required in a preliminary blank titration minus the measure required in the actual titration, multiplied by the factor of the solution as determined by frequent combustions of a standard steel and in agreement with the initial weight of the sample, is equivalent to per cent carbon.

SOLUTIONS REQUIRED

Standard Hydrochloric Acid. Eight cc. of strong hydrochloric acid diluted to one litre. Freshly boiled water should be used in making up the solution. One cc. of this solution is equivalent to approximately .05 per cent carbon on a one gram basis.

Barium Hydroxide. Twenty grams of barium hydroxide crystals are dissolved in one litre of hot freshly boiled water and the flask covered and set aside to cool. When the solution has reached the room temperature, it is filtered as rapidly as possible through a 25 cm. filter into the container. The solution is preferably withdrawn from the container by means of an overflow pipette in conjunction with a suitable guard tube filled with soda lime or caustic potash solution.

Phenolphthalein. One gram dissolved in one litre of ethyl alcohol.

Solution and Combustion Method

The conditions involved in the operation of this method admit of the employment of a greater initial weight of sample than in the previously described Direct Combustion Method.

One gram, or if the barium hydroxide absorbent is to be used, a ten factor weight (.608 gram) of the sample is transferred to a No. 2 beaker or four ounce Erlenmeyer flask; 100 cc. of the solution of copper and ammonium chloride or the potassium salt are added and the covered beaker is placed on a suitable stirring machine or stirred by hand, at a temperature of 60 to 70° C. until in solution; or, if a flask is used, it is placed on a shaking machine or closed with a clean rubber stopper and shaken by hand until solution is complete.

The carbonaceous residue is collected upon a filter of purified ignited asbestos made up in a perforated platinum boat, Gooch crucible or other suitable form of holder. The residue is washed by decantation with dilute hydrochloric acid to the disappearance of color in the washings, then transferred to the filter and washed with cold water until the acid is completely removed. Preliminary drying of the residue is not essential in routine work, but where the refinement of accuracy is desired, it is recommended that the residue be dried in a hot air or steam bath at a temperature of 100° to 105° C. The residue is ignited in a platinum or silica tube, combustion crucible or other form of apparatus and in an atmosphere of pure oxygen or air free from carbon dioxide. The apparatus and the subsequent treatment of this carbonaceous residue may conveniently conform to the description of the method by direct combustion, and the final measure of the carbon established by any of the several optional methods therein described.

SOLUTIONS REQUIRED

Copper and Ammonium Chloride. Three hundred grams of the pure salt are dissolved in one litre of boiling water. After cooling, 60 cc. of strong hydrochloric acid are added and the solution is filtered through a purified asbestos plug into the container.

Copper and Potassium Chloride. One pound dissolved in one litre of water, as above, with subsequent similar treatment.

Caustic Potash. (1.27 sp. gr.). Three hundred grams dissolved in one litre of water.

DETERMINATION OF GRAPHITIC CARBON

One gram or the ten factor weight (.608 gram) is transferred to a No. 2 beaker or a four ounce Erlenmeyer flask, 40 cc. of nitric acid (1.13 sp. gr.) added and gentle heat applied until solution is complete. The solution is then boiled for a few minutes, the residue is collected upon a suitable asbestos or paper filter, washed alternately with hot dilute hydrochloric acid and water until free from iron and finally with hot water until free from acid. If the filtration has been conducted through asbestos filter, the residue may be washed with hot caustic potash solution (1.10 sp. gr.) to remove separated silica. If preferred, a few drops of hydrofluoric acid may be added to the acid solution to dissolve the silica which might otherwise interfere with the filtration.

The analysis may be concluded in either of the following optional ways:

First. The graphitic residue is collected upon a suitable filter, washed with dilute hydrochloric acid and water and ignited in the combustion apparatus, and the measure of the graphitic content established as in the case of total carbon. It will be found convenient in this case to use the ten factor weight of the sample.

Second. The filter and graphitic residue are placed in a crucible and dried to constant weight at a temperature of 110° C., then ignited until the graphitic carbon and the filter paper are completely oxidized and again weighed. The loss in weight minus the weight of the filter paper when used and multiplied by one hundred is equivalent to per cent graphitic carbon on a one gram sample.

DETERMINATION OF COMBINED CARBON

Indirect Method

The per cent graphitic carbon as found above subtracted from that of the total yields the measure of the combined carbon. If desired, a direct estimation of the combined carbon may be conducted by the color comparison method.

Color Comparison Method

The relatively exact chemical characteristics and preliminary heat treatment of the test piece and standard are universally recognized as fundamental bases of accuracy in the determination of the combined carbon of iron or steel by the color comparison method. The universal and continued use of this most convenient method in the analysis of steel products attests its efficiency within the close limits of control possible of attainment in the preparation of the steel standards. The application of the method to the determination of the combined carbon of the various grades of iron is much more limited owing to the larger and varying content of manganese and sulphur, the principal disturbing chemical factors affecting the color of the solution to be compared. It is apparent, however, that with a judicious selection of standards and careful control of all factors involved, the color comparison method may be applied to the determination of the combined carbon content of iron with a quite reasonable degree of accuracy.

The method of procedure as recommended is as follows: One gram of the sample is transferred to a dry clean beaker, flask or tube, as desired. In the presence of graphitic carbon, the use of a magnetized spatula or wire in weighing off the sample is, of course, prohibited. Thirty cc. of nitric acid (1.20 sp. gr.) are added and heat is applied until the sample is decomposed. Graphitic carbon and silica are removed by filtration, and the filtrate retained in a 100 cc. graduated flask or cylinder. The filter is washed with cold water to the disappearance of color; the solution is diluted to volume, thoroughly mixed, and 10 cc. withdrawn with a pipette and transferred to the comparison tube. The color is then compared with the color of the solution of a standard iron in a similar tube and which has been treated in exactly the same manner and with the same relative initial weight. The simple calculation involved in the relative volumes of the two solutions yields the per cent carbon in the sample.

A convenient aliquot portion of the above solution may be employed for the determination of manganese by the persulphate color method.

DETERMINATION OF TITANIUM

Five grams of the sample are transferred to a No. 5 glazed porcelain dish or to a No. 4 beaker, with cover glass; 50 cc. of strong hydrochloric acid are added and the sample is digested until completely decomposed. Practically all of the titanium is said to remain insoluble with the silica and graphitic carbon. The insoluble residue is collected upon an 11 cm. filter, washed a few times with hot water, ignited in a platinum crucible and the silica volatilized with hydrofluoric acid in the presence of a few drops of sulphuric acid. The residue is then carefully ignited to the complete expulsion of the hydrofluoric acid, which if retained prohibits the subsequent colorimetric determination of the titanium.

Should it be desired to determine the usually quite negligible amount of titanium in the filtrate from the insoluble residue, it is recovered as follows: The filtrate in a No. 5 beaker is diluted to 250 cc. and strong ammonia added to the first appearance of a precipitate which slowly dissolves upon stirring. Dilute ammonia (two per cent) is added to a faint permanent precipitate, which is then dissolved by the addition of 15 cc. of a ten per cent solution of hydrochloric acid. The precipitate thus formed should dissolve rather slowly following vigorous stirring of the solution. One hundred cc. or more of a twenty per cent solution of sodium hyposulphite are added and the solution in the beaker is stirred until the iron is completely reduced and the free sulphur begins to separate. The solution is then boiled for ten minutes and the precipitated titanic acid allowed to subside and collected upon an 11 cm. filter. The filter and precipitate are washed free from soluble salts with dilute acetic acid (two per cent) and ignited in the crucible containing the ignited residue from the previously conducted volatilization.

The combined residues are fused with four grams of sodium carbonate, the melt is disintegrated by boiling with hot water, and the insoluble sodium titanate is collected upon a 9 cm. filter and washed with hot water containing a little sodium carbonate. Hot dilute sulphuric acid is added to the crucible which is then heated until the titanate is completely dissolved. The filter is spread upon the bottom of a No. 2 beaker, the contents of the crucible transferred thereto, and the crucible washed thoroughly with hot water. The beaker is then heated until the titanium salt dissolves, when the paper is removed and its burden of titanium sulphate returned to the beaker by washing with hot water. The solution is then transferred to the color comparison tube or if necessary to a graduated flask and aliquot portions taken. Shreds of filter paper which may be observed in the solution are removed by filtration.

In the color comparison, 5 cc. of C. P. hydrogen peroxide are added to the solution in the comparison tube and the solution is diluted to a volume yielding a color convenient for the subsequent comparison. A color equivalent to .005 gram of titanium in 100 cc. of solution will be found convenient. Water acidified with dilute sulphuric acid (equal parts acid and water) is then added to the standard tube to a volume allowing of subsequent necessary increase, 5 cc. of the hydrogen peroxide is added and the standard titanium solution added from a graduated burette in successive small additions until the colors agree. The measure of the standard solution required multiplied by its value in terms of titanium and corrected to agreement with the initial volume and weight is equivalent to per cent titanium. If the color of the solution yielded by a convenient weight of the sample is of insufficient depth for an accurate comparison, adjustment may be made as follows: A measured volume of the standard titanium solution, sufficient to furnish the required depth of color is added to the solution being tested and the comparison conducted as above described. The volume of the standard solution required in the comparison minus the equivalent previously added to the test solution is calculated to per cent titanium. The volume of the two solutions must, of course, be identical in the final comparison.

In preparing the standard titanium solution 1.05 grams of ignited C. P. titanic acid are fused with ten grams of sodium carbonate. The melt is digested with 100 cc. of hot water to the complete solution of the soluble alkali which is then filtered from the insoluble titanate. The residue of sodium titanate is washed with hot water containing a little sodium carbonate and dissolved from the filter with 100 cc. of dilute sulphuric acid (equal parts acid and water) and the solution diluted to one litre. The titanium equivalent of this solution is ascertained by igniting and weighing the precipitated titanic acid of an aliquot portion following a separation with sodium hyposulphite as previously described. The ignited salt will be found to contain approximately 95.6 per cent titanic acid. One cc. of the solution in the above proportion will therefor contain 0.6 mg. of titanium.

A gravimetric determination of the titanium in the iron may be conducted in the same manner, but inasmuch as in the colorimetric method the titanic acid as separated need be only relatively free from contamination by occluded salts, it is apparent that the latter method may be used to advantage, especially where many such determinations are required.

DETERMINATION OF COPPER

Gravimetric Method

Five grams of the sample are transferred to a glazed porcelain dish, 65 cc. of nitric acid (1.20 sp. gr.) are added and the covered dish is heated until solution is practically complete. Twenty-five cc. of dilute sulphuric acid (equal parts acid and water) are then added and the solution is evaporated to fumes of sulphuric anhydride. Ten cc. of the dilute sulphuric acid followed by 50 cc. of hot water are added, the residue is heated until in solution, and the solution is filtered into a No. 4 beaker and the filter washed with hot water. The filtrate is diluted to 300 cc., heated to boiling and, with the addition of 25 cc. of concentrated ammonium bisulphite solution, the boiling continued to the complete reduction of the iron. Thirty cc. of a twenty per cent solution of sodium hyposulphite are then added and the boiling is continued for five minutes or until the precipitated copper sulphide has coagulated. The precipitate is collected upon an ashless 11 cm. filter, washed with dilute nitric acid (two per cent) and hot water, carefully ignited and weighed. The weight of the copper oxide as noted, multiplied by sixteen (80 divided by 5) equals per cent copper. Too great a temperature in the ignition causes the copper oxide to fuse on the crucible. As the copper oxide is somewhat hygroscopic, as are also some porcelain crucibles, less error is encountered by igniting in platinum.

The ignited copper oxide carries with it traces of contaminating iron. If it be desired to correct this usually negligible error, the impure oxide is dissolved in the crucible with 10 cc. of strong nitric acid, the solution transferred to a No. 2 beaker and diluted to 100 cc.; the iron is then removed by an ammonia precipitation. The precipitate so obtained is collected upon a 9 cm. filter, washed with hot water, ignited in the crucible in which the previous ignition was conducted and the weight of ferric oxide noted. This weight is deducted from the weight of the impure copper oxide and the correction applied.

Volumetric Method

The nitric acid solution of the impure copper oxide in the No. 2 beaker obtained as above described, is rapidly evaporated to the removal of the bulk of the free acid, and the solution diluted with cold water to volume of 150 cc. Strong ammonia is then added from a burette until the addition of a final drop causes the permanent blueing of the solution, after which there is added by means of a pipette six drops of acetic acid. Ten cc. of a forty per cent solution of potassium iodide are added and the standard sodium hyposulphite solution is run in until the color of the liberated iodine has almost disappeared. Ten cc. of the starch solution are now added and the addition of the standard sodium hyposulphite solution is continued to the final disappearance of the blue. The number of cubic centimeters of the standard solution required multiplied by its value in terms of copper and divided by five equals per cent copper in the sample.

The value of the standard hypo solution is determined by titration of a solution of pure copper or by titrating the solution of a steel of known copper content. The apparent large excess of the potassium iodide employed is because of its relation to the final endpoint in the titration, the sharpness thereof decreasing in proportion as the excess of the iodide is decreased; the presence of ammonium salts in the solution also tends to lessen the permanency of the endpoint, hence, the necessity for the preliminary evaporation of the acid solution.

If necessary, the time required for the volumetric determination may be materially lessened by initial solution of the sample in 50 cc. of dilute sulphuric acid (one part acid to one part water), and the evaporation to dryness and filtration from the siliceous residue omitted. The iron in this case not being oxidized, the boiling with the ammonium bisulphite is also omitted. The copper oxide so obtained is contaminated to a greater degree by occluded iron, which if it be present in the final titration is prejudicial to a satisfactory endpoint. This iron is, however, readily removed by filtration following the evaporation of the nitric acid solution previous to the addition of the ammonia. It is apparent also, that following the nitric acid solution of the sample, the preliminary treatment with ammonium bisulphite in the gravimetric method may be dispensed with, as the reduction may be accomplished by the addition of a sufficient excess of the sodium hyposulphite solution at the time of the precipitation of the copper sulphide. The precipitate formed under such conditions, however, carries an unduly large burden of separated sulphur, the presence of which would appear undesirable.

SOLUTIONS REQUIRED

Standard Sodium Hyposulphite. Eight grams to one litre. One cc. is equivalent to approximately .002 gram copper.

Starch Solution. The solution as used in the volumetric determination of sulphur.

ANALYSE DE L'ACIDE VANADIQUE COMMERCIAL

NOTE PRÉSENTÉE PAR G. CHESNEAU
Professeur d'analyse minérale et Directeur du Bureau d'Essais de l'Ecole des Mines de Paris

L'industrie minière livre actuellement par tonnes aux métallurgistes de l'acide vanadique destiné à la fabrication du ferrovanadium it des nombreux alliages vanadiféres de plus en plus employés dans les constructions mécaniques. Ces acides vanadiques commerciaux contiennent environ 15 à 20% d'impuretés provenant soit des minerais (oxydes de fer, de manganèse. alumine, silice, arsenic, phosphore, etc., soit des réactifs employés dans le traitement (notamment de la soude qui est entrainée en quantité considérable avec l'acide vanadique, lorsque celui-ci a été obtenu au moyen de vanadate sodique produit par fusion du minerai avec du carbonate de soude). Si l'acide vanadique a été simplement desséché, il est facilement attaquable par les acides et l'analyse ne présente pas d'autres difficultés que celles, d'ailleurs très grandes, des séparations habituelles du vanadium d'avec les autres éléments; mais, comme il contient alors près de 10% d'eau les fabricants d'acide vanadique trouvent préférable en général de le calciner pour le rendre anhydre, de façon à augmenter sa teneur en acide vanadique pur et à le rendre directement utilisable dans les traitements métallurgiques. Or, une fois calciné, l'cide vaanadique commercial n'est plus que partiellement attaqué par les acides, et son analyse complète offre alors de grandes difficultés: il me parait donc intéressant de faire connaître la méthode à laquelle m'a conduit leur étude.

1. *Humidité; perte au feu.* L'humidité se détermine sur 1 gr. chauffé à 120° et la perte au feu sur la même prise d'essai, calcinée au rouge au moufle en capsule de platine tarée; il peut y avoir *gain* au lieu de *perte* au feu, si le produit commercial a été chauffé en atmosphère réductrice ou en présence de corps réducteurs, ayant donné des oxydes inférieurs du vanadium.

2. *Acide vanadique; silice; fer; manganèse; chaux; magnésie.* 1 gr. du produit bien pulvérisé est fondu en creuset de platine avec 2 à 3 gr. de carbonate de soude mélangé de 1/10 de nitre. La masse refroidie est reprise par l'eau bouillante: V_2O_5, SiO_2 et Al_2O_3 passent en solution, tandis que les oxydes de fer et de manganèse restent insolubles avec les carbonates de chaux et la magnésie.

Le résidu insoluble lavé sur filtre est redissous par l'acide chlorhydrique et analysé par les méthodes habituelles; le paroxyde de fer obtenu et le filtrat final de la magnésie contiennent quelques milligrammes d'acide vanadique entràiné: on reprend le peroxyde de fer par fusion au carbonate de soude ét lessivage à l'eau chaude qu'on rajoute après l'avoir audifiée par l'acide azotique, au filtrat de la magnésie également audifié, on concentre et dans la liqueur réduite à un petit volume on dose colorimétiquement à l'eau oxygénée cette trace d'acide vanadique.

La solution alcaline contenant V_2O_5 SiO_2 et Al_2O_3 est audifiée par l'acide azotique évaporée à sec pour insolubiliser la silice, puis reprise par l'acide azotique; on filtre la silice puis le filtrat est rendu faiblement ammoniacal et chauffé; s'il se produit un précipité d'alumine (ou de PO_4Al et AsO_4Al) on le filtre calcine et pèse puis y dose comme-ci dessus colorimétrique ment les traces de V_2O_5 entrainé.

Dans le filtrat ammoniacal bouillant on précipite l'acide vanadique au moyen du nitrate de baryum par la méthode de *A. Carnot*[1] donnant le corps $V_2O_5\ 2BaC$ qui calciné contient 37, 24% de V_2O_5. Le précipité n'est pas il est vrai rigoureusement complet mais cette méthode offre ainsi que je l'ai constaté, le très grand avantage sur d'autres vanadates plus insolubles que le corps obtenu a une composition bien constante et que la méthode n'ayant introduit dans la solution que des sels incolores il est très facile aprës avoir concentré et acidifié la liqueur d'y doser colorimétriquement à l'eau oxygénée les quelques milligrammes de V_2O_5 restés en solution.

Du poids de vanadate de baryum obtenu, on doit, le cas échéant, retrancher sous forme de phosphate et d'arséniate de baryum

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[1] Comptes-rendus de l'Académie des Sciences de Paris, t. 104, p. 1803; 1887.

trimétallique les quantités correspondant aux teneurs de $P_2 O_5$ et $As_2 O_5$ obtenues plus loin (et dépassant celle qui a pu ètre entrainée par l'alumine précipitée ci-dessus).

3. *Soude.* La soude est dosée aisément par la méthode classique de *Lawrence Smith*[1] sur 1 gr. mais en ayant soin d'ajou ter au mélange de carbonate de chaux (8 gr.) et de chlorhydrate d'ammoniaque (1 gr.) 3 gr. de carbonate de baryum pour retenir sûrement l'acide vanadique dans le résidu insoluble; on obtient ainsi du chlorure de sodium pur et des filtrats sans trace appréciable d'acide vanadique.

4. *Arsenic et phosphore.* On fait fondre 5 gr. du produit avec 10 gr. de carbonate de soude la masse est reprise par l'eau bouillante, on acidifie par HCl, traite à froid par SO_2 pour réduire l'acide arsénique à l'état arsénieux; chasse SO_2 par la chaleur, puis fait passer à froid un courant d'hydrogéne sulfuré et dose enfin l'arsenic dans le précipité par les méthodes ordinaires.

Le filtrat, bouilli pour expulser $H_2 S$, est traité par 2 à 3 cmc. d'acide sulfurique pur, puis concentré à chaud jusqu'à fumées blanches de $SO_4 H_2$ pour expulser HCl; on a sinsi un petit volume de liqueur bleue contenant le vanadium à l'état d'acide hypovanadique, auquel on ajoute son volume de réactifmolybdique et quelques grammes de nitrate d'ammoniaque puis chauffe 2 h. à 40°: Comme à cette température l'acide hypovanadique n'est oxydé que très lentement par l'acide azotique étendu, tout le phosphore est précipité sans que la liqueur cesse d'etre bleue et le précipité de phosphomolybdate d'ammoniaque n'entraine pas de quantités appréciables d'acide vanadique.

Cette méthode appliquée à un échantillon d'acide vanadique commercial, prélevé sur un millier de kilogrammes, m'a donné les résultats suivants:

	Pour 100:
Acide vanadique ($V_2 O_5$)	84,9
Soude (Na_2O)	9,6
Peroxyde de fer (Fe_2O_3)	3,9
Oxyde de manganèse (Mn_3O_4)	0,2
Chaux (CaO)	0,6

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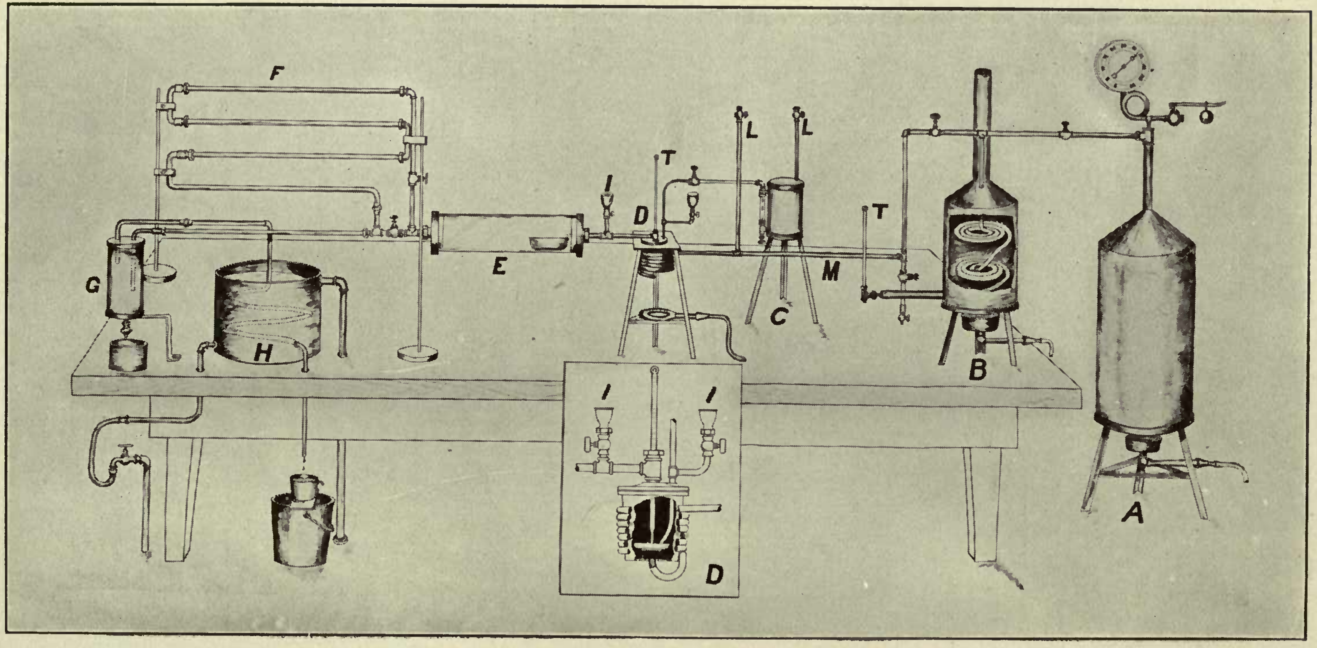
[1] American Journal of Science and Art, t. 1, p. 269; 1871.

	Pour 100:
Magnésie	traces
Silice (SiO_2)	0,5
Acide arsénique (As_2O_5)	0,65
Acide phosphorique (P_2O_5)	0,02
Humidité	0,2
Total:	100,57
Gain à la calcination	0,3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APPARATUS FOR THE EXAMINATION AND STUDY OF THE BEHAVIOR OF VALVE AND CYLINDER OILS AND OTHER PETROLEUM LUBRICATING OILS IN SATURATED AND SUPERHEATED STEAM, CARBON DIOXIDE, AIR AND OTHER CASES

By P. H. Conradson

Chief Chemist, Galena-Signal Oil Company, Franklin, Pa.

The introduction of highly superheated steam in locomotive and stationary engine practice has brought about the necessity of adding tests to the ones usually made of cylinder oils, whether straight petroleum stock, or the mixture of same with smaller or larger amount of saponifiable fats.

The writer has constructed and used an apparatus for some time, in the investigation of cylinder oils suitable for the lubrication of valves and cylinders, in connection with the use of highly superheated steam in locomotive service.

The apparatus consists essentially as follows (See the photographic cut):

A—Small steam boiler with gas, steam gauge and pipe connections.

B—Superheater with armored thermometer "T" and steam connections (a small circulating water heater with double copper coils, answers very well).

C—Slight feed lubricator with connections.

D—Steam vessel (a conical cast iron retort for distilling mercury, about 95 mm. deep and about 75 mm. in diameter at top provided with two strong screw clamps to keep the lid tight, answers very well) surrounded on the outside as indicated in the photographic cut by a coil of copper pipe 5 to 6 mm. inside diameter, for further heating of the steam and gases used in the tests: this coil is tapped into the bottom of the steam vessel containing, upon a suitable support, a dish about 25 cc. capacity (in ointment box about 5 mm. in diameter, 18 to 20 mm. high) into which the oil to be examined either is fed drop by drop from the sight feed lubricator "C" or a given amount of oil is poured into the cup "I." Through the lid is inserted an armored thermometer "T," shown on photograph reaching down into the dish.

The steam vessel thus arranged and connected up is surrounded and covered by a suitable asbestos hood. "L," pipe connections for the gases used.

E—Glass cylinder of heavy glass about 200 mm. long 18 to 20 mm. inside diameter, containing as shown in the photograph a small rectangular boat or dish; beyond "E" is a glass tubing system "F" connected up with brass fittings; each glass tube is about 500 mm. long, 8 to 9 mm. inside diameter, and at the further end is attached a steam separator and oil collecting vessel "G," consisting of an ordinary glass chimney fitted up with brass caps, and to this by means of copper tubing is connected the condenser "H."

In this apparatus any desired temperature may be maintained at least up to 1000° Fah., which is 300 to 400 degrees higher than is required under most exacting service conditions, as far as superheated steam temperature is concerned.

In studying the behavior of valve and cylinder oils in an atmosphere of superheated steam, the steam is passed from the small steam boiler through the superheater "B" and into the steam vessel "D" through its pipe coil (lamp being lit under "D"), and out through E, F, G, and H.

When the temperature reaches and is regulated in "D" to 400° Fah., oil is fed drop by drop from the sight feed lubricator "C" or the cup "I" is filled; the steam is shut off and the valve in the cup "I" opened, letting the oil run into the dish in "D," the steam valve is then very gradually and carefully opened so as to let through any desired amount of steam.

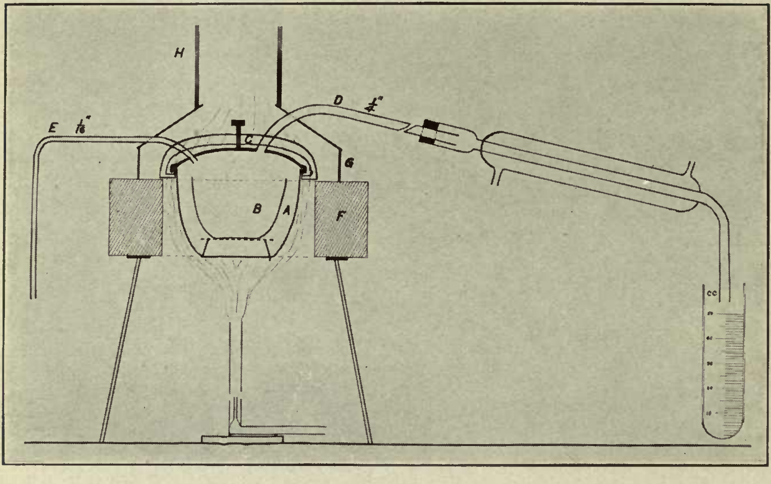
The temperature in "D" is maintained for a given length of time at or near 400° Fah., noting if any oil vapors are coming over; by shutting and opening the steam valve it is easy to see if any vapors are coming over with the steam.

The temperature is increased in increments of 25 to 50° Fah., at a time, until the desired temperature is reached, noting the behavior of the oil vapors passing on with the steam through the glass pipe system, etc. It is interesting to note the behavior of the cylinder oils containing rather a large percentage of saponifiable fats or fat oils. These generally come over to a great extent at much lower temperatures than the main portions of the petroleum stock oils that are generally used in compounding first-class cylinder oils.

In further study of the behavior of oils, the boat in the glass cylinder "E" may be filled through the cup "I" to the left, and subjected at various temperatures in slow currents of superheated steam, carbon dioxide and air or mixtures of these. The glass cylinder "E" during the last test is surrounded by heavy asbestos covering to prevent radiation.

The cylinder oils may leave a residue in the dish in "D" at steam temperatures below 700° Fah.; if so, such residue should give a clear solution in 90 cc. 0.65 sp. gr. (87°B) petroleum ether (Pennsylvania) and show no precipitate on standing. At steam temperatures of 850 to 900° Fah., generally all the oil has volatilized with the steam, and good oils should leave no carbonaceous or coky residue.

While this apparatus was principally designed for the study and behavior of valve and cylinder oils in atmospheres of steam at various temperatures as above indicated, it can very readily be adapted for the study of other oils at various temperatures in currents of air, carbon dioxide or other gases or mixtures of these with and without steam.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APPARATUS AND METHOD FOR CARBON TEST AND ASH RESIDUE IN PETROLEUM LUBRICATING OILS

By P. H. Conradson
Franklin, Pa.

In the examination of lubricating oils, especially those intended for gas and oil engines, air compressors, steam turbines, valve and cylinder oils, etc., the writer has found that the carbon residue from the so called "carbon test" at times contains other materials than carbon, such as chemicals from imperfect refining treatment, which would be considered as carbon unless further examined.

The following method and apparatus as shown in accompanying photograph have proven satisfactory in most cases.

The apparatus consists of an iron crucible or retort (A) (Skidmore's Normal School or similar) of about 200 cc. capacity. Approximate inside dimensions: diameter on top 80 mm. ($3\frac{1}{8}$ in.), bottom 45 mm. ($1\frac{3}{4}$ in.), height 55 mm. ($2\frac{1}{4}$ in.). Inside of the crucible is placed upon a suitable support either a glass crystallizing dish (B) about 65 mm. ($2\frac{5}{8}$ in.) in diameter or a platinum dish about 70 to 80 cc. capacity; the latter is preferred for further study of the carbon residue. In the lid of the crucible or retort are attached two tubes: one, an exit or delivery pipe (D) 7 to 8 mm. ($\frac{1}{4}$ in.) in diameter bent as shown in the cut, and if so desired attached to a condenser, the other (E) with small bore 2 mm. (1/16 in.) in diameter. The object of the latter is to blow out the heavy fumes generally produced, at the end of the distillation process.

The test is conducted as follows: 35 grams of the oil are placed in the weighed dish which is set in iron retort or crucible, the cover with its pipe connections is securely clamped down (C) (an asbestos washer is found suitable to make a tight joint).

The apparatus thus ready is put on an asbestos block resting on a tripod and covered as indicated in the photograph with a sheet iron or asbestos hood (G) and on top of this a clay chimney (H) so as to distribute the heat uniformly during the process. To get the upper part of the apparatus hot at the beginning, a large gas flame is used at the start for a few minutes, then lowered; the distillation should be uniform and at the rate of 1 cc. per minute. The long exit pipe should be kept comparatively cool with water-soaked waste in case a condenser is not used. At the end of the distillation, the flame is raised gradually to make the bottom and lower part of the apparatus red hot at least when heavy fire test oils such as cylinder oils are tested, and through the inlet pipe attached to a rubber tubing is momentarily blown at the last CO_2 or other suitable gases to drive out the heavy, dense fumes or vapors.

After cooling, the dish containing the carbonaceous residue is weighed, the latter ground fine and leached out first by boiling with water (water solution is tested with litmus paper for alkalinity and a few drops with Silver Nitrate solution for chlorides), next digested and boiled with dilute hydrochloric acid (1+1), filtered, washed, dried and weighed again. The difference in weight, if any, gives approximately the amount of foreign matter in the carbon residue. The carbon residue transferred back to the platinum dish is carefully burned off with a little pure ammonium nitrate. If any residue is left it is weighed and deducted from the last carbon weight and dissolved in hydrochloric acid. The water and hydrochloric acid solutions are united and examined, qualitatively or quantitatively as the case may require, for impurities such as iron, alumina, lime, sulphuric acid and soda. (Some petroleum lubricating oils are compounded with lead, aluminum, zinc, lime or magnesium oleates held either in solution or suspension or both; before making the above test it is well to ascertain first if any of these compounds are present).

	Carbon Residue per cent	Impurities in Carbon Residue per cent
Turbine Oil	0.02	None
1—Gas Engine Oil	0.53	0.126 NA_2SO_4
2—Gas Engine Oil	0.71	0.103 NA_2SO_4
3—Air Compressor Oil	0.66	0.092 NA_2SO_4
4—Motor Oil	0.78	0.059 NA_2SO_4

Sulphur determination in No. 1 Gas Engine Oil gave according to Conradson's method:

In products of combustion (lamp), 0.08% Sulphur.

In wick from the oil (0.074% SO_3), 0.131% NA_2SO_4.

APPARATUS AND METHOD FOR SULPHUR DETERMINATION IN PETROLEUM ILLUMINATING AND LUBRICATING OILS

By P. H. Conradson
Franklin, Pa.

The methods generally used in determining the sulphur in petroleum, illuminating and lubricating oils do not fully give either the total amount of sulphur compounds that might be present or how they occur. The writer has found that in many inferior, poorly refined or treated petroleum oils large percentages of the total sulphur compounds present may be due to sulphonates or sulphates, which altogether escape notice in the so called lamp methods where the oil is only partly consumed in the lamp; while in the direct oxidation methods no distinction is made.

In the examination of the illuminating (kerosene) oils used in railroad service, such as in locomotive headlights or track signal lamps (long time burner lamps) which latter require an oil with hardly any diminution in the intensity of light or candle power for 175 to 250 hours' continuous burning with no attention; or lubricating oils, such as used in steam turbines, gas or oil engines, superheated steam valve and cylinder lubrication, high pressure air compressors or high vacuum air pumps; it is essential to differentiate between the sulphur compounds that might be present in the oils. Therefore, the writer has found it necessary not only to burn a larger amount of oil in the lamps, but also to consume all the oil in the oil fount and make a careful examination of the sulphur compounds that may remain in the wick from the oil.

The accompanying photographic cut of the apparatus is self explanatory — using ordinary small kerosene burners with chimneys well washed and dried cotton wicks about 3 mm. ($\frac{1}{8}$ in.) in width. The lamp founts for the illuminating oils are ordinary glass beakers; for the lubricating oils, funnels having the stems cut off and fastened to a metal socket. The burners are inserted in a small disk (lid of an ointment box with a hole cut to fit the burner). Filter tubes of strong glass with stem bent at right angles to fit snugly over the long arm of the stoppered absorption tubes; the latter are about 350 mm. (14 in.) in length between the constriction and exit tube, the diameter about 25 to 35 mm. (1 in. to 1¼ in.), and contain small glass beads to a depth of about 80 mm. (3 in.). (In the cut the second absorption tube of the apparatus to the right is wrongly connected.)

The products of combustion are aspirated through carbonate of soda solution containing 6 grams of Na_2CO_3 in one liter of water and standardized with 1/10 normal hydrochloric or sulphuric acid. In testing, place 25 to 50 cc. of the soda solution in the first absorption tube; at the end of the operation the soda solution is run into a beaker and the chimneys, glass filter tubes and absorption tubes are rinsed out with water and the solution with the washings is either titrated, using methyl orange as an indicator, or the solution may be oxidized with bromine and hydrochloric acid precipitated with barium chloride solution in the usual way. Calculate to sulphur (S). The wicks are separately treated and examined for sulphur compounds that may remain in the same from the oil as hereinafter described.

ILLUMINATING OILS

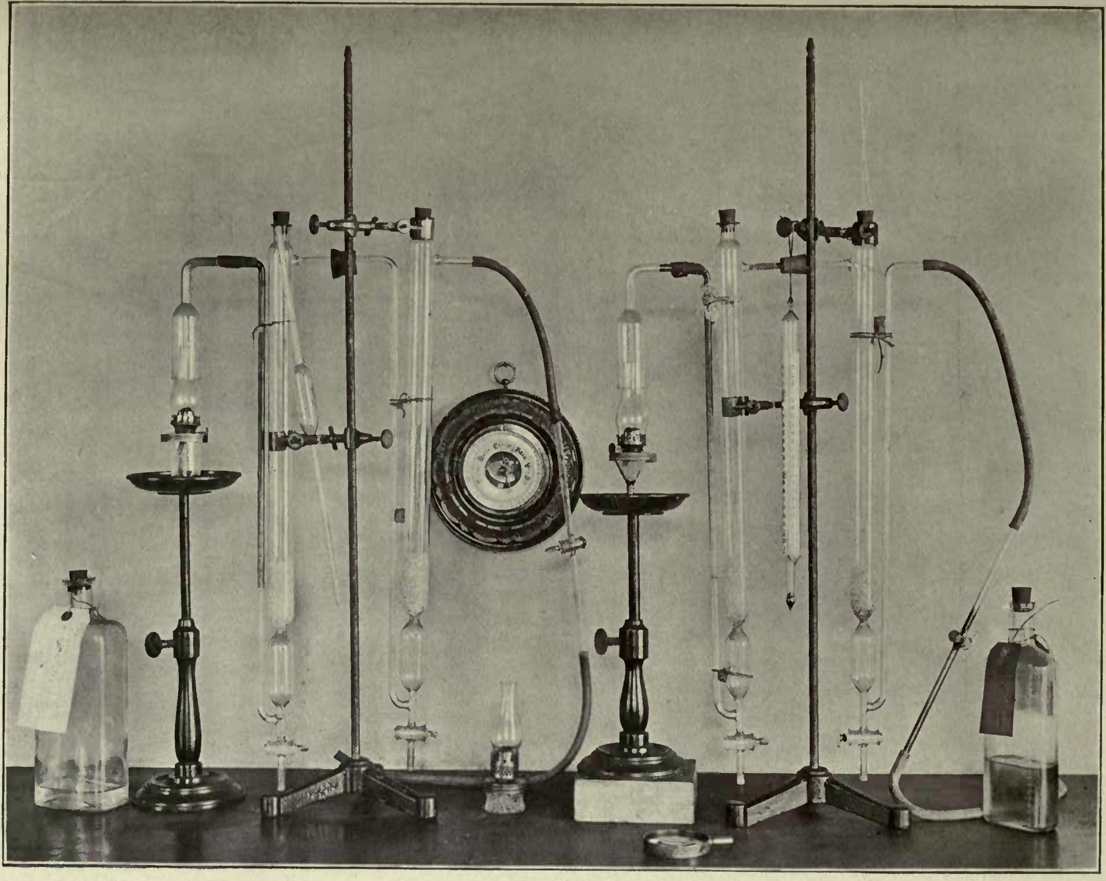
For low sulphur oils such as kerosenes made from Pennsylvania crudes, 15 to 20 grams of oil are used.

For kerosenes made from Western crudes containing larger percentages of sulphur compounds, 10 to 15 grams are used.

For kerosene oils intended for severe railroad service, either for headlight oil purposes or in long time burner signal lamps, it is well to make two sulphur determinations, one as above indicated, the other as follows:

425 cc. of the oil are carefully distilled in a 600 cc. Engler's distilling flask at the rate of 2 to 4 cc. per minute (the slower rate at the beginning and at the end), until 400 cc. have come over; the Engler's flask is placed on an asbestos gauze and covered over with asbestos wool up to the top of the neck. The thermometer bulb as usual is placed opposite the exit tube.

The 25 cc. residue in the distilling flask is transferred to a bottle



Apparatus and Method for Sulphur Determination in Illuminating and Lubricating Oils.

and if as often happens with ordinary or poorly refined kerosene oils a deposit or sediment is formed, more or less adhering to the sides and bottom of the flask, it should be carefully removed and added to the residue in the bottle as follows: Use successively ethyl ether, chloroform, 95% ethyl alcohol and hot water, as the case may require. The liquids are united and evaporated in a small dish and the residue is transferred to the bottle containing the 25 cc. oil residue with some of the latter. The sulphur compounds are then determined by burning the whole or part of the above well mixed residue to dryness in the apparatus above described.

LUBRICATING OILS

Five to ten grams of lubricating oils are burned to dryness in the lamps as stated with kerosenes. Spindle oils, thin turbine oils and automobile oils will feed through the wicks until they are all consumed, with possibly once or twice trimming of the formed crust; with thick, high viscosity oils, 5 to 8 cc. of highly refined low sulphur kerosene are added and the mixture is burned to dryness or practically so and then 2 cc. more of the kerosene oil are added and burned to dryness.

The soda solution and washings are treated as above described, deducting for the sulphur in the 5 to 10 cc. of added kerosene.

The wicks from the above described lamp tests are treated as follows: cut same in small pieces, transfer to a 50 cc. porcelain crucible, add 0.200 gram pure dried carbonate of soda and 5 cc. 1.42 sp. gr. nitric acid, digest on steam or water bath (cover crucible with inverted lid) till the fibers are disintegrated, then add 2 grams pure crystallized magnesium nitrate, continue the digestion, gradually raising the temperature on hot plate or protected gas flame till the organic matter is destroyed and most of the nitrates decomposed, leaving a white residue; after cooling add sufficient bromine water and hydrochloric acid, boil, dilute and precipitate with barium chloride in the usual way and calculate to sulphuric acid (SO_3). This includes the SO_3 both in form of sulphate and sulphonates, if both are present; if it is desired to estimate the latter separately, boil the wicks with 10 to 15 cc. strong barium hydrate solution, dilute to 100 cc. with boiling water, filter and wash. The filtrate is either oxidized with bromine and hydrochloric acid, or evaporated with a few drops of nitric acid to dryness and slightly ignited, and the residue treated with hydrochloric acid and boiling water. The insoluble $BaSO_4$ in either case is calculated to SO_3 in sulphonates.

The remaining wicks with any insoluble barium salts are then oxidized with nitric acid and magnesium nitrate, the residue is taken up by boiling with bromine water and hydrochloric acid; the insoluble if any (barium sulphate) calculate to SO_3 present in the oil as sulphates.

The usual precaution of making blank tests with the chemicals or reagents and wicks should not be omitted.

Illuminating Oils	Sulphur in lamp calculated to S per cent	Sulphur compounds in wick from sulphonates, and sulphates calculated to SO_3. per cent
1 Kerosene Original	0.015 S.	None
2 Kerosene Original	0.035 S.	Trace
2a Kerosene in 25 cc. Residue	0.038 S.	Trace
3 Kerosene Original	0.071 S.	0.0075
3a Kerosene in 25 cc. Residue	0.0135 S.	0.013
4 Kerosene Original	0.018 S.	None
4a Kerosene in 25 cc. Residue	0.057 S.	
Lubricating Oils		
1 Turbine Oil	0.035 SO_3	None
2 Turbine Oil	0.098 SO_3	0.098
3 Engine Oil	0.354 SO_3	0.018
4 Machinery Oil	0.345 SO_3	0.032
5 Heavy Gas Engine Oil	0.080 SO_3	0.074

A STUDY OF THE SENSITIVENESS OF THE BEAD AND LEAD DIOXIDE TESTS FOR MANGANESE WITH SPECIAL REFERENCE TO THE INTERFERENCE OF IRON

By L. J. Curtman and A. D. St. John
New York

The object of this work was to determine first the delicacy of the bead and lead dioxide tests for manganese when this metal alone is present and second the influence of iron on these tests, since in the ordinary qualitative procedure, the manganese and iron are tested for in the same precipitate.

The Bead Test.— The bead tests were made in the customary way; that is a sodium carbonate bead on a loop of platinum wire of approximately 3 mm. in diameter with a volume of about 0.03 cc. was fused with a small quantity of the metallic compound, slightly cooled, and then touched while still quite hot to powdered potassium chlorate. A special procedure referred to below as "reheating," consisted in bringing the carbonate bead containing the manganese compound and adhering potassium chlorate into the upper part of the Bunsen flame, heating to quiet fusion[1], and finally cooling, preferably by contact with a cold surface, such as a porcelain plate, until almost cold. By this "reheating" process a more intense coloration was produced, and in cases where large amounts of iron were present, it had the effect of concentrating the coloration in certain parts of the bead notably near the wire.

Tests were first made to determine the minimum quantity of manganese which would give a green coloration to the bead. To this end one drop (1.05 cc.) of a standard manganese chloride solution was carefully absorbed in a sodium carbonate bead that had been previously fused and cooled; the wet mass was then slowly and cautiously dried by heating the wire (away from the

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[1] Care must be exercised in this fusion to lose none of the bead through sputtering which may be caused by the use of too much chlorate or by too rapid heating.

bead) and finally fused and brought in contact with potassium chlorate. This procedure obviated the apparent difficulty of introducing qualitative amounts of precipitate into the bead and was the method employed in all the bead tests except where otherwise stated. The following results were obtained:

TABLE I

SUBSTANCE $MnCl_2.4H_2O$

Quantity of Mn	Result
0.05 mg.	Very good green
0.02 mg.	Very good green
0.005 mg.	Good green
0.002 mg.	Fair green
0.001 mg.	Doubtful but fair on reheating
0.0005 mg.	Trace of green on reheating — limit

If we consider the volume of the bead 0.03 cc. and its sp. gr. 1. (in order to make a rough comparison with other color reactions which are carried out in aqueous solution), the limiting test would show a delicacy of one part in 60,000.

Having determined the sensitiveness of the test when manganese alone is present, the next step was to investigate the interfering influence of iron. Accordingly standard solutions of $FeCl_3.6H_2O$ and $MnCl_2.4H_2O$ were mixed in varying proportions and precipitated by the addition of an excess of sodium hydroxide. A small portion of the filtered precipitate was taken up on the bead and the test completed in the usual way. The following results were obtained.

TABLE II

Parts Mn	Parts Fe	Result
1	1	Very good
1	2	Very good
1	3	Good
1	4	Fair
1	5	Fair
1	6	Fair

Up to this ratio a small amount of the wet precipitate was used equal to about one quarter of the bulk of the bead. With increasingly large amounts of iron, however, more of the precipitate was taken up, and reheating resorted to with the following results.

TABLE III

Parts Mn	Parts Fe	Result
1	25	Good
1	50	Good
1	100	Good
1	500	Good
1	1000	Fair

In the last two tests the blast lamp was used, and a quantity of the precipitate equal approximately to three or four times the volume of the bead was taken up in small portions, successively dried, and reheated several times. These results suggested that the iron did not interfere except in so far as it prevented sufficient manganese from being introduced into the bead to give the test; for if the same quantity of precipitate is to be employed in each test, it is obvious that the higher the ratio of iron to manganese, the smaller will be the quantity of the latter that will be contained in the portion taken for the test. The tests were therefore repeated with sufficient manganese (0.005 mg.) in each case to give a good color and to this amount were added varying quantities of iron. In these tests the solutions were not precipitated but absorbed in the bead in the manner already described.

The following results were obtained:

TABLE IV

Parts Mn	Parts Fe	Result
1 (0.005 mg.)	100	Good
1 (0.005 mg.)	200	Good
1	500	Good
1 (0.005 mg.)	1000	Good
1 (0.005 mg.)	2000	Good

In all the above experiments the beads were reheated; in the last test, this was repeated several times, potassium chlorate being added at each reheating. The iron present in the above tests was vastly more than could be dissolved in the bead and in consequence appeared as a brown coating completely enveloping the bead and masking the green color due to the manganese; it was found, however, that by reheating several times with more potassium chlorate this coating was driven to one side, causing the green color beneath to be exposed. It therefore appears that provided enough manganese is introduced into the bead to give a fair test, the amount of iron present has no effect other than to enclose the bead in a brown coating, which difficulty may be overcome as indicated above.

The Lead Dioxide Test.— To determine the sensitiveness of this test when manganese alone is present, diminishing amounts of a standard solution of manganese chloride were treated in test tubes with one to two grams of lead dioxide[1], 0.5 cc. conc. nitric acid and sufficient water to make the total volume 5 cc. The mixture was then gently boiled, allowed to settle and the supernatant liquid examined as to color. The following results were obtained:

TABLE V

		Result
5 cc. = 5.0	mg. Mn.	Deep purple
5 cc. = 2.5	mg. Mn.	Deep purple
5 cc. = 0.5	mg. Mn.	Deep purple
5 cc. = 0.25	mg. Mn.	Purple
5 cc. = 0.125	mg. Mn.	Purple
5 cc. = 0.05	mg. Mn.	Pink
5 cc. = 0.025	mg. Mn.	Faint pink
5 cc. = 0.005	mg. Mn.	Very faint pink
5 cc. = 0.002[2]	mg. Mn.	Limit

The limit test shows a delicacy of one part in 2,500,000.

The influence of iron on the sensitiveness of the test was determined by the following procedure: varying mixtures of standard solutions of manganese chloride and iron chloride were precipitated with a slight excess of sodium hydroxide, the precipitates filtered and dissolved in a hot mixture of 0.5 cc. conc. nitric acid and 4.5 cc. of water and finally treated with lead dioxide and boiled. The same results were also obtained with the solutions without precipitation, except that the salts used were $Fe(NO_3)_3.9H_2O$ and $MnSO_4.6H_2O$ in order to prevent the formation of aqua regia. The following results were obtained:

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[1] Merck's Reagent PbO_2 was employed throughout this work and was found to be free of manganese.

[2] Noyes, Bray and Spear (J.A:C. S. *30*, 556) have shown that the lead dioxide test is easily sensitive to 0.02 mg. Mn.

TABLE VI

Parts Mn	Parts Fe	Result
1 (0.02 mg.)	10	Good
1 (0.02 mg.)	20	Good
1 (0.02 mg.)	50	Good
1 (0.02 mg.)	100	Fair
1 (0.02 mg.)	200	Fair
1 (0.02 mg.)	300	Faint
1 (0.02 mg.)	400	Faint
1 (0.02 mg.)	500	Limit

The last result gave a nearly colorless solution. The effect of iron in discharging the color due to manganese recalls the use of manganese dioxide in glass manufacture. The absence of a yellow color when a large amount of iron is present might be taken to indicate its decolorization by the presence of manganese; it appears, however, that this cannot be depended upon for the reason that an iron solution of the concentration used in the limiting test was found to be decolorized by the lead dioxide and nitric acid treatment even when no manganese was present; hence the nearly colorless solution obtained above is apparently not due to the mixture of the permanganate pink and the yellow iron.

It was thought desirable to make a few further tests to determine the influence of varying amounts of iron upon a larger constant quantity of manganese than that employed above. The results obtained are given below:

TABLE VII

Parts Mn	Parts Fe	Color	Result
1 (0.2 mg.)	500	Reddish pink	Good
1 (0.2 mg.)	1000	Reddish yellow	Fair
1 (0.2 mg.)	2000	Reddish brown	Doubtful[1]

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[1] The color given by the last test could not be readily distinguished from a solution containing 400 mg. of Fe as $Fe(NO_3)_3$ in 5 cc. It may also be noted that a solution of this concentration of iron was noticeably decolorized by the nitric acid and lead dioxide treatment.

From the results of Tables VI and VII it appears that the lead dioxide test for manganese is unreliable in the presence of three or four hundred parts of iron, unless a fairly large amount of manganese is present such as 0.2 mg. when a somewhat larger ratio of iron does not interfere with the test. On the other hand, the bead test is efficient with larger amounts of iron provided enough manganese (0.005 mg.) is introduced into the bead and provided the precautions cited under Table IV are followed.

THE DETERMINATION OF THE SENSITIVENESS OF THE HYDROXIDE REACTIONS FOR THE COMMON METALS

By L. J. Curtman and A. D. St. John
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The hydroxide reactions of the metals are perhaps the most common as well as the most important of those which take place in the wet way; yet no systematic work has been done to determine the delicacy of these reactions. The present work was therefore undertaken to supply this information, the need for which was felt in qualitative work. From the fact that the hydroxides studied were formed by precipitation, it might appear that the desired results could be calculated from the figures for the respective solubility products of the hydroxides; but it unfortunately happens that, with few exceptions, these figures have not as yet been determined; moreover, this information, even if available, would give but a rough idea of the sensitivity limit, for the reason that the final result of a sensitivity determination is largely an optical phenomenon that is controlled by factors some of which are not included in the law of mass action. Chief among these factors are those which affect the visibility of the precipitate in very dilute solutions; such as its form, density, and color. In order to obtain comparable results, all the experiments were carried out under uniform conditions. The general procedure was as follows: In separate experiments diminishing amounts of metal, in the form of a solution of one of its salts, were treated in test tubes with a slight excess of a ten per cent solution of either ammonia or sodium hydroxide, depending upon the solubility of the precipitate in an excess of either, and the tubes examined for a precipitate. The final volume in each case, including the reagent added, was 5 cc. The following results were obtained.

Lead.— A standard solution of lead nitrate containing a trace of nitric acid was employed in these tests. The precipitant was a 10 per cent solution of ammonia. The results are tabulated below:

	Cold	Boiled
5 cc. = 25 mg. Pb	large precipitate	large precipitate
5 cc. = 12.5 mg. Pb	slight precipitate	large precipitate
5 cc. = 5.0 mg. Pb	cloudiness	small precipitate
5 cc. = 2.5 mg. Pb	slight cloudiness	slight precipitate
5 cc. = 1.0 mg. Pb	very faint cloudiness	slight cloudiness
5 cc. = 0.75 mg. Pb	just visible cloudiness	limit

The most uniform results were obtained by boiling. The precipitate was white and divided. The result obtained with 0.75 mg. of lead was just visible without eye strain and represents a concentration of one part in 6500. No hydrolysis was observed in blanks either in the cold or on boiling.

Silver.— A solution of silver nitrate was employed in these tests. The precipitant was a 10 per cent solution of sodium hydroxide. All samples were boiled. The following results were obtained:

5 cc. = 25.0 mg. Ag.	heavy precipitate
5 cc. = 5.0 mg. Ag.	slight precipitate
5 cc. = 2.5 mg. Ag.	cloudiness
5 cc. = 1.0 mg. Ag.	slight cloudiness
5 cc. = 0.5 mg. Ag.	faint cloudiness
5 cc. = 0.25 mg. Ag.	faint cloudiness
5 cc. = 0.125 mg. Ag.	limit

The end product was brownish. The limit test was given by a solution of silver, the concentration of which was one part in 40,000.

Mercury.— (ous). A solution of mercurous nitrate containing approximately one per cent of concentrated nitric acid, was employed in these tests. The following results were obtained:

	NaOH	NH_4OH
5 cc. = 25.0 mg. Hg	large precipitate	large precipitate
5 cc. = 5.0 mg. Hg	heavy precipitate	heavy precipitate
5 cc. = 2.5 mg. Hg	heavy precipitate	heavy precipitate
5 cc. = 1.0 mg. Hg	slight precipitate	slight precipitate
5 cc. = 0.5 mg. Hg	slight precipitate or coloration	very faint precipitate which increases on standing.
5 cc. = 0.25 mg. Hg	slight precipitate or coloration	limit on standing two minutes.
5 cc. = 0.10 mg. Hg	very slight precipitate or coloration	
5 cc. = 0.05 mg. Hg	very faint precipitate or coloration	
5 cc. = 0.025 mg. Hg	limit. Appears light gray, away from the source of light.	

The above results indicate that a ten per cent sodium hydroxide solution is a more sensitive reagent for the detection of mercurous mercury than an ammoniacal solution of the same strength. With the former the limiting test was given by a solution whose concentration was one part in 200,000 while with the latter reagent the limit was one part in 20,000.

Mercury (ic).— The following results were obtained with a solution of mercuric chloride:

	NaOH	NH_4OH
5 cc. = 25.0 mg. Hg	heavy precipitate	heavy precipitate
5 cc. = 12.5 mg. Hg	slight precipitate	fair sized precipitate
5 cc. = 5.0 mg. Hg	slight precipitate	slight precipitate
5 cc. = 2.5 mg. Hg	limit	slight precipitate
5 cc. = 1.0 mg. Hg		coloration ½ minute
5 cc. = 0.5 mg. Hg		slight coloration ½ minute
5 cc. = 0.375 mg. Hg		limit

The precipitates obtained with sodium hydroxide were yellow becoming orange with dilution. With ammonia the precipitates were white.

The limiting results obtained above show that with sodium hydroxide one part of mercury in 2000 can be detected while with ammonia the delicacy is one part in 13,000.

Bismuth.— In the following tests, a solution of bismuth nitrate acid with nitric acid was used. The following results were obtained with ammonia as the precipitant:

	Cold	Boiled
5 cc. = 25.0 mg. Bi	white gelatinous ppt.	white gelatinous ppt.
5 cc. = 5.0 mg. Bi	white gelatinous ppt.	white gelatinous precipitate[1]
5 cc. = 2.5 mg. Bi	slight gelatinous ppt.	white gelatinous precipitate[1]
5 cc. = 1.0 mg. Bi	limit	faint precipitate
5 cc. = 0.5 mg. Bi		limit

In the cold it was found difficult to estimate the quantity of gelatinous precipitates; boiling facilitates this. The sensitiveness of the test in a boiling solution is shown to be one part in 10,000.

Copper.— The following results were obtained with a solution of copper nitrate using a sodium hydroxide solution as the precipitant.

	Cold	Boiled
5 cc. = 25.0 mg. Cu.	heavy precipitate	heavy precipitate
5 cc. = 5.0 mg. Cu.	light precipitate	light precipitate which settles
5 cc. = 2.5 mg. Cu.	slight precipitate	slight precipitate which settles
5 cc. = 1.0 mg. Cu.	limit	faint precipitate
5 cc. = 0.5 mg. Cu.		limit

In the cold the color of the precipitates was bluish-white; when boiled they were black becoming brown on dilution. The limit test in a boiling solution shows a delicacy of one part in 10,000.

Cadmium.— A solution of cadmium nitrate was employed in

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[1] The precipitate coagulated and settled.

these tests with sodium hydroxide solution as the precipitant. The results obtained are given below.

		Cold	Boiled
5 cc. = 25.0	mg. Cd.	heavy precipitate	heavy precipitate (white)
5 cc. = 5.0	mg. Cd.	heavy precipitate	heavy precipitate which settled
5 cc. = 2.5	mg. Cd.	slight precipitate	slight precipitate which settled
5 cc. = 1.0	mg. Cd.	cloudiness	cloudiness
5 cc. = 0.5	mg. Cd.	slight cloudiness	cloudiness
5 cc. = 0.25	mg. Cd.	faint cloudiness	slight cloudiness
5 cc. = 0.125	mg. Cd.	limit	limit

In all the above experiments in which less than one milligram was present in 5 cc., more conspicuous results were obtained on standing one minute. The limit tests show this reaction to possess a delicacy of one part in 40,000.

Iron.— The following results were obtained with a solution of ferric chloride. The precipitant chosen was ammonia.

5 cc. = 25	mg. Fe.	heavy precipitate
5 cc. = 5.0	mg. Fe.	heavy precipitate
5 cc. = 2.5	mg. Fe.	light precipitate
5 cc. = 1.0	mg. Fe.	light precipitate which looks like a coloration
5 cc. = 0.5	mg. Fe.	light precipitate which looks like a coloration
5 cc. = 0.25	mg. Fe.	very light precipitate which looks like a coloration
5 cc. = 0.125	mg. Fe.	faint color
5 cc. = 0.060	mg. Fe.	limit

On boiling the precipitate becomes darker brown, and is more noticeable in small amounts. All the precipitates in quantities greater than one milligram coagulate and settle on boiling. The limiting test above shows the test to be exceedingly sensitive, producing a visible result in a concentration of one part in 80,000.

Aluminium.— All the results given below were obtained with a solution of aluminium chloride to which a slight excess of ammonia was added and the mixture boiled in each case.

5 cc. = 25.0	mg. Al.	heavy gelatinous precipitate
5 cc. = 5.0	mg. Al.	heavy gelatinous precipitate
5 cc. = 2.5	mg. Al.	light precipitate
5 cc. = 1.0	mg. Al.	light precipitate
5 cc. = 0.5	mg. Al.	very light precipitate
5 cc. = 0.25	mg. Al.	very light precipitate
5 cc. = 0.125	mg. Al.	faint precipitate
5 cc. = 0.05		limit

With amounts greater than 0.5 mg. the precipitates coagulated in one or more isolated clots. With smaller amounts, however, the precipitates do not coagulate in large pieces but remain in a finely divided state. The delicacy of the test is one part in 100,000.

Chromium.— A solution of chromium nitrate was employed in the tests given below:

		NaOH	NH_4OH
5 cc. = 25.0	mg. Cr.	heavy precipitate (green)	heavy precipitate (gray)
5 cc. = 5.0	mg. Cr.	medium sized ppt.	medium sized ppt.
5 cc. = 2.5	mg. Cr.	slight precipitate	slight precipitate
5 cc. = 1.0	mg. Cr.	faint precipitate	slight precipitate
5 cc. = 0.5	mg. Cr.	limit	very slight ppt.
5 cc. = 0.25	mg. Cr.		very slight ppt.
5 cc. = 0.125	mg. Cr.		very slight ppt.
5 cc. = 0.06	mg. Cr.		faint precipitate
5 cc. = 0.03	mg. Cr.		limit

All the precipitates were boiled and allowed to settle. With the lower amounts of metal the precipitates were slightly coagulated; while in the limiting tests the precipitates showed a decided tendency to form in the finely divided state. The limit test shows a delicacy of one in 170,000.

Zinc.— The following results were obtained with a solution of zinc nitrate. Ammonia was used in slight excess and the mixture boiled.

5 cc. 25.0 mg. Zn.	dense white precipitate
5 cc. 5.0 mg. Zn.	dense white precipitate
5 cc. 2.5 mg. Zn.	slight precipitate
5 cc. 1.0 mg. Zn.	slight precipitate
5 cc. 0.5 mg. Zn.	slight precipitate
5 cc. 0.25 mg. Zn.	cloudiness
5 cc. 0.12 mg. Zn.	faint cloudiness
5 cc. 0.06 mg. Zn.	limit

The limit test shows a delicacy of one part in 80,000.

Nickel.— A solution of nickel chloride was employed in carrying out the following tests. The precipitant was sodium hydroxide.

5 cc. = 25.0 mg. Ni	heavy gelatinous precipitate (light green)
5 cc. = 5.0 mg. Ni	slight precipitate
5 cc. = 2.5 mg. Ni	slight precipitate
5 cc. = 1.0 mg. Ni	slight precipitate
5 cc. = 0.5 mg. Ni	few flakes
5 cc. = 0.25 mg. Ni	few flakes
5 cc. = 0.125 mg. Ni	few flakes
5 cc. = 0.06 mg. Ni	limit

Not less than 0.5 mg. can be readily distinguished without boiling.

The limit test shows a delicacy of one part in 80,000.

Cobalt.— For these tests a solution of cobalt nitrate was used. The reagent was sodium hydroxide.

5 cc. = 25.0 mg. Co.	heavy precipitate (blue becoming a dirty orange), coagulates and settles on boiling
5 cc. = 5.0 mg. Co.	heavy precipitate
5 cc. = 2.5 mg. Co.	slight precipitate
5 cc. = 1.0 mg. Co.	slight precipitate
5 cc. = 0.5 mg. Co.	very slight precipitate
5 cc. = 0.25 mg. Co.	faint precipitate
5 cc. = 0.125 mg. Co.	faint precipitate
5 cc. = 0.06 mg. Co.	limit

Not less than 0.25 mg. can be seen in the cold. The limit test shows a concentration of one part in 80,000.

Manganese.— The following results were obtained with a solution of manganese chloride. In each test a slight excess of ammonia was added and the mixture boiled.

5 cc. = 25.0 mg. Mn	heavy precipitate (orange)
5 cc. = 5.0 mg. Mn	heavy precipitate (red-brown)
5 cc. = 2.5 mg. Mn	medium sized precipitate
5 cc. = 1.0 mg. Mn	slight precipitate (dark red)
5 cc. = 0.5 mg. Mn	slight precipitate (black)
5 cc. = 0.25 mg. Mn	slight precipitate (black)
5 cc. = 0.12 mg. Mn	faint precipitate (black)
5 cc. = 0.06 mg. Mn	faint precipitate (black)
5 cc. = 0.03 mg. Mn	limit

With sodium hydroxide as reagent, the same results were obtained. With 5.0 mg. and less, the precipitate appears like a coloration before boiling.

The limit test shows a delicacy of one part in 170,000.

Magnesium.— A solution of magnesium sulphate was used in these tests with sodium hydroxide as the precipitant.

5 cc. = 25.0 mg. Mg.	heavy gelatinous precipitate
5 cc. = 5.0 mg. Mg.	heavy gelatinous precipitate
5 cc. = 2.5 mg. Mg.	heavy gelatinous precipitate
5 cc. = 1.0 mg. Mg.	slight precipitate
5 cc. = 0.5 mg. Mg.	limit

The limit test shows a delicacy of one part in 10,000.

A METHOD FOR THE SYSTEMATIC QUALITATIVE DETECTION OF BARIUM AND STRONTIUM

By L. J. Curtman and E. M. Frankel
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The previous work of the authors[1] has shown that the systematic qualitative detection of barium is distinctly unreliable. They have devised a scheme of analysis by which small amounts of the alkaline earth metals may be detected. The method consists in the precipitation of the alkaline earth metals, together with part of the lead as sulphates with dilute sulphuric acid and alcohol, from a solution of definite acidity. After extracting the lead sulphate with ammonium acetate, the alkaline earth sulphates are converted to carbonates by boiling with sodium carbonate solution. The carbonates are then dissolved in acetic acid and the resulting solution analyzed in the usual manner. Numerous test analyses prove the method to be trustworthy.

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[1] J. A. C. S., *33*, 724, 1911.

THE INFLUENCE OF NON-VOLATILE ORGANIC MATTER AND CERTAIN ACIDS ON THE PRECIPITATION OF THE AMMONIUM SULPHIDE GROUP OF METALS

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The effect of a number of non-volatile organic substances to prevent or hinder the precipitation of Al, Cr and Fe by NH_4OH was investigated. The following was found to be the order of interference: Citric acid, tartaric acid, dextrin, sucrose, glucose, and lactose. The first offered the greatest interference while sucrose, glucose and lactose interfered very slightly in the precipitation of the trivalent metals of Group III. Tables are given showing the effect of each of the above substances under conditions which prevail in qualitative work. A study was also made of the influence of certain acids in causing the precipitation of the alkaline earth metals and Mg in the third group. It was found that two grams of NH_4Cl which are formed in the course of the analysis, are sufficient to prevent any interference by boric acid or borates; with fluorides, however, this was not found to be the case, even when the quantity of NH_4Cl was increased. The effect of varying quantities of oxalates and phosphates respectively on the precipitation of Ba, Sr, Ca and Mg in the third group was also investigated.

THE SAMPLING OF GOLD BULLION[1]

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At the Seventh International Congress of Applied Chemistry I presented a paper[3] on "The Assay and Valuation of Gold Bullion" in which are briefly mentioned a few illustrations of different methods of sampling gold bullion, particularly cyanide bars. Since then I have carried on an extensive investigation upon the sampling of gold bullion in relation to its effects upon the assay results in connection with the statement of accounts between the smaller assay offices of the United States which purchase gold bullion and the mints where the purchases are redeposited.

Under the name of gold bullion are included metals of widely different composition. We may have practically pure metal, 999.75 fine or even more in gold, alloys of gold and silver with only trifling amounts of base metal, alloys of gold and copper with trifling amounts of other metals, ternary alloys of gold, silver and copper, or gold, silver and lead, and most complex alloys of 5 to 8 or more constituents of ordinary occurrence, besides some of the rarer metals occasionally. In any or all of these classes we may have one or more of the metalloids, which may add to our difficulties.

Of course, with metal 999.75 fine in gold there is only slight opportunity for different samples to differ in fineness, but on such fine metal we expect the assays to agree very closely and the sampling must be done with the utmost care. When possible, dip or granulation samples of the molten metal should be taken, but when necessary to sample bars the chief point to guard against is surface dirt.

In the case of four melts of fine gold, which had been carefully

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[1] Published by permission of the Director of the Mint.

[2] Assayer, Mint Bureau, U. S. Treasury, Washington, D. C.

[3] Published in Trans. Am. Inst. Mining Engineers Vol. XL, p. 780, and in Annual Report of the Director of the Mint for the year 1908-1909, p. 25.

sampled by both dips and chips, one of the chip bars and an independent bar were chipped and the chips assayed. Table I summarizes the results:

TABLE I

FINE GOLD SAMPLING

Original Report	Sample Bar 2nd Sample	2nd Bar
997.9 fine	997.7 fine 998. fine	997.9 fine
997.5 fine	997.4 fine .3 fine	997.4 fine
997.4 fine	997.4 fine .4 fine	997.3 fine
997.2 fine	996.9 fine	996.9 fine

In the case of four melts of much higher grade metal independent samples were taken and assayed after the melts had been reported by the Assayer and Table II summarizes the results.

TABLE II

FINE GOLD SAMPLING

Original Report	Resamples
999.8 fine	999.7 fine .7 fine
999.7 fine	999.7 fine .7 fine
999.7 fine	999.7 fine .6 fine
999.6 fine	999.5 fine .5 fine

Our standard gold, coin gold, is 900 fine in gold and 100 fine in copper. When made from pure metals it does not segregate. Four melts of standard gold were carefully sampled by both dips and chips and reported by the assayer. Subsequently one of the sample bars and a second bar were chipped and the chips were assayed. Table III summarizes the result.

TABLE III

STANDARD GOLD SAMPLING

Original Report	Sample Bar	2nd Bar
900 fine	899.8 fine .9 fine	899.8 fine
899.9 fine	899.8 fine	899.8 fine
899.8 fine	899.7 fine	899.6 fine
899.7 fine	899.7 fine .8 fine	899.5 fine

In the cases already cited the question of sampling is a very simple matter and the variations in the results shown may just as well be due to the assaying itself as to the sampling. When, however, we come to consider miscellaneous bullion of more complex composition the sampling assumes greater importance.

If we have a bar of strictly homogeneous metal, manifestly it would make no difference how the sample was taken, for any part of the metal would be just the same as the balance of the metal. Bars that are practically homogeneous are not uncommon, and such bars would not have to be melted for the purpose of sampling, provided always that we could be certain that they were homogeneous.

Only two classes of alloys can form homogeneous bars; those that are solid solutions and the eutectics, and unfortunately there are no characteristics by which the homogeneity of a bar of gold bullion may be readily established. As a general proposition it is safe enough to assume that a brittle bar of gold bullion will not be homogeneous. We may, of course, happen to get a bullion of eutectic composition, which would be both brittle and homogeneous, but eutectics undoubtedly form a very small proportion of the ordinary run of gold bullion. On the other hand it is far from safe to assume that a ductile bar is homogeneous.

The alloys of gold and silver and gold and copper form continuous series of solid solutions and they may carry small amounts of other metals without showing marked segregation. Several cases are shown in the examples cited beyond where there is remarkable agreement in the assays of different samples of gold and silver alloys containing small amounts of impurities, thus showing the practical absence of segregation. Alloys of gold and copper are quite similar in their heat behavior to the gold-silver alloys, but I do not happen to have any satisfactory series of samples of these carrying small amounts of other metals.

When we come to the ternary alloys our knowledge of their behavior on heating and cooling is too scant to admit of valid generalizations and this is even more so with regard to the alloys of increasing complexity.

Considering now the sampling of general miscellaneous gold bullion, there is only one universally satisfactory method of taking a sample of such bullion that shall truly represent the metal sampled. This consists in pouring a small portion of the well-mixed molten metal into water so as to produce small globules or granulations of the metal. As this is generally done by dipping out a portion of the molten metal in a small cup such a sample is frequently called a "dip," and this name is generally used throughout this paper. These samples are, however, often called "granulations" and they are sometimes made by pouring directly out of the crucible into the water, the operation of casting being interrupted for the purpose.

As already indicated, there are indeed various cases where other styles of sampling may be sufficiently satisfactory, and there are, moreover, many cases where it is desirable or even necessary to sample a bar of solid bullion without melting it. In such cases a chip may be cut off from the bar by an ordinary cold chisel or by a chisel especially designed for the purpose. Power-driven punches with especially designed tools may be used. Machines are also built which bite out a triangular piece of metal by means of a projection on a lever operated by a cam. Where much chip sampling is done, especially on small bars, these machines are great time and labor savers. A third method of sampling consists in boring into the bar, generally with a power drill, and using the drillings for the assay sample.

In taking a chip sample there is but little choice in the location of the sample. It must necessarily be taken from a corner or along some edge of the bar. In the systematic sampling of large bars, generally two chips are cut; one from the top and one from the bottom of the bar and properly identified.

In taking drill samples there is a wide choice in the location of the drill holes and in the sampling of large bars more or less of a plan in placing the holes is often followed. It is a common practice in the mint service to drill half way through a bar at diagonally opposite corners on top of the bar and unite the drillings for the top sample. The remaining corners are drilled half way through from the bottom and the drills mixed for the bottom sample. Occasionally the four drills are kept separate, especially when sampling very base bars. Occasionally also holes are drilled near the center of the bar.

Drill samples are often more satisfactory than chip samples, especially where large numbers of bars of fairly uniform size and composition are sampled in accordance with a well-designed plan. Drill samples of brittle bars are, however, liable to be unsatisfactory because the fine and coarse portions may differ considerably in composition.

In the purchase of gold bullion by the Mint Service of the United States the size of the deposit has an important bearing upon the question of sampling. A very large proportion of the deposits will weigh less than 100 ounces each. Manifestly slight differences in the samples on such bars will be immaterial. When, however, the weight of a deposit reaches 300 ounces the samples become important and with bars weighing 700 to 1200 ounces correct sampling becomes essential.

Limiting ourselves now for the most part to these large-sized bars of miscellaneous bullion, I propose to illustrate some of the general principles underlying the question of sampling gold bullion by specific cases drawn from actual practice. In considering the illustrations the assay results given must not be too rigidly interpreted. Besides the variations in the results due to variations in the samples there are three other variants that must be kept in mind constantly; the chapter of accidents, the personal equation of the assayer and the effect of the composition of the metal upon the assaying as distinct from its effect upon the sampling. This last point will be especially dealt with by various illustrations. Making reasonable allowances for these variants it is thought that the illustrations are sufficiently conclusive upon the main points involved.

To begin with, alloys of gold and silver containing only small amounts of base metal, four bars, each one carrying less than four base, were chipped top and bottom and each one of the eight samples was assayed in three laboratories. A fifth bar carrying ten base was treated in the same way. Table IV summarizes the results reported.

TABLE IV

Sampling Gold-Silver Alloys Low in Base by Chips

Fineness	Assays		Fineness	Assays		Fineness	Assays		Fineness	Assays		Fineness	Assays	
872.3	1		875.7		1	883.3	1	1	884.2	2		873.8		1
.4	2		.8	1	2	.4		6	.3		1	4.0	1	
.5	5	4	.9	2	3	.5	4	2	.4	1	4	.2	2	1
.6		2	6.0	4	2	.6	2	1	.5	1	2	.3	1	
.7		3	.1	1	1	.7	3		.6	1		.4	2	1
3.0	1	1	.2	2	1				.7		1	.5	2	4
												.6		1
												.7	1	
Total	9	10		10	10		10	10		5	8		9	8
Silver	124			121			114			111			116	

Each one of the above bars may be taken as a single product, but a bar obtained by melting 39 small bars of miscellaneous origin into a mass-melt exhibits a remarkable agreement of chip samples. This mass weighed a little over 1300 ounces and was .143 fine in silver. It was chipped top and bottom at the assay office and twice at the mint of redeposit. The assay office samples were assayed in duplicate there and the four mint samples were assayed in four laboratories. Forty-four assays were made on the six chip samples. Table V summarizes the results reported.

TABLE V

Sampling a Mass Melt by Chips

1 assay showed	679.7 fine in gold
4	.8
2	.9
2	80.1
5	.2
8	.3
3	.4
4	.5
7	.6
5	.7
2	.8
1	.9
44	

A bar carrying over 90 base and weighing 606 ounces was chipped top and bottom and the samples assayed at the purchasing office. At the receiving mint it was drilled top and bottom and the drills were assayed in four service laboratories. Table VI summarizes these assays.

TABLE VI

CHIP AND DRILL SAMPLES AGREEING

Fineness	Chip	Drill
741.6		1
.7		1
.8		1
.9		2
2.0		2
.1	2	3
.2	2	1
.3		4
.4		5
Total	4	20
Silver	165	

A bar weighing over 800 ounces presents another remarkable case of the presence of considerable base metal without producing marked segregation. This bar was drilled top and bottom and the drillings were united to form one sample. Two other sets of drills, top and bottom, were taken from the same bar and each sample was kept separate. These five samples were assayed 69 times in five laboratories. Table VII summarizes the results reported.

TABLE VII

SAMPLING GOLD-SILVER ALLOY, CONTAINING CONSIDERABLE BASE, BY DRILLS

6	assays showed	351.0 fine in gold
10	assays showed	.1 fine in gold
13	assays showed	.2 fine in gold
14	assays showed	.3 fine in gold
15	assays showed	.4 fine in gold
6	assays showed	.5 fine in gold
2	assays showed	.6 fine in gold
3	assays showed	.7 fine in gold
69		

This bar was 604 fine in silver and 44.5 fine in base metals.

Two other bars containing less base metal but also considerably less gold yielded much less satisfactory results. These bars weighed nearly 1200 ounces each. They were drilled, top and bottom, and the drillings united to form one sample. One bar was drilled twice again, top and bottom, and the other three times, top and bottom, each drilling being kept separate. These twelve samples were assayed in five laboratories and Table VIII summarizes the results.

TABLE VIII

DRILL SAMPLING GOLD-SILVER ALLOY LOW IN GOLD AND BASE

Fineness	1st Drill	2nd Drill		3rd Drill		Fineness	1st Drill	2nd Drill		3d Drill		4th Drill	
		T	B	T	B			T	B	T	B	T	B
290.2				2		290.6	1						
.6	1	1		2		.9	1						
.7		1		2		1.1	1	1					
.8		1		2		.5	1						
.9		2		2		.9	1	2					
1.0				3		2.0	1	2				1	
.1	1	1		1		.1	2						
.2		2				.2		2			2	2	
.3		2		1		.3	1	1			1	3	1
.4	2	2	1		2	.4		2	1		4	2	3
.5	4		1			.5	3	2	2		2	3	3
.6	2	1			2	.6	4		4		1	1	2
.7	2					.7		1	4		1	1	3
.8					1	.8		1	1		1	1	
.9	1		1		1	.9							2
2.0					1	3.0			2	1	1		
.1			1			.1				4	1	1	
.2	2		2			.2		1		4			
.3			2		1	.3				2			
.4		1	3			.6				1			
.5			1			.9				1			
.7			1		1								
.8			1		2								
.9					1								
3.0			1		1								
.1					1								
Total	15	14	15	15	14		16	15	14	13	14	15	14
Silver		670								671			

On the other hand, a ductile bar 778 fine in gold with only 9 base yielded unsatisfactory results for this grade of metal. This bar weighed over 1500 ounces and was drilled top and bottom, the drillings being mixed for one sample. Being ductile it was chipped twice top and bottom at the mint of redeposit. These six samples were kept separate. The bar was remelted with a loss of .38 ounces, and two dip samples were taken. The cold bar was again drilled, top and bottom. These eleven samples were assayed in four service laboratories and Table IX summarizes the results reported.

TABLE IX

Sampling Ductile Gold-Silver Alloy, Low in Base

Fineness	1st Drill	2nd Drill		1st Chip		2nd Chip		Remelt			
								Drill		Dip	
		T	B	T	B	T	B	T	B	T	B
777.2						1					
.3						2					
.5											
.6											
.7						3		1			
.8	1										
.9					1						
8.0					1			1			
.1	1						2	2			
.2	1			2	2		1	2			
.3	1	3	2	2	3		3	2	2		1
.4	1	1	4		1		3	2			3
.5	3	4	3		1			2	3	2	5
.6	3	1	2		2		1		5	6	1
.7	1			1					2	1	2
.8										1	
.9		1								1	
9.0				1							
Total Silver, 212.5	12	10	11	6	11	6	10	12	12	11	12

The following case exhibits what is probably the very best agreement between various samples and between an assay office and a mint that it is possible to attain under everyday working conditions:

A deposit of approximately 3000 ounces was melted in the assay office and two dip samples were taken. It was cast into three bars and two chip samples were taken from each bar. At the mint of redeposit two chip samples were cut out from each bar. The mint samples were forwarded to the Bureau and thence sent to the assay office and afterwards returned to the mint to be assayed, neither institution being informed what the samples were.

In all, ten samples were taken from this deposit, and 47 assays were made at the two institutions. Table X summarizes the assays reported.

TABLE X

AGREEMENT OF ASSAYS ON VARIOUS SAMPLES AT TWO INSTITUTIONS

1 assay showed 875.5 fine in gold
1 assay showed .6 fine in gold
4 assays showed .7 fine in gold
4 assays showed .8 fine in gold
14 assays showed .9 fine in gold
12 assays showed 6.0 fine in gold
6 assays showed .1 fine in gold
4 assays showed .2 fine in gold
1 assay showed .3 fine in gold
—
47

If we eliminate the results that were reported only once each, we have 44 assays ranging from 875.7 to 876.2. This deposit might, therefore, be properly reported by either institution at either 875.75 or 876. It did not contain over four base.

On three bars the purchasing office took chip and dip samples and on a fourth bar took dip and drill samples. The mint of redeposit cut two chip samples from each bar. These samples were assayed in various service laboratories and Table XI summarizes the results on the various styles of samples.

TABLE XI

SAMPLING IN VARIOUS WAYS WITH SATISFACTORY AGREEMENT

Fineness	Dip	Chip	Chip	Fineness	Dip	Drill	Chip	Fineness	Dip	Chip	Chip	Fineness	Dip	Chip	Chip
861.4		1	2	895.1	1		2	858.5	1		1	883.2			1
.5			1	.2			3	.7		1		.3		2	
.7	1	1		.3		1	4	.9			1	.4	1	1	1
.8		4	1	.4	1		2	9.0	1	3	1	.5	2	1	6
.9	3	1	4	.5	1	2	1	.1	1	1	2	.6			1
2.0	3	3	6	.6	1	1	2	.2	3	3	7	.7		1	4
.1	3	1	3	.7	2	2	1	.3	1	1	2	.8	5	4	
.2	1	1		.8	3	3		.4	3		1	.9	3	3	3
.3	2	1		.9	3	4		.5	5	1		4.0	3	2	1
.4	1			6.0	1		1	.6		3	3	.1			1
				.1	1			.7	1			.2			1
				.2		1									
Totals	14	13	17		14	14	16		16	13	18		14	14	19
Silver	134					98				137				113	

On three bars the purchasing office took dip and drill samples and the mint of redeposit took top and bottom drill samples. These samples were assayed in various service laboratories and the results are summarized in Table XII, showing a considerable amount of agreement between the chips and the drills taken at the separate offices but a better agreement is desirable.

TABLE XII. DIP AND DRILL SAMPLES PARTIALLY SATISFACTORY

Fineness	Dip	Drill	Drill	Fineness	Dip	Drill	Drill	Fineness	Dip	Drill	Drill
822.4	1			973.4		1		972.1		1	
.7	1			.5		1		.2	1	1	
.8			2	.6			1	.3	3		3
.9	1	1	1	.8		1	1	.4	4	1	
3.0	3	1	2	4.0			2	.5			1
.1	3	2	1	.1		1		.6	3	1	1
.2	2	4		.2	2		2	.7	1		2
.3		3	1	.3	2			.8			2
.4	1	2	4	.4	1		1	.9		1	
.5	1			.5	2	1	2	3.0		2	2
.6			2	.6	1			.1		3	
.7		1	1	.7		1	2	.2	1		
.8			4	.8	3	2	4	.3	1	1	1
.9			1	.9	1		2	.4		1	1
4.1			1	5.0		4	1	.5			2
				.1	1	1		.6			1
				.2		1	2	.8		1	1
				.3	1		1	4.3		1	
								5.7			2
Totals	13	14	20		14	14	21		14	14	19
Silver		162				4			Practically none		

On four bars the purchasing office took dip and drill samples and the mint of redeposit cut two chips from each bar. These samples were assayed in various laboratories in the service and Table XIII summarizes the results reported, showing the chip samples to be unsatisfactory.

TABLE XIII. CHIP SAMPLES UNSATISFACTORY

Fineness	Dip	Drill	Chip	Fineness	Dip	Drill	Chip	Fineness	Dip	Drill	Chip	Fineness	Dip	Drill	Chip
821.8			1	892.3			1	898.0			1	820.7	1		
2.3			3	.6			2	.1			4	.8			2
.5			1	.7			5	.2			2	.9			2
.6			1	.8			2	.3		1	3	1.0	4		1
.7	2	1	1	.9	1		4	.4	1	2	2	.1	1		
.9			1	3.1		2		.6	1	2	1	.2	2		
3.0	1	1	2	.2	1	1	1	.7	3		1	.3	1		
.1	4	3	3	.3	4	2	1	.8	2	2	1	.4	3	2	
.2	3			.4		1		.9	3	3		.5	1	1	
.3	1	2		.5	5	4		9.0	3	2		.6		1	
.4		1	1	.6	3			.1	1		1	.7	1	3	1
.5	4	2	1	.7		1	1	.4			1	.8	1	3	1
.6	1	3	2	.8		1		.8		1		.9			2
				.9		1		.9		1		2.0		1	2
												.1		2	
												.5			1
Totals	16	13	17		14	13	17		14	14	1		15	13	12
Silver		160				97					887			172	

On three bars the purchasing office took dip and chip samples and the receiving mint cut two chips. These samples were assayed in various laboratories in the service and Table XIV summarizes the results reported, showing that the mint chip samples were entirely unsatisfactory.

TABLE XIV
SECOND CHIP SAMPLES UNSATISFACTORY

Fineness	Dip	Chip	Chip	Fineness	Dip	Chip	Chip	Fineness	Dip	Chip	Chip
879.8			1	890.3			1	867.6			1
80.0			1	.5			2	.8			1
.1			2	.6			2	8.1			2
.6			1	.8			1	.2			1
1.3			1	.9			4	.3			1
.4			1	1.0			1	.5			4
.5			2	.1			1	.6			4
.6			1	.2			1	.7			1
.7			2	.3		2	1	.8		1	
.9		1		.4	2			9.0		1	1
2.0		1	1	.5		2		.3	1		
.1			1	.6	4	1		.5		1	
.2		2		.7	5	1		.6	1	5	
.3	2	3		.8	2	4		.7	1	1	
.4	3	1		.9		5		.8	2	1	
.5	2	4		2.0	4	1		.9	1	1	
.6	2		1	.2	1	3		70.0	1	2	
.7	4			.3		1		.1	3	1	
.8		3						.2	1	2	
.9	2							.3	4	2	
3.0	3	1						.4	1		
.1	1	1						.5	2	1	
.2		1						.6	1		
								.7	1		
								.9	1		
								1.0	1		
								.1		2	
Totals	19	18	15		18	20	14		22	21	16
Silver		90				98				95	

A very complete set of samples from five bars contained in one shipment made by a purchasing office to a mint for redeposit shows what may happen under everyday working conditions in handling moderate grade bullion. Everything considered, the first set of samples may be taken as fairly satisfactory, but the last set is totally unsatisfactory. At the office of purchase two dips and two drills were taken from each bar. At the mint of redeposit two drills and two chips were taken. Each one of these eight samples on each bar was assayed in various service laboratories and Table XV summarizes the results reported, the assays on each set of two samples being grouped.

TABLE XV

SAMPLING FIVE BARS OF MISCELLANEOUS BULLION

Fineness	Dip	Drill	Drill	Chip	Fineness	Dip	Drill	Drill	Chip	Fineness	Dip	Drill	Drill	Chip
630.3		1	1		755.0			1	1	544.2				1
.4		1		1	.1			1		.3				1
.5				2	.2				2	.6				1
.6	3				.3			1	2	.7				1
.7	1	1	2	3	.4			3	2	.9				1
.8			2	1	.5		1	1		5.0				2
.9	2	1	2	1	.6			1	4	.1			1	1
1.0	2	2	2	2	.7				1	.2				1
.1	3				.9		1	1		.3				2
.2	2	2		1	6.0			1		.4	1			1
.3	1	2	1		.1		1	1	1	.5			1	
.4	1	2			.2		2	3	1	.6			1	1
.5	1	2	1	1	.3		1			.7			1	
.6			2		.4		1			.8		1	1	1
.7		1	1		.5	1		1		.9	2		1	
					.6	2		1		6.0	2			
					.7	2	2			.1	3		1	
					.8	1	1			.2	1		1	
					.9	1	1			.3	1	2		
					7.2	3				.4	3	1	1	
					.3	1	1			.5	2	2		
					.4	2				.6	1	2	1	
					.5	1				.7		1		
										.8		1	1	
										.9	2	1		
										7.0			1	
										.2		2	1	
										.3			1	
Totals	16	15	14	12		14	12	16	14		18	13	14	14
Silver		330					203					444		

TABLE XV—*Continued*
SAMPLING FIVE BARS OF MISCELLANEOUS

Fineness	Dip	Drill	Drill	Chip	Fineness	Dip	Drill	Drill	Chip
549.4				1	568.5				1
.7				1	9.6				1
50.5				1	573.9				1
1.0				1	4.6				1
.4				1	5.4				1
.7				2	.7				1
.8				1	6.4				1
.9	1		1		.5				1
2.1	1			2	7.0				2
.2			1		.2				1
.3				1	.3			1	
.5			1	1	.4				1
.6	1		3		.6			1	
.7	3		2	1	.8			1	
.8	2	1	1		.9			1	
.9	4	4	3		8.0			2	
3.0	2				.1			1	
.1	4	5	1		.3	1			
.2	3	3			.4		1		
.3		3			.5		1	1	
.4		1	1		.6		3	2	
.5	1				.7	3	2	2	1
.6			2		.8	3	1		
					.9	4	2	1	
					9.0	4	1	1	
					.1		3		
					.2	1	1		1
					.3	2			
					.4	1	1		
					.5	1			
					.6		1		
					.7		1		
Totals	22	17	16	13		20	18	14	14
Silver		410					335		

A small bar resulting from melting up scrap material has a most interesting and instructive sample history. The bar weighed a trifle over 31 ounces and was shipped from the assay office at 826 fine in gold. At the receiving mint it was drilled top and bottom and while the assays on these samples agreed fairly well, yet they averaged considerably below 826. The bar was again drilled top and bottom and these samples yielded very erratic assays. The bar was then melted and two dip samples were taken. The solid bar was again drilled top and bottom. These eight samples were assayed in four service laboratories and Table XVI summarizes the results reported.

TABLE XVI
SAMPLING A SMALL UNSATISFACTORY BAR

Fineness	Drill		Drill		Remelt			
					Drill		Dip	
	T	B	T	B	T	B	1st	2d
823.0				1				
.5				1				
.7				1				
.9				1				
4.3				1				
.4				2				
.7		1						
5.1							1	2
.2		2	1					
.3		1	1				1	
.4	2	2					1	
.5	4	2						
.6	2	2			1		3	1
.7	1					1		1
.8	1		1			3	3	
.9			1			1	1	1
6.0	1	1	1		2		3	
.1					1	1		
.2					2	2		2
.3			2			1		2
.4					1			1
.5			1		1			2
.6			2		2			
7.0			1					
Totals	11	11	11	7	10	9	13	12
Silver		143						

On three bars drills were taken from diagonally opposite corners on top of the bar and also near the center of the bar. The other two corners were drilled from the bottom of the bar and a drill was taken near the center of the bottom. All the top drills were mixed to make one sample and all of the bottom drills to make another. These samples were assayed in two laboratories and Table XVII summarizes the results reported, to which are added for comparison duplicate assays of two dip samples of each bar made in one of the laboratories.

TABLE XVII

SAMPLING BY TOP AND BOTTOM DRILLS

1st Bar			2d Bar			3d Bar		
Fineness	Bottom	Top	Fineness	Bottom	Top	Fineness	Bottom	Top
883.7	2		884.8	3		888.7	1	
.9	4		.9	3		.8	1	
884.0	1		885.0	4		.9	1	
.1	6		.1	3		889.0	2	
.2	3		.2	3		.1	3	
.3	1		.3	1		.2	2	
.4	1		.4	5		.3	1	
.5	1		.5	2		.4	2	
.7		1	.6	1		.5	2	1
885.1		5	.7	1		.6	1	
.2		2	886.2		4	.7	1	
.3		1	.3		3	.8	3	
.4		3	.5		6	890.0		2
.5		2	.6		4	.1		3
.6		4	.7		1	.2		2
.7		2	.8		1	.3		1
			887.0		1	.6		2
						891.1		1
						.3		1
						.4		1
						.6		1
						.7		1
						.8		1
						.9		1
						892.2		2
Totals	19	20		26	20		20	20

Dip Samples		Dip Samples		Dip Samples	
840.0	3	885.3	1	889.1	2
.1	1	.4	1	.2	2
		.5	1		
		.7	1		

With the exception of the single assay at 889.5 on the third bar, all the top assays are above the highest bottom assay on each bar. All the top assays are above the dip assays in each one of these cases. Each one of the bars was less than five fine in silver.

As a general proposition a drill sample will often be better and more satisfactory than a chip sample simply because it represents a larger volume of the metal, but a drill sample of a brittle bullion may be open to a serious objection because the fine particles of the sample are generally liable to be quite different in composition from the coarse portions, so that even if the drill sample as a whole should be fairly representative of the bar, yet it would be necessary to have the half gram weighed up for the assay composed of fine and coarse material in just the same proportions as the whole sample. Manifestly this will seldom be the case.

Drill samples of two closely related bars were sifted on an 80-mesh screen and yielded the following results:

	1st Bullion	2nd Bullion
Coarse Portion	290.3 fine .4 fine	291.4 fine .5 fine
Fine Portion	287.8 fine	290.1 fine

Two other drills of these same bars were sifted. The portion between 20 and 40 mesh and that finer than 60 mesh were assayed with the following results:

	1st Bullion	2nd Bullion
20–40 mesh	290.4 fine 1.9 fine	291.9 fine 2.3 fine
60 mesh	289.6 fine 90.3 fine	290.3 fine .8 fine

Two other bullions treated like the last illustration showed:

	1st Bullion	2nd Bullion
20–40 mesh	351.7 fine .9 fine	573.2 fine .4 fine
60 mesh	350.2 fine .5 fine	566.6 fine 7.3 fine

An entirely different bullion sifted differently showed:

40–60 mesh	585.3 fine .4 fine	100 mesh	584.6 fine .7 fine

A rich bullion sifted like the last showed:

40–60 mesh	889.2 fine .2 fine	100 mesh	887.8 fine

Five samples of a bullion which had given discordant assays were subjected to sifting tests and the resulting samples assayed. Four drill samples were sifted on 100 mesh, when the coarse and fine portions yielded the following results:

A		B		C		D	
Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
615	612.7	615.3	612.2	613.9	612.9	612.8	608.
617	614.4	.9	.3	615.1	613.1	616.6	609.4
		617.9	613.7		614.1		610.5

Just over a gram of the small pieces of a dip sample was crushed and assayed in duplicate. Coarser pieces were crushed and sifted on 80 mesh. The three samples yielded the following results:

Whole Dip Sample	Crushed Dip Sample	
	Coarse	Fine
614.8	614.8	614.8
615.	615.2	.9

This bullion carried bismuth.

No class of bullion has given assayers the world over so much trouble as the so-called cyanide bullion. Not all bullion produced by cyanide mills is troublesome. Hundreds of bars produced by such mills have passed through our mint service without the slightest trouble. It is easy enough to produce a high-grade refined bar from the zinc-box precipitate, but when this precipitate is melted direct and put into bars without proper refining there is liable to be no end of trouble with the assays. Unfortunately, too, in some instances the precipitate is not as thoroughly cleaned from zinc before drying as it might be. These dirty unrefined bars are the ones that are usually spoken of as cyanide bars with so much disparagement.

Over 15 years ago Roberts-Austen[1] gave a startling illustration of the difficulties and uncertainties of assaying this class of bullion. A bar weighing 393 ounces was sampled and assayed in the usual manner and paid for at £965. The gold from this bar was separated and refined by itself and was found to be worth £1028. This meant a loss of £63 or over $300 to the former owner of the bar.

It is generally assumed that the zinc remaining in the bullion is the cause of the trouble but no clear and systematic explanation of its action has yet been given. It is quite probable that its action differs in different bullions according to the presence or absence of other metals and is complex. I have for instance published[2] 50 assays made in eight laboratories on a synthetic bullion approximately 590 fine in gold, 245 fine in silver, 130 fine in zinc, with a little copper and a very little lead, which ranged from 588.9 to 589.9 fine in gold. Clearly the zinc did not seriously interfere with the actual assaying in this case.

I have also published[3] 207 assays made on three bars of bullion produced in the celebrated Mercur mill showing widely varying assays. By a qualitative analysis, this bullion was found to carry both cadmium and nickel, and four other bullions from cyanide mills in Montana showed these metals. At present I am carrying

[1] Annual Report Deputy Master and Comptroller of the Mint, No. 27, 1896, p. 38.

[2] Trans. Am. Inst. Mining Engineers, Vol. XL, p. 794.
Annual Report Director of the Mint, 1908–9, p. 34.

[3] Engineering and Mining Journal, Vol. XCIII, p. 733.

on, as occasion permits, a series of test assays on synthetic alloys of gold, zinc and cadmium.

From our tests in sampling cyanide bullion I am satisfied that much of the variation ordinarily shown by the assays on this class of bullion is due to differences in the samples arising from the effect of the zinc upon the physical structure of the metal, but aside from this there are many cases where the composition of the metal directly affects the assay work itself.

The illustrations of top and bottom drilling given in Table XVII are from cyanide bars. Five of these samples show that individual samples of cyanide bullion may give fairly satisfactory results, but that two such samples from the same bar may leave the question of the actual content of gold in the bar in doubt.

Again three bars from the same mill were sampled by dips twice each and the six samples were assayed in various laboratories in the service, giving widely varying results and showing the effect of the composition of the metal upon the actual assaying. Table XVIII summarizes the results reported.

TABLE XVIII. EFFECTS OF COMPOSITION UPON THE ASSAY WORK

Fineness	1st Dip	2nd Dip	Fineness	1st Dip	2nd Dip	Fineness	1st Dip	2nd Dip
784.9		1	816.6		1	821.9	1	
5.2		3	.8		2	2.0	2	
.3	1		7.0		1	.2	3	
.4	3	1	.2		1	.3	2	2
.5	2	1	.3	1		.4	1	3
.6	1	2	.4	2	1	.5	1	2
.7	3		.5	1		.6	2	
.8	1		.6	3	2	.7	2	
.9	2	3	.7	2		.8	4	1
6.0	1	1	.8	1	1	.9	1	
.2	1		.9	2	3	3.0		2
.3		1	8.0	1	1	.1		3
.5	1		.1	3		.2	1	2
.6	1	2	.2		2	.5		1
.8		1	.3	1	1	.6		2
7.0	1	3	.4	1		.7		1
			.5		2			
			.6		2			
			.7		1			
			.8	1	1			
			9.0	1	1			
			.1		1			
			.2	2				
			.3		1			
Totals	18	19		22	25		2	19

These bars range from 5 to 10 fine in silver.

Three bars deposited at one time by a cyanide mill furnish an excellent illustration of the general condition in handling this class of bullion. Two drills and two dips were taken from each bar and the 12 samples were sent to various laboratories in the service for assay. Table XIX summarizes the results reported, together with the original assays at the office of deposit, the assays on each kind of sample being grouped.

TABLE XIX. SAMPLING CYANIDE BULLION

	1st Bar			2nd Bar			3rd Bar	
Fineness	Drills	Dips	Fineness	Drills	Dips	Fineness	Drills	Dips
826.9	1		816.9	1		831.5	1	
7.2	2		7.2	1		2.1		1
.3	1		.3	3		.3		3
.4	1		.5	1		.4		1
.6	1		8.3		1	.6		1
.7	3		.4	1		.8	1	2
.8	1		.5		1	.9	1	1
8.3		1	.6	1	1	3.0		4
.4	2		.7		1	.1	1	3
.5	4		.8		1	.3	1	2
.6	1	1	.9	1	2	.4	1	3
.7	1	4	9.0	1	1	.5	3	6
.8	2	1	.1	2	1	.6	1	1
9.0	1	3	.2		1	.7	1	1
.1	2	2	.3		1	.8	2	1
.2	3	3	.4		1	.9		1
.3	1	5	.5	1	3	4.0	1	2
.4	1	2	.6	2	3	.1	1	2
.5	1	5	.7		2	.4	1	1
.6	1	3	.8		2	.7	1	
.7		1	.9		4	5.0	1	
.8		3	820.0	4	4	.4	2	
.9	2	1	.1		1	.5	1	
830.0		4	.2	2	2	.6	1	
.1		1	.3		2	.9	1	
.3		1	.5		1			
.4	1		.6	1	2			
.5		1	.7	2	1			
.8	1		.8	2				
			.9	2				
			1.0	1	1			
			.2	1				
			.4	1				
			.5	1				
			.8	1				
			2.1	1				
Totals	34	42		34	40		23	36

All of these bars carried less than 5 of silver.

In one office receiving a great deal of high-grade bullion it is the general experience that the chip samples will run somewhat below the dip samples on this rich material. Illustrations already given show that there is no fixed relation generally exhibited between the dip and drill samples as to the content of gold. Where many bars of practically uniform composition are drilled in accordance with a well-designed plan, a more or less fixed relationship between the drill and dip assays might appear. Such a plan was developed at one time for certain deposits at one of our mints.

TABLE XX. SAMPLING CYANIDE BULLION BY DRILLS AND DIPS

	1st Bar			2nd Bar	
Fineness	Drills	Dips	Fineness	Drills	Dips
894.7	1		905.6	1	
.8	2		6.1	2	
5.0	1		.2	2	
.2	1		.6		1
.3		1	.8	1	1
.5	1		.9	1	
.7		1	7.0	1	
.8	2	2	.1	1	1
.9	1		.2		2
6.0	1		.3		2
.1	1	1	.4		2
.2	2	1	.5	1	2
.3	3	3	.6		2
.4	2	1	.7	2	4
.5	2	3	.8	1	2
.6	3	1	.9	2	5
.7	2	3	8.0	2	
.8	1	2	.1	1	
.9	1	2	.3	1	1
7.0	1		.4	2	
.1		1	.5	2	
.2		1	.7	1	1
.5	1		.9	1	
8.0	1		9.0	1	
.1	2		.4	1	
.6	1		.5	3	
.7	1		.6	2	
9.2	1		.7	1	
.4	1		.8	1	
.6	2		.9	1	
.8	3		10.3	2	
			.4	1	
			.5	1	
			.7	1	
			.8	1	
			1.0	1	
			.4	1	
			.8	1	
			.9	1	
			2.0	1	
Totals	41	23		46	26

The foregoing table shows that with cyanide bars a drill sample may give much higher assays than a dip sample. On the first bar 13 assays of the drill samples are above the highest assay on the dip samples and on the second bar 22 drill assays exceeded the highest dip assays. Two cyanide bars, each weighing about 850 ounces and practically free from silver, were drilled top and bottom and these four samples, together with four corresponding dips, were sent to various service laboratories for assay. Table XX summarizes the results reported, together with the original mint assays, the assays on each kind of sample being grouped.

Undoubtedly much of the trouble with these cyanide bars would be avoided by a better cleaning of the zinc-box precipitate. It is, however, easy enough to refine the impure bullion by strongly oxidizing fusions in the crucible, but this is expensive in labor and reagents and there is some loss of gold. I have previously published[1] an illustration of this.

A cyanide bar weighing 643.30 ounces was melted with a loss of 6.07 ounces and 10 assays on various kinds of samples were made with the following results:

1 assay showed 844.6 fine in gold
1 assay showed 6.3 fine in gold
1 assay showed .6 fine in gold
2 assays showed 7.0 fine in gold
1 assay showed .2 fine in gold
2 assays showed .6 fine in gold
1 assay showed .8 fine in gold
1 assay showed 8.0 fine in gold
—
10

The bar was melted seven times when it weighed 502.01 ounces, showing a total loss of 141.29 and an estimated loss of 3.75 ounces of gold. Eight assays were made on various samples of the final metal with the following results:

1 assay showed 933.2 fine in gold
2 assays showed .3 fine in gold
2 assays showed .4 fine in gold
1 assay showed .5 fine in gold
2 assays showed .7 fine in gold
—
8

The final bar was 21 fine in silver.

[1] Trans. Amer. Inst. Mining Engineers, Vol. XL, p. 789.
Annual Report Director of the Mint, 1908, 9, p. 31.

A great deal of old scrap material of the most heterogeneous character is purchased at some of our offices and many of these deposits are small. On these small bars the question of sampling and assaying is not so important, but before the purchasing offices ship these small deposits to a mint they are united into mass melts when difficulties may appear in the sampling and become important. Nine small bars were united to make a mass melt of 338 ounces. Dip and drill samples were taken at the purchasing office and the bar was drilled, top and bottom, at the receiving mint. These samples were assayed in various service laboratories and Table XXI summarizes the results reported.

TABLE XXI

SAMPLING MASS MELT

Fineness	Dip	Drill	Drill
500.7			1
.8			1
1.1			1
.7			1
.8			2
.9	1		
2.0		2	
.1		1	
.4	4		2
.5			2
.6			2
.8	1		1
.9	1	1	1
3.0	1	1	1
.1		2	1
.2		1	
.4		2	1
.5	1		
.6		2	
.7	1		
.8			1
.9	2	1	
4.0			1
.2			2
.7	1	1	
	—	—	—
Totals	13	14	21
Silver		225	

What is probably the very worst case of disagreeing samples and assays ever investigated by the Mint Bureau was afforded by a bar weighing 774.39 ounces carrying nearly 400 base, largely copper, which was shipped to a mint as being 568 fine in gold.

Three sets of drills, top and bottom, were taken, and proving very unsatisfactory the bar was remelted with a loss of 4.6 ounces. Two dip samples were taken and the bar was again drilled, top and bottom. These ten samples were assayed in four laboratories in the service and 113 assays were made. Table XXII summarizes these assays.

TABLE XXII

SAMPLING BAR 400 BASE, LARGELY COPPER

			BAR					REMELT			
Fineness	1st Drill		2nd Drill		3rd Drill		Fineness	Drill		Dip	
	T	B	T	B	T	B		T	B	A	B
564.7						1	571.2		2		
5.3						1	.3		1		
.6					1		.7		1		
6.2					2		.8	1			
.4					1		.9				1
7.0					1		2.0	1	1	1	
.1		1			1		.6		2	1	1
.4						2	.8	1		1	
.5		1					3.0		1		
.6					1	1	.2	1	2		
.8	1						.5	1			1
8.0						1	.6			1	
.3		1					.7		1		
.4		1					.8		1	1	
.5		1					.9	1		2	1
.6		1					4.0	2		2	1
.7	1			1			.1	1		1	1
.8	1			1			.2	1			
9.1		1					.3	1		1	1
.2		2					.4	1			1
.4	3	1					.6			1	1
.5		1	1				.8			1	
.6				1			5.0			1	2
.7	1	1		1			.5				1
.8			1				.7				1
.9			1				6.0				1
570.0				2							
.1	1										
.2	1		2								
.3				1							
.4			1								
.5	1			1							
.6	2		2								
.7			2	1							
.8				1							
.9			1								
1.0				1							
.3				1							
Totals	12	12	11	12	7	6		12	12	14	14

The presence of so much copper in this metal undoubtedly affected the actual assaying as well as the sampling of the bar.

In describing the taking of dip samples I have spoken of the molten metal being "well mixed." This condition is absolutely essential to proper sampling. It is quite possible that in some of the cases already mentioned the molten metal had not been thoroughly mixed when the samples were taken. In the following case the molten metal certainly was not well mixed.

Two dip samples were assayed in duplicate by the writer, showing a decided difference between the two samples. On a reassay in duplicate the same difference appeared. Each sample was also assayed once in two other laboratories. Table XXIII summarizes the results.

TABLE XXIII

DIFFERING DIP SAMPLES

	1st Sample	2nd Sample
Bureau	615.6 fine	612.8 fine
	6.0 fine	.8 fine
Reassay	615.5 fine	611.5 fine
	6.3 fine	.1 fine
2nd Laboratory	615.3 fine	612.2 fine
3rd Laboratory	615.5 fine	611.9 fine

Many melters, samplers, and assayers have an idea that unsatisfactory chip and drill samples can be corrected by simply melting the bar and taking fresh samples. There are, of course, cases where there was carelessness in the original melting and sampling which can be cured by careful remelting and resampling, but in a vast majority of cases simple melting does little or no good. If there is a real difference of importance between two chips or two drills or between chips and drills of the same bar, it is due to the fact that the metal segregates on solidifying. This is a function of the chemical composition of the metal and, under practical conditions, a remelting which does not materially change the composition can accomplish very little in reducing the segregation.

If the chemical composition of the metal is such that it interferes with the actual assay work, manifestly a remelting which does not change the composition of the bar will accomplish no good.

It therefore follows that when the assay reports on an ordinary bar of miscellaneous bullion differ so widely as to be unsatisfactory, it should be melted and refined by strong oxidation. This will of course reduce the weight of the bar, but the loss in weight is nearly all base metal in most cases. The actual loss of gold will generally be small, except where a large amount, 50 ounces or more, of base must be removed as in the case of many cyanide bars, when the loss may become considerable. In the case already cited the removal of 141.29 ounces from a bar weighing originally 643.30 ounces caused a loss of about 3.75 ounces of gold.

A bar carrying about 35 silver and weighing 494.26 ounces yielded varying assays on the gold and was remelted with a loss of .63 ounces. Again the assays were unsatisfactory and it was remelted with a further loss of 1.09 ounces but without improvement in the assays. It was finally melted with a further loss of 5.20 ounces and still gave unsatisfactory assays. Two dip samples were taken at each melting and the eight samples were assayed in various service laboratories. Table XXIV summarizes the results reported.

TABLE XXIV

DIP SAMPLES ON FOUR MELTINGS

1st Melt		2d Melt		3d Melt		4th Melt	
Fineness	Assays	Fineness	Assays	Fineness	Assays	Fineness	Assays
806.0	1	809.9	1	812.8	1	818.3	1
.1	1	10.1	2	3.0	1	.4	1
.3	2	.6	3	.2	2	.8	1
.4	2	.7	1	.3	1	9.1	1
.5	1	.8	2	.6	2	.2	1
.7	1	.9	1	.7	1	.3	1
.8	2	1.0	2	.8	1	.5	1
.9	3	.1	1	.9	1	.9	1
7.0	2	.3	1	4.2	1	20.2	2
.1	1	.6	2	.6	2	.5	3
.2	3	.8	2	.8	2	.6	1
.4	2	2.2	1	.9	1	.8	1
.5	2	.3	1	5.0	3	1.0	1
.6	3			.3	1	.3	1
.7	2					.4	2
.8	3						
.9	1						
8.0	1						
.1	2						
.2	3						
.3	1						
.5	2						
Totals	41		20		20		19

Another bar carrying about 35 silver and weighing 666.91 ounces was drilled at the ends and in the center and the drills yielded the following results:

End Drills		Center Drills	
Fineness	Assays	Fineness	Assays
664.1	1	695.4	1
.5	1	7.4	1
5.5	2	703.0	2

This bar was remelted and two dip samples were taken, while the cold bar was again drilled at the ends and in the center. After melting, however, even with the loss of 33.29 ounces the metal remained unsatisfactory as shown by the following assays:

Dips		Drills			
		Ends		Center	
Fineness	Assays	Fineness	Assays	Fineness	Assays
705.5	1	699.5	2	706.7	1
6.6	1	.9	1	7.9	1
.8	1	701.3	1	8.9	1
7.8	1	.6	1	725.0	1
.9	1	.8	1	6.3	1
8.3	1			7.	1
.5	1				
.7	1				

From these gold assays the silver cannot be given with any exactness but it was probably about 40.

CONCLUSIONS

The foregoing data are summarized in the following conclusions:

In sampling deposits of miscellaneous gold bullion weighing over 300 ounces:

There are various cases where either a chip or a drill sample may be satisfactory.

There are various cases where a drill sample is better than a chip sample.

Where the assayer is acquainted with the metal he may accept a chip or drill sample.

On an unknown bullion it is unsafe to accept any sample except a properly prepared dip sample.

In many cases, particularly of cyanide bullion, the composition of the metal interferes with the actual assaying and the bullion must be refined before one can expect to determine the gold accurately.

A NEW TECHNICAL METHOD OF SPELTER ANALYSIS

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The subject of spelter analysis engaged the attention of the VI[1] Congress in Rome, 1906. Mr. Nissenson, Director of the Stolberg Laboratory in Westfalen, Germany, presented an exhaustive paper over the methods employed by them and invited other chemists to publish theirs, for comparison and possible unification.

I desire now to present a scheme, involving the application of an original method for lead, which, at the same time, effects a separation from cadmium. The fundamental reactions were described in the Journal of the American Chemical Society, September, 1904, and subsequently in the Engineering and Mining Journal July 25, 1908, and May 22, 1909. The last two papers deal also with its application to ores. It is based on the following reactions:

a. $Pb(NO_3)_2+4NH_4OH+(NH_4)_2S_2O_8=\mathit{PbO_2}+2NH_4NO_3+2(NH_4)_2SO_4+2H_2O$

b. $PbO_2+H_2O_2+2HNO_3=Pb(NO_3)_2+2H_2O+O_2$

c. $5H_2O_2+2KMnO_4+6HNO_3=2KNO_3+2Mn(NO_3)_2+8H_2O+5O_2$

Hence:

$2KMnO_4=5H_2O_2=5Pb$

Since the theoretical factor $\frac{5Pb}{10Fe}=1.851$ gives too low results, the empirical factor 1.92 was chosen,—giving results agreeing exactly with the standard gravimetric method—whenever a preliminary separation of lead is not necessary, and 1.95 for ores where such separation is essential. The reason for requiring a

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[1] Bericht der Internationalen Analysen Kommission an der VI Internationalen Kongress für Angewandte Chemie in Rom, 1906. Page 50.

higher factor than the theoretical is believed due to the lead peroxide carrying one-half molecule of water.

Solution of the spelter sample is effected by dilute hydrochloric acid according to Oswald Gunther[1] or dilute sulphuric according to Nissenson[2], until nearly all zinc is dissolved. This procedure makes it possible to operate on a large sample and each 0.1 cc. of potassium permanganate (0.568 grams to the liter) equals 0.001% lead, when 19.2 grams spelter is taken. The insoluble lead, cadmium and some zinc is filtered off, washed, dissolved in nitric acid, diluted, ammonia and ammonium persulphate added to peroxidize the lead. After filtering the cadmium may be precipitated in the filtrate by hydrogen sulphide.

The substitution of trichloracetic acid, according to Fox[3], for any one of the mineral acids usually employed in separating cadmium and zinc, has been found advantageous, since it is not dissociated to the same extent as hydrochloric or sulphuric acids, and even rather concentrated solutions do not prevent the complete precipitation of cadmium. In the case of mineral acids the strength must be kept within narrow limits, as is well known. A slight excess prevents the complete precipitation of cadmium, while insufficient acid causes zinc to be precipitated along and makes several re-precipitations necessary. By means of trichloracetic acid usually only one re-precipitation is called for, unless it is accompanied by more zinc than was aimed at originally in dissolving.

ANALYTICAL METHOD

Weigh out 19.2 grams of the spelter and place in No. 3 beaker. Add 200 cc. ordinary water and 44 cc. conc. hydrochloric acid, or 100 cc. water and 50 cc. dilute sulphuric acid (1:3); allow to stand over night whenever cadmium is to be determined, if lead alone is wanted a few hours' time will do. Filter off metallics, consisting chiefly of lead, cadmium and some undissolved zinc, and wash with hot water. Transfer whatever metallics are on the filter paper back into the beaker by means of a jet of water. This can be accomplished without loss if done at once before the

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[1] Ibid

[2] Ibid

[3] Journal Chem. Soc. London, 1907, page 964.

paper gets dry. Now add 10 cc. conc. nitric acid, boil until brown fumes cease to come off. Filter and wash if traces of tin or antimony are indicated, which is very seldom the case. If filtered and washed the volume will probably be large enough; if not filtered, add 100 cc. distilled water, 30 cc. conc. ammonia and 5 to 10 grams ammonium persulphate, depending on size of precipitate. Should lead be unusually high, say over 1.00%, it is best to add half of the persulphate before adding the ammonia. Boil five minutes and allow ten more for the precipitate to settle. Then filter while still warm through double 11 or 12.0 cm. No. 1 F filters. Wash four times with a hot 10% ammonia solution and five times with hot water. Transfer filter with precipitate back into same beaker in which precipitation was made. Add 25 cc. hydrogen peroxide solution (10 to 50 cc. hydrogen peroxide U. S. P. strength to the liter, plus 50 cc. conc. nitric acid). Stir until dissolved, add 15 cc. nitric acid, 1.20 sp. gr. plus 75 to 100 cc. distilled water and titrate the excess of the hydrogen peroxide by standard potassium permanganate of the strength indicated above. For instance, if 25 cc. H_2O_2 blank requires 80.0 cc. $KMnO_4$ and the sample 34.5 cc. then the lead equals 80.0—34.5 0.455%. If 25 cc. of the H_2O_2 solution should fail to dissolve the lead peroxide, add another 25 cc. and double the blank. The accompanying samples taken from practice, shows that a new method checks exactly with the long chromate method:

	Ericson method	Gravimetric[1] as chromate
Refined spelter	0.052% lead	0.055% lead
Refined spelter	0.082	0.083
Refined spelter	0.043	0.044
Prime Western spelter	0.530	0.538
Prime Western spelter	0.533	0.531
Special spelter	1.272 1.283	1.279

For spelter rather high in lead, it will be advisable to check the lead factor against a standard spelter, under identical conditions.

[1] Tilitz. Praktische Leitfaden für Zinkhütten-laboratorien, page 27.

CADMIUM DETERMINATION

Boil the ammoniacal filtrate from lead until nearly neutral and a white precipitate appears, then take off hot plate and add 40 cc. dilute sulphuric acid 1:3 and boil about ten minutes. Add water to make the volume about 200 cc. and saturate with hydrogen sulphide gas, adding a little water occasionally. Allow the precipitate to settle, filter through double filters and wash a few times with water. Redissolve on the filter the cadmium sulphide contaminated with zinc sulphide, in as little warm dilute hydrochloric acid as possible and wash with warm water. If copper is present, the sulphide remains insoluble on the filter. It may be ignited and weighed as CuO.

The filtrate containing the chlorides of cadmium and zinc is nearly neutralized with dilute ammonia and about 8 grams of trichloracetic acid dissolved in water added, or enough to dissolve the CdS formed by neutralization. Add distilled water to about 200 cc. volume and re-precipitate Cd by H_2S. Allow to settle, filter and determine by any of the usual methods, preferably as sulphate or phosphate. Duplicate determinations usually agree within a few hundreds of one per cent.

Iron is determined in a separate sample by dissolving 10 grams in 75 cc. dilute sulphuric acid and allowed to stand until practically all dissolved, then a few drops of platinic chloride added to effect complete solution, then titrate with the same standard permanganate solution used for lead. Each 0.1 cc. $KMnO_4$ solution equals 0.001% iron on a 10 gram sample basis.

The method outlined above takes care of the usual constituents called for in spelter analysis, such as lead, iron and cadmium. Zinc is taken by difference. Copper, tin and antimony are indicated and may also be determined, whenever present. The lead method is a marvel of accuracy and gives very concordant results. In making this claim, I am aware of recent criticism in regard to shortcomings of most analytical methods proposed. This one will be found, on investigation, to be a notable exception, and its daily use for several years has fully demonstrated its reliability.

A STUDY OF SOME METHODS FOR THE DETERMINATION OF ALDEHYDES

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INTRODUCTION

The great and constantly growing commercial importance of aldehydes makes definite methods of analysis of great value. It is, therefore, not surprising to note that the literature on the subject is quite extensive. Although a considerable amount of work has been done in comparing certain of the methods with a view to determining the most accurate, it is worthy of note that little has been done to determine the general applicability of some of the methods nor has a systematic quantitative study of the behavior of certain typical aldehydes towards various reagents been undertaken.

On account of the reactivity of the carbonyl group, aldehydes are capable of taking part in many reactions. Those which in addition to the aldehyde group also have other characteristic groups will in turn take part in special reactions peculiar to those groups.

Methods may therefore be classified as general when the characteristic reactions of the aldehyde group alone are considered, and *special* when the properties of any of the other groups present are taken advantage of for purposes of analysis.

Among the general methods (*a*) the combination of aldehydes with bisulphite; (*b*) the use of neutral sulphite; and (*c*) the precipitation of aldehydes as hydrazones by means of substituted hydrazines were considered promising and deserving of closer study.

This paper is part of "A Quantitative Study of Some Aldehyde Reactions." The study was suggested by Professor H. C. Sherman of Columbia University and was carried out under his direction. The writer takes this opportunity for thanking Professor

Sherman. He also wishes to mention that part of the work was carried out at the Laboratory of the College of the City of New York through the courtesy of the Director.

PURPOSE AND PLAN

The part of the work taken up in this paper consists in the determination of how quantitative the general methods mentioned above are with the following typical aldehydes:

Formaldehyde, benzaldehyde, salicyl aldehyde, p-oxy benzaldehyde, anisaldehyde, and vanillin.

The purest material possible was procured, its purity ascertained by the application of well-known tests, by redistillation at reduced pressure, recrystallization, or sublimation. Also, wherever possible the best tested or approved special methods were used as checks.

THE COMBINATION WITH BISULPHITE

Bertagnini[1] in 1853, established the fact that bisulphite combined with substances of aldehydic nature. In 1892[2] this was introduced by Schimmel and company, for the determination of cinnamic aldehyde in cassia oil. It now plays an important part in the valuation of citral and cinnamic aldehyde-containing oils. The method of determination consists in treating a known volume of oil with sodium bisulphite in a cassia flask, shaking well and allowing to stand for some time. The oil is then brought up to the graduated portion of the flask, and the volume of uncombined oil is read off. The aldehyde present is thus determined by difference.

In 1901, M. Ripper[3] suggested using a dilute bisulphite solution with dilute aldehyde solutions, and determining the excess bisulphite with a standard iodine solution. Ripper uses potassium bisulphite and claims good results with formaldehyde, acetaldehyde, benzaldehyde, and vanillin. The method as applied here was essentially that of Ripper with the exception that solutions of various concentrations were employed. The conditions which gave the best results are described below.

[1] Die "Atherischen Ole" Semnaler, I, 156.

[2] "Atherischen Ole" Gildmeister and Hoffman (23, p. 602).

[3] Monatsh, *8*, 637.

The preponderance of opinion seemed to be in favor of the Romijin[1] iodine method, as the most reliable for commercially pure solutions of formaldehyde. It was therefore selected as the check method in determining how quantitative the other methods were.

The formaldehyde used was Kahlbaum's pure, which had previously shown 33.76 per cent aldehyde by the Blank[2] and Finkenbeiner method.

More consistent results were obtained with the Romijin method when the conditions were modified so as to use twice the amount originally recommended. The error in measuring a small amount of solution is thus decreased. The conditions as used are therefore as follows: Ten cubic centimeters of a solution of formaldehyde containing about five grams to the half liter were treated in a stoppered Erlenmeyer flask with forty cubic centimeters of a standard iodine solution about tenth normal, made up with thirty-five grams potassium iodide per liter, ten cubic centimeters normal sodium hydroxide added, and allowed to stand fifteen minutes; ten cubic centimeters normal sulphuric acid were then added, and the excess iodine determined with about tenth normal thiosulphate. By means of a flask, the amount of iodine used up by the aldehyde present is ascertained, and from the factor, one gram iodine is equivalent to 0.11858 grams formaldehyde, the aldehyde equivalent of one cubic centimeter iodine solution can be obtained. The average of fourteen determinations by this method showed 33.86 per cent aldehyde.

Solutions of sodium bisulphite were now used upon an aldehyde solution of the above mentioned concentration. A three per cent bisulphite solution gave results which approached the closest to those obtained above with the Romijin method. The figures in Table I were obtained by treating 25 cc. aldehyde solution containing 5 grams to half a liter, with 25 cc. 3 per cent bisulphite solution, in a stoppered Erlenmeyer flask. After standing about fifteen minutes, during which a blank is run, the excess bisulphite is titrated with tenth normal iodine and the per cent aldehyde

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[1] Z. Anal. chem. *36*, 18.
[2] Ber. *31*, 2979.

calculated from the iodine equivalent of the formaldehyde[1] mentioned above.

For use with bisulphite, a high grade of commercial benzaldehyde was first distilled at the ordinary pressure and that fraction which came over at 178.5°-179°, corrected, using a standardized thermometer, was collected and redistilled in vacuum. At 110 mm. the boiling point of the aldehyde was found to be 112.5°, corrected. The main portion was then fractionated in vacuum, and that part which distilled over at 112.5°-113° at 110 mm. was caught in an amber-colored bottle, and tightly stoppered at once. Oxidation was therefore reduced to a minimum.

A one per cent aldehyde solution in 100 cc. 95 per cent alcohol and 400 cc. water was prepared, and varying amounts of this solution were treated with different quantities of sodium bisulphite solutions ranging in concentration from 1-6 per cent and the excess determined with standard iodine. Results above 95 per cent, however, were not obtained. The aldehyde-bisulphite compound is apparently hydrolized very easily into bisulphite and aldehyde, for in all cases when the reaction mixture was titrated with iodine, the endpoint could not be made to persist for more than the fraction of a second. If the titration were continued until a permanent endpoint was obtained the amount of iodine used would almost be equal to that required by the bisulphite alone. Attempts to render the reaction more quantitative did not prove very successful. The addition of neutral sodium sulphite to take care of the acid formed during the titration and which promoted the splitting of the addition compound, appeared to give better results but still only about 95 per cent of the theoretical.

The figures in the table were obtained by treating 25 cc. of the 1 per cent aldehyde with 25 cc. of a 3 per cent sodium bisulphite and allowing the mixture to stand about 25 minutes in a stoppered Erlenmeyer flask before titrating the excess bisulphite.

Salicyl aldehyde was purified by fractionation under reduced pressure and only that which distilled at 139°-139.5° at 160 mm. or 166°-166.5° at 360 mm. was treated similarly to benzaldehyde; the results indicated only about 82 per cent material showing

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[1] W. Kerp, Z. Nahr. Genussen, *6*, 66. Also Centr. '04, II, 57.

that this aldehyde bisulphite compound was much less stable than the corresponding benzaldehyde compound. In order to ascertain whether the greater instability of the addition compound was due to the proximity of the acid hydroxyl group, experiments were conducted with p-oxy benzaldehyde.

Kahlbaum's p-oxy benzaldehyde was purified by sublimation and the fine snow-white needle-like crystals were found to have a melting point of 115°-116°. These were then used for the various determinations. With bisulphite the results were mainly 87-89 per cent of the theory. Thus, showing that while the hydroylsis of the aldehyde-bisulphite compound was greater in this case than for benzaldehyde[1], it was considerably smaller than for salicyl aldehyde. The presence and proximity of the hydroxyl group apparently influence the stability of the bisulphite addition compound.

On account of the relation between anisaldehyde and vanillin on one hand, and benzaldehyde, salicyl and p-oxy benzaldehyde on the other, it was considered very interesting to note how the former would behave in the various determinations.

Anisaldehyde was therefore purified by repeated fractionation under reduced pressure and that which distilled at 195°-195.5° corrected at 205 mm. pressure was used in the determinations. The results with bisulphite showed only about 90 per cent of the theoretical amount present. This would indicate that while the anisaldehyde bisulphite compound was more easily hydrolized than that with benzaldehyde, it was not as readily hydrolized as the corresponding p-oxy compound and still less than that with salicyl aldehyde.

Vanillin which was specially purified by Isakovics as well as material prepared by Kahlbaum and Fritzsche Bros. was used in the determinations. When the conditions with bisulphite used heretofore were applied to vanillin the results of a hundred determinations on the three brands ranged from 93-96 per cent of the theory. Attempts to make the reaction more quantitative by increasing the concentration of the bisulphite, using alcohol instead of water as a solvent, titrating in an ice bath, or taking care of the acid formed, did not very materially change the figures.

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[1] See Table I.

Vanillin apparently is hydrolized to a smaller extent than any of the others tried excepting formaldehyde.

TABLE I

BISULPHITE RESULTS OF THE DIFFERENT ALDEHYDES AS PER CENT OF THE THEORETICAL

Formaldehyde[1]	Benzaldehyde	Salicylald.	P-oxy Benzald.	Anisald.	Vanillin
33.42	93.45	80.48	88.40	89.90	A. material
33.42	92.79	81.58	88.86	90.40	95.19
					95.59
33.42	93.34	82.01	88.40	90.17	95.21
					95.77
33.34	92.02	82.23	89.10		95.21
					95.64
33.40	93.12	82.23	89.10		95.20
					94.98
33.19	93.55		85.66		
					B. material
33.31	93.12		85.38		
					94.50
33.21	94.98		85.50		94.40
					94.50
33.36	95.19		87.09		94.63
					94.31
33.51	94.77		86.77		94.18
33.42	92.89		87.09		C. material
	93.71				95.75
Aver. 33.34					95.75
	93.61				95.35
					95.72
	94.03				95.50
	93.82				

In the table the figures were obtained by treating an approximately one per cent aldehyde solution with 10-25 cc. three per

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[1] Romijin results = 33.86%.

cent sodium bisulphite solution in a stoppered Erlenmeyer flask and titrating after 15-25 minutes (depending upon the aldehyde) with a standard iodine solution, until the blue color with starch persisted for an instant. The difference between the amount of iodine required by a blank run under similar conditions and that required in the determination gave the iodine equivalent to the amount of aldehyde used. The per cent was calculated by using the factors obtained from the amount of aldehyde equivalent to one gram iodine, thus:

1 gram iodine is equivalent to 0.11858 grams formaldehyde
1 gram iodine is equivalent to 0.41178 grams benzaldehyde
1 gram iodine is equivalent to 0.48081 grams salicyl and p-oxy benzaldehyde
1 gram iodine is equivalent to 0.5360 grams anisicaldehyde
1 gram iodine is equivalent to 0.5990 grams vanillin.

W. Kerp[1] finds that the sodium bisulphite addition compounds of aldehydes and ketones are hydrolized in water. This is increased by a rise in temperature and lowered by an increase in concentration. He finds that the formaldehyde compound is least hydrolized; acetaldehyde five times as great; benzaldehyde, thirty-one times as readily; acetone 155 times, and glucose 500-1200 times as fast as with the formaldehyde compound. A study of Table I will give an idea of the relative ease with which the addition compounds are probably hydrolized.

Another cause for low results, though of less importance than that caused by hydrolysis, would be the error in reading the burette. Thus, if that error be placed at about 0.01 cc. for a concentrated bisulphite this would amount to about 0.1 cc. of iodine solution, which alone is sufficient to cause an error of several tenths of a per cent on the amount of vanillin taken, for an analysis.

R. H. Williams[2], working in this laboratory compared the Legler,[3] Blank[4] and Finkenbeiner, with the Romijin[5] iodine and cyanide

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[1] Z. Nahr. Genussen, *6*, 66.
[2] J. Am. Chem. Soc., *27*, 596.
[3] Ber., *16*, 1333.
[4] Ber., *31*, 2979.
[5] J. Anal. Chem., *36*, 18.

methods on formaldehyde and concludes that the condensation methods give lower results because the reaction is not complete, or the oxidation methods give higher results because the oxidation goes further than the equation would show. The bisulphite method belonging to the former class, probably gives lower results than the iodine method with formaldehyde, for the reason mentioned above.

USE OF SODIUM SULPHITE IN THE DETERMINATION OF ALDEHYDES

According to some investigators, when neutral sodium sulphite in water solution acts on an aldehyde or ketone, sodium hydroxide is liberated thus:

$$R.\ COH + Na_2SO_3 + H_2O = R.\ C(OH)NaHSO_3 + NaOH.$$

The use of this reaction for the quantitative determination of aldehydes was first suggested by Tiemann[1]. Later Sadtler[2] stated that this reaction was more or less general for the quantitative determination of some saturated and unsaturated aliphatic, and aromatic aldehydes, and some ketones. The method as worked out by him consists in titrating the alkali with normal acid. From the equation the amount of aldehyde present could be calculated.

A 20 per cent sodium sulphite solution was prepared and neutralized as closely as possible using phenolphthalein as indicator. When this solution was used with dilute aldehyde solutions, and tenth normal acid used in the titration, the results obtained were quite far from the theoretical. This may in part be due to the difficulty of obtaining a sharp endpoint in titrating sodium sulphite a half of 1 cc. acid, more or less, producing no effect on the endpoint. When, however, the concentrated aldehyde was used, normal or half normal acid could be used for the titration, and on account of the large amounts of acid used up, 0.1 or 0.2 cc. did not cause a serious error. The determination on formaldehyde was therefore carried out as follows:

Two to five grams of aldehyde were weighed into a stoppered Erlenmeyer flask and neutralized with tenth normal sodium

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[1] (Berl.) Ber., *31* ('98), 3317.

[2] Am. J. Pharm. ('04), *76*, 84; J. Soc. Chem. Ind., *23* ('04), 303; J. Am. Chem. Soc., *27* ('05), 1321.

hydroxide and two drops phenolphthalein; now 50 cc. of the neutral sodium sulphite solution were added for each two grams of aldehyde, the mixture allowed to stand about half an hour and titrated with half normal sulphuric acid to absence of a pink color. The amount of acid required by a blank containing an amount of sulphite equal to that left uncombined in the determination is subtracted from the amount required in the determination. This is the correction recommended by Russ[1] and Larsen. Sadtler[2], however, in the case of citral uses the same amount of sulphite as in the determination. He does not say whether that is also the condition in the case of formaldehyde. If, however, the blank contains the same amount of sulphite as the determination, the results are about 0.75 per cent less than shown in Table II. The results obtained by this method check very closely with those obtained by the bisulphite method, being almost identical with them.

With benzaldehyde the conditions described in the Pharmacopoeia, 8th Revision, gave low results similar to those obtained with dilute solutions. As a result of comparative experiments in which the concentration of aldehyde, the amount of sulphite, the presence of alcohol or kerosene as diluent, and the interval before titration were the factors varied, the conditions which were found to be most satisfactory were as follows:

About a gram of benzaldehyde was weighed into a well-stoppered flask, 10 cc. alcohol added, and a little water about 10 cc. to wash down the sides of the flask. The aldehyde was then neutralized with the tenth normal alkali using 6 drops of 1 per cent phenolphthalein as an indicator. Then 50 cc. neutral sodium sulphite were added and titrated with half normal sulphuric acid until the pink color disappeared. A blank containing 35 cc. sulphite, the amount calculated to be left unabsorbed, was carried out alongside of the determination, and the amount of acid required to render colorless, subtracted from the total acid in the determination.

The alkali required to neutralize the aldehyde was calculated to benzoic acid, and this weight of acid subtracted from the weight

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[1] Mitt. Technol. Gewerb. Uns., Wien (2) *16*, 85; (Centr., '06, II, 363).
[2] J. Soc. Chem. Ind., *23*, 303.

of the sample before calculating the per cent aldehyde. In this way results of about 99 per cent of the theoretical were obtained for the benzaldehyde used.

With salicyl aldehyde and p-oxy benzaldehyde before the addition of sodium sulphite the acidity was neutralized with half normal sodium hydroxide and phenolphthalein. During the neutralization or after the addition of the sulphite, colored compounds were formed rendering it impossible to titrate with any degree of accuracy.

Anisic aldehyde behaves like benzaldehyde in that a clear solution is obtained which is not colored as with salicyl aldehyde and p-oxy benzaldehyde. The determination of the endpoint is, however, more difficult; phenolphthalein must be added in the course of the titration, the color being rather flitting.

The results that were obtained indicated only about 94 per cent aldehyde when the determination was conducted under the conditions established under benzaldehyde.

In the case of vanillin, as with salicyl aldehyde and p-oxy benzaldehyde, it was found very difficult to indicate the end of the titration with any degree of accuracy, whether the solution was titrated cold or hot. The solution at first was only slightly off color, this could not however be dissipated by adding acid, and the endpoint could not be determined.

TABLE II

RESULTS WITH NEUTRAL SULPHITE IN PER CENT

1. Formalde.[1]	Benzald.	Salicylald.	P-oxy Benzald.	Anisicald.	Vanillin.
33.20	97.31	Not possible to indicate with any degree of accuracy.	91.60	92.67	Not possible to indicate with any degree of accuracy.
33.40	98.76		89.60	94.09	
33.46	99.00		83.72	94.25	
33.22	98.77	52-54%	83.18	93.46	
33.29	98.64		83.76	93.64	
33.18	98.05		76.09	92.33	
33.17	99.09		80.45	94.90	
33.42					
33.51					
Av. 33.32	Av. 98.52				

[1] Romijin Method=33.86%.

Attention may be directed here to the view of Seyewetz[1] and Gibbello. They claim that when neutral sodium sulphite is added to formaldehyde, no reaction takes place until acid is added. The bisulphite then formed combines with the aldehyde. Since the formaldehyde bisulphite compound reacts neutral to phenolphthalein, the sulphuric acid does not decolorize the indicator until all the formaldehyde has gone into combination with the bisulphite.

$$2Na_2SO_3 + 2CH_2O + H_2SO_4 = 2NaHSO_3.CH_2O + Na_2SO_4.$$

The writer is inclined to agree with this explanation for the following reasons:

1. When sulphite is added to the aldehyde used, the characteristic odor of the latter is not dissipated even on long standing until acid had been added in sufficient amount to form bisulphite to combine with all the aldehyde present.

2. If during the titration the acid should be poured in quite rapidly with shaking, the solution will turn entirely colorless long before it should do so. On shaking for some time, however, it turns pink again, and the titration can be continued. This is observed only slightly with formaldehyde but is very marked with benzaldehyde and anisaldehyde. The behavior described would seem to indicate that more bisulphite was formed than could be absorbed at once; on thorough agitation, however, the reaction proceeded to completion and all the bisulphite used up.

3. In the course of the titration, the pink color does not seem to diminish much in intensity, until very near the end.

In the case of benzaldehyde and anisaldehyde it was moreover possible to get experimental proof of the absence of a reaction liberating alkali, as follows:

Five cc. of the aldehyde were pipetted into a cassia flask filled to the divisions on the neck, with neutral sodium sulphite. The benzaldehyde remaining on top, the amount added could be readily measured, so that the pipette reading was verified. After standing in this way for twelve days with frequent shaking, it was observed that the aldehyde on top had not changed in amount. When 5 cc. of the clear sulphite solution was pipetted out from the

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[1] Bull Soc. Chim. (3) *31*, 691 ('04).

bottom of the flask, 1.1 cc. half normal acid were required for neutralization, while a blank of 5 cc. sulphite required 1.15 cc. of the acid. No alkali was, therefore liberated. The result was similar in the case of anisaldehyde.

In the case of the sulphite method a considerable amount of practice is required before the results will be uniform and concordant. Gildmeister[1] and Hoffmann say that it is impossible to titrate sulphite solutions sharply so that the endpoint of the reaction can only be approximately determined. Accurate results are therefore not to be obtained with it. In spite of this disadvantage for concentrated solutions, the simplicity of the process and rapidity of execution makes this method quite desirable. As may be seen from Table II the results for formaldehyde are close enough to make it quite reliable. Benzaldehyde also may be determined with a fair degree of accuracy.

THE CONVERSION OF ALDEHYDE INTO HYDRAZONES.

A. Use of P-brom Phenyl Hydrazine.

J. Hanus[2] suggested the use of p-brom phenyl hydrazine for precipitating vanillin quantitatively. An attempt was therefore made to apply this method to the other aldehydes.

The solutions used were approximately of one per cent concentration; wherever possible water alone was used as the solvent or the substance brought into solution with as small a quantity of alcohol or acetic acid as would be required to keep it in solution when the desired concentration was obtained by diluting with water.

The precipitant was prepared fresh when required by dissolving in the necessary volume of hot water and filtering before use.

Attempts to precipitate formaldehyde with p-brom phenyl hydrazine did not result successfully; the precipitate did not settle and ran through the filter.

With benzaldehyde under various conditions the results did not show more than about 93 per cent aldehyde. The hydrazone did not form well, was sticky, and gave a rather turbid filtrate.

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[1] Atherischen Ole (2) 604.

[2] Z. Unters. Nahr. Gen. *3*, 531 ('00).

Similarly, the hydrazone obtained with salicyl aldehyde resembled the benzaldehyde hydrazone and indicated only about 93 per cent aldehyde.

A well formed and easily handled hydrazone, however, was formed with p-oxy benzaldehyde; 25 cc. of a 1 per cent water solution of the crystals using 40 cc. alcohol to the half liter, were treated with 75 cc. hot water containing in solution 2-3 times as much hydrazine as the aldehyde to be precipitated. The precipitation was conducted at 50° C. and the precipitate allowed to stand five hours. It was then filtered on a Gooch crucible, washed with hot water to absence of a reaction with silver nitrate and dried at 105°. The weight of the hydrazone multiplied by 0.4193 gives the weight of aldehyde present.

$$C_6H_4OH.COH + C_6H_4.B_2NH.NH_2$$
$$= C_6H_4OH.CH{:}N.NH.C_6H_4B_2 + H_2O.$$

Theoretical results were obtained under the conditions described.

Anisaldehyde gave results in the neighborhood of 99 per cent when an acetic acid solution of 90 cc. glacial acid to half a liter of a one per cent aldehyde was used. The precipitation was carried out under conditions similar to those described above with the exception that the precipitate was allowed to stand one hour instead of five and was dried at 100. The weight of hydrazone multiplied by 0.4460 gives the aldehyde present.

The conditions for the precipitation of vanillin with p-brom phenyl hydrazine are essentially as described by Hanus[1]; 0.5 gram of the hydrazine being 2-3 times the theoretical amount, was dissolved in 75 cc. of hot water, filtered, and added to 25 cc. of the 0.75-1 per cent water solution of vanillin which was previously warmed. The temperature at the precipitation was kept at about 50° C. The precipitate settles in about half an hour and is allowed to stand for about five hours; it is then filtered on a Gooch crucible, washed with hot water until the washings no longer reduce silver nitrate, dried at 100° and weighed.

The weight of the hydrazine multiplied by 0.4738 gives the weight of vanillin present.

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[1] Z. Unters. Nahr. Gen., *3*, 532 ('00).

TABLE III

PERCENTAGE RESULTS WITH P–BROM PHENYL HYDRAZINE

Formald	Benzald	Salicylald.	P-oxy Benzald	Anisald[1]	Vanillin
A well defined precipitate did not form.	93.55	93.24	99.82	99.50	A. —
	91.12	93.21	100.09	99.11	98.75
					98.50
	91.92	93.04	99.88	99.09	99.07
					99.18
	93.42	93.25			
	93.05	93.44			B. —
					98.88
		94.25			98.72
					99.21
		94.35			99.40
					99.37
					C. —
					99.09
					99.32
					99.25
					99.02
					98.86
					98.81

From the table it may be noticed that those aldehydes which were solid, vanillin, and p-oxy benzaldehyde, tended to give hydrazones which were most suited for quantitative determination. The lower the molecular weights of those that are liquid, the less quantitative are the results.

B. The Use of P-Nitro Phenyl Hydrazine.

W. Alberda van Epenstein[2] and J. J. Blanksman found that p-nitro phenyl hydrazine precipitated acetone, acetaldehyde, and benzaldehyde, quantitatively. Although they give only single determinations in each case to support their contention, the

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[1] The results here were corrected for anisic acid by titrating 25 cc. with tenth normal alkali and subtracting the weight of acid thus found from the weight of aldehyde present before calculating the per cent.

[2] Receuil Trav. Chim. Pays Bas, *24* ('05) 33.

method was considered promising and was taken up more fully with the aldehydes considered in order to ascertain how generally applicable it might be.

The solutions of the aldehydes employed here were the same as those used with p-brom phenyl hydrazine. The precipitant was dissolved in 30 per cent acetic acid or in dilute hydrochloric acid and the solution filtered. This was prepared fresh when wanted.

When this reagent was employed with formaldehyde, a well defined precipitate formed at once and was easily handled; the results, however, did not check with those obtained by the other methods, showing only about 26 per cent aldehyde.

As a result of various trials the conditions which gave the most consistent results with benzaldehyde were as follows:

A one per cent solution of benzaldehyde in 12 per cent acetic acid was prepared; 25 cc. of this solution were diluted with 50 cc. water, and 30 cc. 30 per cent acetic acid containing about twice as much of the p-nitro phenyl hydrazine as demanded by theory were added. The precipitate was allowed to stand five hours, then filtered on a Gooch crucible, washed with 10 per cent acetic acid to absence of a strong color with dilute alkali, dried in an oven at 105-110°, and the weight multiplied by 0.4400 to obtain the weight of benzaldehyde. If the weight of benzoic acid is separately determined, by titration with alkali, and subtracted from the weight of aldehyde, taken for analysis, the method proves to be about 99 per cent. It is therefore the most accurate method for benzaldehyde at present known.

For salicylic aldehyde, the conditions which gave the most quantitative results were essentially the same as for benzaldehyde:

To 20 cc. of one per cent solution of the aldehyde in 15 per cent acetic acid were added 50 cc. of water and 25 cc. of 30 per cent acetic acid containing 0.6 gram of the hydrazine. The precipitate was allowed to stand one hour, filtered on a Gooch crucible, washed with 10 per cent acetic acid, to absence of a strong color with dilute alkali, and dried at 105-110°.

The weight of the hydrazine multiplied by 0.4747 gives the weight of aldehyde present. The figures obtained under these conditions are quite concordant though only about 95.5 per cent of the theoretical.

When the conditions described above were applied to the determination of anisaldehyde, p-oxy benzaldehyde, and vanillin, the results obtained were about 100 per cent, 101.5 per cent and 102 per cent for the respective aldehydes. After considerable variation of conditions, the p-nitro phenyl hydrazine was dissolved in very dilute hydrochloric acid about twice normal strength and added drop by drop from a pipette to the aldehyde solution which had previously been diluted with 75 cc. water and warmed. The mixture was stirred vigorously while the precipitant was added, and the precipitate allowed to stand half an hour before filtration. It was washed on the Gooch crucible with a little of the dilute hydrochloric acid, and finally with water until the washings only gave an opalescence with silver nitrate. A few available figures with vanillin show results very close to the theoretical. The writer believes[1] that by this treatment co-precipitation will be decreased to a minimum.

The factors for calculating the aldehyde from the weight of the hydrazone are 0.4747 for p-oxy benzaldehyde; 0.50188 for anisic aldehyde, and 0.5353 for vanillin.

TABLE IV

PERCENTAGE RESULTS WITH P-NITRO PHENYL HYDRAZINE

Formald	Benzald	Salicylald	Anisicald	P-oxy Benzald[2]	Vanillin[2]
25.67	98.63	95.16	100.25	101.5	100.52
	98.62	95.38	99.79	101.09	100.40
	98.71	95.36	99.70	101.82	100.00
	98.12	95.42	100.10	101.68	99.77
	99.42	minimum	99.98		
		figures	99.85		
		94.50			
		94.63			

The hydrazones formed with p-nitro phenyl hydrazine are on the whole less soluble and better formed physically than those

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[1] Experiments on this point are still in progress.

[2] See text preceding page.

obtained with the p-brom compound. It is therefore possible to get better results with it than with the brom derivative.

TABLE V

COMPARISON OF THE RESULTS BY THE DIFFERENT METHODS ON FORMALDEHYDE, BENZALDEHYDE AND VANILLIN

	Iodine	Bi-sulphite	Neutral Sulphite	p-brom ph.hydraz	p-nitro ph.hydraz	Alkali-metric[1]
	per cent	per cent	per cent	per cent	per cent	per cent
Formaldehyde	33.86 average	33.34 average	33.32 average		about 26	99.06 average
Benzaldehyde		93-95	98.52 average	about 93	98.70 average	
Vanillin	about 95.5 average	about 95.5 average	see text	99.03 average	about 100 see text	

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[1] The Wellman method for determining vanillin by titrating with alcoholic potash. Pharm. Ztg. '98, 634:

One gram of vanillin is introduced into a 200 cc. stoppered flask and 25 cc. alcohol and 25 cc. half normal alcoholic potash added; the excess of alkali is titrated with half normal acid and phenolphthalein. The strength of the alcoholic potash with the addition of alcohol is first determined, and the difference between the two titrations multiplied by 0.076 gives the weight of vanillin.

$$C_6H_3.OCH_3.COH.OH + KOH = C_6H_3.OCH_3.COH.OK + H_2O$$

(*Résumé*)

INFLUENCE DE L'HYDROGENE SULFURE SUR LA PRECIPITATION QUANTITATIVE DE CERTAINS HYDROXYDES PAR L'HYPOSULFITE DE SODIUM

PAR DR. R. HAC
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La méthode Chancel, dans laquelle la précipitation des sels d'alumine par l'hyposulfite de sodium devait être utilisée pour le dosage et la séparation de l'aluminium, n'a pas eu de succès. Il n'est pas même possible de précipiter d'une manière quantitative les sels d'aluminium seuls; c'est pourquoi les expériences qui avaient pour but la séparation exacte du fer de l'aluminium et de celui-ci du glucinium ont fourni des résultats absolument inexactes. Malgré cela on voit apparaitre dans la littérature chimique des méthodes pour la séparation du fer et de l'aluminium, qui ne sont que des modifications de la manière de travailler indiquée par Chancel.

En appliquant cette méthode, dont la base théorique est le degré différent d'hydrolyse de ces deux sels métalliques, on doit nécessairement tenir compte de l'acide sulfureux, qui se forme par la décomposition de l'hyposulfite, ainsi que des propriétés des sulfites des métaux en question.

D'une manière générale les solutions aqueuses des sulfites de métaux plus électropositifs se décomposent moins facilement et la séparation quantitative de certains hydroxydes dépend de l'élimination parfaite de l'oxyde sulfureux d'une solution donnée.

Par l'ébullition seule l'oxyde sulfureux n'est éliminé que bien difficilement, bien rapidement au contraire lorsqu'on fait passer dans le liquide bouillant un courant d'hydrogène sulfuré.

1. Des solutions diluées de sels d'alumine, maintenues en ébullition et saturées d'hydrogène sulfuré, l'aluminium se sépare déjà

au bout d'une demi-heure; à une température inférieure, c'est à dire de 90 à 98° C, cette séparation n'est terminée qu'au bout de trois heures.

2. Les solutions de sels ferreux sont précipitées à l'ébullition par l'action de l'hydrogène sulfuré.

3. Les solutions des sels de glucinium ne se précipitent pas lorsqu'on les fait bouillir avec une solution d'hyposulfite de sodium. Par contre il y a séparation quantitative lorsqu'on y fait passer en même temps de l'hydrogène sulfuré pendant au moins deux heures.

4. Les solutions des sels de thorium sont précipitées, comme on le sait, d'une, façon quantitative par une ébullition avec l'hyposulfite de sodium seul.

5. Les solutions des sels cériques (par ex. $CeCl_3$) ne donnent pas de précipité par l'ébullition avec l'hyposulfite de sodium. L'action simultanée de l'hydrogène sulfuré ne change pas sensiblement cet résultat, vu qu'il se forme un précipité négligeable.

Il s'en suit que de cette simple façon il est possible de précipiter l'aluminium quantitativement de ses sels, mais que l'on ne peut pas se servir de cette réaction pour la séparation quantitative de l'aluminium d'avec le fer et le glucinium. Il en est de même pour la séparation du thorium et du cérium par la méthode Chancel.

ACCELERATION CATALYTIQUE DE LA REDUCTION DES NITRATES PAR LA METHODE SCHLOESING

PAR DR. R. HAC

Laboratoire de chimie analytique (prof. T. Hanus) de l'Ecole polytéchnique tchèque de Prague (Bohème.)

Lors du dosage de l'acide nitrique dans les précipités phosphomolybdiques j'ai observé un dégagement très vif de NO, lorsqu'on faisait bouillir le liquide après la réduction. En travaillant de cette manière l'opération exigeait bien moins de temps que lors du dosage de l'acide nitrique dans d'autres substances. Des expériences ultérieures ont démontré qu'il faut attribuer cette accélération à l'influence des combinaisons molybdéniques qui s'étaient formées par l'action réductrice du $FeCl_2$ sur l'acide molybdique.

Pour cette raison j'ai fait une série d'expériences ayant pour but d'établir la proportion dans laquelle cette accélération s'effectue et de constater s'il on obtient ce résultat seulement avec des composés de molybdène où encore en employant des combinaisons d'autres éléments analogues.

Dans la réaction non catalysée le gaz NO se dégage lentement et en petites bulles, tandis qu'avec l'emploi de MoO_3 comme catalyseur il y a formation quasi instantanée de grandes bulles du dit gaz et il n'est guère nécessaire d'évaporer le liquide pour le chasser entièrement.

Pour évaluer l'effet catalyseur du MoO_3, je me suis servi d'un appareil permettant de mesurer, dans des conditions égales, le volume de NO dégagé d'un côté par le $FeCl_2$ seul et de l'autre en présence de MoO_3.

L'addition de WO_3, V_2O_5, U_3O_8, $K_2Cr_2O_7$, H_2PtCl_6, $MnCl_2$ et TiO_2 au $FeCl_2$ n'a produit aucun effet catalyseur sur la réduction de l'acide nitrique.

Les produits que l'on obtient en réduisant par le zinc les acides H_2MoO_4, H_2WO_4, H_4TiO_4 et les sels uranyliques réduisent, comme on le sait, l'acide nitrique. Cette réduction, comme j'ai pu constater, ne donne toutefois jamais un rendement théorique de NO.

Avant tout j'ai fixé mon attention sur les sels correspondants aux oxydes Mo_2O_3 et Ti_2O_3. Dans le premier cas, la majeure partie (environ 75% dans mes essais) de l'acide nitrique est réduite en ammoniaque, dans le second il se forme NO, mais le rendement n'est pas quantitatif.

Par contre, en combinant le $FeCl_2$ avec le MoO_3, il y a dans tous les cas réduction quantitative de l'acide nitrique en NO.

Remarques sur le dosage de l'acide nitrique.

On place la solution, dans laquelle on veut doser les nitrates, dans un ballon, on l'additione d'environ 0.2 g de Na_2MoO_4 où 0.1 g de MoO_3. On fait bouillir le liquide afin d'en chasser l'air. Après y avoir introduit le chlorure ferreux et l'acide chlorhydrique on maintient le mélange pendant cinq minutes à la température du bain-marie. Puis on distille et recueille l'oxyde NO sur mercure. La petite quantité d'acide chlorhydrique, entraîné est éliminé par l'introduction d'un peu de potasse caustique dans la burette. On fait la lecture au bout d'une demi-heure jusqu'à une heure et l'on calcule avec le volume lu directement. Le gaz NO est pratiquement pur.

0.1015g KNO_3 ont fourni: 22.62 cm^3 de NO (pour conditions normales),
calculé: 22.47 cm^3 de NO; différence: +0.15 cm^3;
0.1023g KNO_3 ont fourni: 22.78 cm^3 de NO (pour conditions normales),
calculé: 22.63 cm^3 de NO; différence: +0.15 cm^3;
0.0730g KNO_3 ont fourni: 16.28 cm^3 de NO (pour conditions normales),
calculé: 16.16 cm^3 de NO; différence: +0.12 cm^3.

	ont donné de NO:		trouvé:	différence:
0.0920g KNO_3,	20.46 cm^3	(p. cond. norm.),	0.0921g KNO_3,	+0.0001g
0.0990g KNO_3,	21.81	(p. cond. norm.),	0.0985g KNO_3,	—0.0005g

Te me réserve d'étudier la réduction de l'acide nitrique par d'autres substances réductrices en présence de différents corps catalyseurs.

(*Resumé*)

L'EMPLOI DE L'HYDRAZINE ET DE CERTAINS DE CES DERIVES POUR LE DOSAGE PONDERAL DU CHROME

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La réaction de l'hydrate d'hydrazine et de ces sels avec les chromates alcalins a été étudié exclusivement pour des solutions acides. Elle sert surtout pour le dosage volumétrique des deux substances en question dans lequel on mesure le volume de l'azote mis en liberté.

Nous avons trové que cette réaction se prête également au dosage pondéral du chrome, lorsque ce dernier se trouve dans la solution aqueuse sous forme de l'anion CrO_4'' et que le milieu est alcalin ou sensiblement neutre. La réaction s'effectue d'abord dans le même sens qu'en milieu acide, c'est-à-dire d'après le schéma.

$$4\,CrO_4'' + 3\,N_2H_5{}^{\cdot} + 17H^{\cdot} = 4Cr^{\cdot\cdot\cdot} + 16H_2O$$

De la solution de sel chromique ainsi formé le chrome se sépare quantitativement comme $Cr(OH)_3$, si l'on semplit certaines conditions, qui se rapportent à la proportion relative des corps réagissants, au temps de l'ébullition et à la présence des certains corps catalyseurs. L'hydrate de chrome se précipite des solutions des chromates acalins non seulement par l'hydrate d'hydrazine, (lequel précipite les sels chromiques, déjà par suite de sa basicité) mais encore par le sulfate d'hydrazine, (qui ne précipite pas les sels chromiques) et par certains derivés de l'hydrazine de nature basique ou neutre. Nous avons en effet pu constater que la phénylhydrazine et la thiosémicarbazide réduisent les chromates en sels chromiques et en précipitent en même temps l'hydrate chromique.

Nous faisons remarquer que la précipitation par l'hydrazine et les derivés hydraziniques citées plus haut est assez lente et peut exiger plusieures heures et même davantage. La raison en est que l'hydroxyde chromique est de nature colloide. Si toutefois on additione la solution à précipiter de certains sels—le chlorine d'ammonium convient le mieux,—la précipitation est quantitative et quasi instantanée. L'influence favorable du NH_4Cl apparait le plus nettement lors de la réaction entre l'ion CrO_4'' et la thiosémicarbazide.

Des expériences faites avec l'hydrate d'hydrazine et le sulfate d'hydrazine nous ont montré qu'une séparation quantitative d'hydroxyde chromique n'a lieu que quand il y a certaines proportions entre le réactif et sel à précipiter let convénient n'apparait pas dans le cas de la thiosémicarbazide, vu qu'un excès de celle-ci-si grand qu'il fût—n'exerce aucune influence défavorable sur la précision du résultat.

Voici maintenant de quelle façon il faut procéder pour le dosage du chrome au moyen de la thiosémicarbazide. A la solution neutre de chromate on ajoute un excès de NH_4Cl (sur un molecule de chromate au moins cinque molecules de sel d'ammonium), puis on additione le liquide de thiosémicarbazide on excès et porte à l'ébullition. La précipité d'hydroxyde de chrome qui se dépose rapidement, est mis sur filtre etc. Nous n'avons pas besoin d'ajouter que le liquide filtré doit être liquide et incolore.

La méthode que nous venons de décrire convient surtout pour le dosage du chrome à côté du fer et de l'aluminium. La solution contenant des sels de fer, d'aluminium et de chrome est additionée d'amoniaque et exydée par l'eau oxygenée. Dans les cas où la proportion du sel chromique dans le mélange serait considérable on est obligé de répéter cette opération.

On sépare des précipités d'hydroxyde ferrique et d'aluminium par filtration, neutralise le liquide filtré par d'acide chlorhydrique, et traite le chromate formé pa la thiosémicarbazide. Cette méthode est plus rapide et précise que les méthodes volumétriques usuelles. Nous la recomendons surtout pour l'analyse du chrome dans la chromite et le ferrochrome.

Pour montrer au lecteur l'exatitude de notre méthode, voici quelques chiffres:

Resultats obtenus:

(*a*) *avec l'hydrate d'hydrazine:*

Pesé g Cr	Trouvé g Cr	Différence g Cr	P. 100
0.01355g	0.01352g	+0.00003g	100.22
0.04059g	0.04055g	+0.00004g	100.09
0.06764g	0.06759g	0.00005g	100.07
0.1081g	0.1081g	± δ	100.
0.13514g	0.13517g	—0.00003g	99.98

(*b*) *avec le sulfate d'hydrazine:*

Pesé g Cr	Trouvé g Cr	Différence g Cr	P. 100
0.06474g	0.06488g	—0.00012g	99.82
0.0811g	0.0811g	± δ	100.
0.09221g	0.09232g	—0.00011g	99.88
0.11337g	0.11354g	—0.00017	99.85
0.14575g	0.14598g	—0.00023	99.84

(*c*) *avec la thiosémicarbazide:*

Pesé g Cr	Trouvé g Cr	Différence g Cr	P. 100
0.0159g	0.0159g	± δg	100.
0.0795g	0.0796g	—0.0001g	99.88
0.1114g	0.1114g	± δ	100.
0.1275g	0.1273g	+0.0002g	100.16
0.1431g	0.1432g	—0.0001g	99.93

Séparation de l'aluminium et du chrome (précipité avec la thiosémicarbazide):

Pesé g Al_2O_3	Pesé g Cr_2O_3	Trouvé g Al_2O_3	Trouvé g Cr_2O_3	Différence		P. 100	
				g Al_2O_3	g Cr_2O_3	Al_2O_3	Cr_2O_3
0.0559g	0.1575g	0.0560g	0.1578g	—0.0001g	—0.0003g	99.81	99.81
0.0936g	0.1124g	0.0933g	0.1127g	+0.0003g	—0.0003g	100.32	99.73
0.1304g	0.0678g	0.1307g	0.0677g	—0.0003g	+0.0001g	99.77	100.15
0.1677g	0.0225g	0.1680g	0.0225g	—0.0003	δ	99.82	100.
0.0188g	0.2028g	0.0187g	0.2029g	+0.0001g	—0.0001g	100.53	99.94

Separation du fer d'avec le chrome (Précipité pa la thiosemicarbazide)

Pesé g Fe_2O_3	Pesé g Cr_2O_3	Trouvé g Fe_2O_3	Trouvé g Cr_2O_3	Différence		P. 100	
				g Fe_2O_3	g Cr_2O_3	Fe_2O_3	Cr_2O_3
0.0630g	0.1582g	0.0628g	0.1578g	+0.0002g	+0.0004g	100.31	100.24
0.1048g	0.1125g	0.1047g	0.1127g	+0.0001g	—0.0002	100.10	99.82
0.1885g	0.0224g	0.1884g	0.0225g	+0.0001g	—0.0001	100.08	99.56
0.1888g	0.0225g	0.1884	0.0225g	—0.0004g	$\pm\delta$	99.79	100.

SUR UNE MODIFICATION DU PROCEDE DE MARSH POUR LE DOSAGE DE L'ARSENIC

PAR M. ALEXANDRE HEBERT, PARIS

I

Jusqu'ici pour doser l'arsenic en très petite quantité ou à l'état de traces, les chimistes ont toujours eu recours à la méthode classique de Marsh. Ce procédé, dans ces dernières années, a été perfectionné dans tous ses détails par M. Armand Gautier et par M. Gabriel Bertrand qui sont arrivés à pousser sa sensibilité à un point tel que l'on peut déceler jusqu'à un quart de millième de milligramme d'arsenic. Dans ces procédés, l'hydrogène est produit par la réaction de l'acide sulfurique sur le zinc et la sensibilité qu'on leur demande exige, non seulement la pureté absolue, au point de vue de l'arsenic, de l'acide employé, mais aussi celle du zinc et des autres adjuvants employés à la production de l'hydrogène.

Or, pour exécuter divers dosages d'antimoine, nous avons eu occasion de mettre en oeuvre un procédé assez peu répandu, dû à Van Bylert[1] basé sur la décomposition facile d'hydrogène antimoiné et destiné, dans l'idée de son auteur, à déterminer l'antimoine dans un alliage. Il consiste en principe à amalgamer d'abord l'alliage avec un grand excès de mercure. Cet amalgame liquide était introduit dans un appareil monté comme celui de Marsh, au contact d'acide sulfurique étendu; l'attaque de l'antimoine n'a pas lieu dans ces conditions. Mais si l'on ajoute, dans l'appareil, de l'amalgame de sodium, il se fait par double décomposition de l'antimoniure de sodium qui, au contact de l'eau acidulée, dégage une quantité équivalente d'hydrogène antimonié. L'auteur indique d'ailleurs que sa méthode n'est pas parfaite et qu'une petite portion de l'antimoine échappe à la réaction; il donne un mode opératoire à suivre pour la récupérer.

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[1] Ber. d. deustch. chem. gesellsch. 1890 p. 2968.

II

L'hydrogène arsenié étant de décomposition plus facile et plus intégrale que l'hydrogène antimonié, nous avons pensé à appliquer le principe de la méthode de Van Bylert au dosage de l'arsenic, et nous l'avons mis en oeuvre de la façon suivante :

Un courant de gaz carbonique pur produit par un appareil continu et passant dans des flacons laveurs munis des dispositifs de sûreté habituels, se rend dans un flacon de Wolff tribulé où aura lieu la réaction, et dont la tribulure centrale est munie d'un bouchon traversé par un tube à entonnoir à robinet. Le gaz sort par la tubulure opposée à celle de son entrée et passe ensuite dans l'équipage habituel destiné à opérer la décomposition de l'hydrogène arsenié produit dans le flacon à réaction: tube large garni de tampons d'ouate, tube capillaire chauffé par une petite grille à gaz sur une partie de sa longueur, puis refroidi ensuite par une bande de papier mouillé; ce dispositif étant celui recommandé ou perfectionné par les auteurs dont nous avons parlé au début de notre note.

L'opération est conduite de la façon suivante: dans le fond du flacon à réaction, on met une petite couche de mercure pur, mais de façon que l'extrémité du tube entonnoir à robinet ne plonge pas dans ce mercure, pour ne pas gêner par sa pression l'introduction ultérieure des autres liquides dans ce flacon. On balaye alors l'appareil par un courant d'acide carbonique pour ne pas y laisser de traces d'air qui contrariraient la sensibilité de la réaction. On allume alors la petite rampe à gaz chauffant le tube capillaire et quand la portion chauffée de celui-ci est portée au rouge, on introduit dans le flacon à réaction par l'entonnoir à robinet le liquide arsenical dans lequel on veut doser l'arsenic; on rince ensuite cet entonnoir avec 40 c.c. d'acide sulfurique pur au dizième en ayant soin dans ces dernières opérations de ne pas introduire d'air dans le flacon à réaction. A ce moment, on modère considérablement la vitesse du courant d'acide carbonique qui peut être réglée par un robinet placé à la sortie de l'appareil à production continue de ce gaz. On verse alors dans l'entonnoir du flacon à réaction 100 grammes d'amalgame de sodium bien liquide (obtenu antérieurement en dissolvant peu à peu dans 100 gr. de mercure chaud 0 gr. 5 de sodium bien décapé, coupé en petits morceaux.) Cet amalgame est introduit goutte à goutte par le robinet dans le flacon à réaction. Cette addition doit durer une demi heure environ et le robinet doit être fermé avant l'écoulement total, toujours pour éviter l'introduction d'air. On obtient ainsi, au sein de l'atmosphère carbonique qui remplit l'appareil, un dégagement très lent et très graduel d'hydrogène qui entraîne aussi l'hydrogène arsenié qui se forme dans ces conditions aux dépens du liquide arsenical qu'on a introduit au début de l'expérience. Cet hydrogène arsenié ainsi entrainé est décomposé par son passage dans la partie chauffée du tube capillaire et l'arsenic libéré se dépose sous forme d'anneau dans la portion refroidie de ce même tube. Quand le dégagement d'hydrogène a cessé dans le flacon a réaction, on balaye l'atmosphère de l'appareil par un courant plus rapide de gaz carbonique qui entraîne les dernières traces d'hydrogène arsenié. Après un quart d'heure de ce balayage, on éteint la rampe à gaz et, après refroidissement, on démonte l'appareil pour examiner ou peser l'anneau produit, selon son importance, et avec les précautions nécessaires.

Le flacon a réaction est vidé à chaque essai et le mercure qu'il contenait est régénéré et purifié. Un semblable essai dure 1 heure environ.

III

Ce procédé qui est au fond une combinaison de la méthode de Van Bylert et des perfectionnements d'A. Gautier et de G. Bertrand, nous a donné de bons résultats. En employant des réactifs que des dosages à blanc nous ont montré exempts de toute trace d'arsenic, nous avons retrouvé pondéralement les anneaux correspondant des quantités d'arsenic introduites intentionnellement supérieures à 1 millig. et nous avons retrouvé les proportions d'arsenic inférieures à cette teneur par comparaison avec des anneaux obtenus avec des quantités d'arsenic données et obtenues par la méthode de Marsh, modifiée par A. Gautier et G. Bertrand. De même que ces derniers savants, nous avons pu déterminer des teneurs en arsenic descendant jusqu'au demi-millième et même jusqu'au quart de millième de milligramme. La méthode que nous indiquons est assez rapide, met en oeuvre des réactifs ou des produits qui ne contiennent généralement pas de traces d'arsenic et donne une sensibilité de même ordre que les anciens procédés. C'est pourquoi nous avons cru devoir la signaler.

(*Contribution from the John Harrison Laboratory of the University of Pennsylvania*)

THE RAPID DETERMINATION OF MAGNESIA IN LIMESTONE BY MEANS OF THE HYDROGEN ELECTRODE

By Joel H. Hildebrand and Herbert S. Harned

The detrimental effect of magnesia in mortar and cement makes its estimation in limestone a matter of considerable importance. Unfortunately, however, the ordinary method of determining magnesium in the presence of calcium has required the preliminary precipitation of the iron, calcium, etc., before the separation of the magnesium. The skill and experience necessary to make a good separation of calcium and magnesium, and the time necessary to complete both of these precipitations are disadvantages which the user of lime would doubtless often be glad to overcome. The method here described allows the determination of magnesia in limestone with an accuracy more than adequate for all technical purposes, and in a very short time.

PRINCIPLE OF THE METHOD

If hydroxyl ions are added to a solution containing both calcium and magnesium ions, the smaller solubility of magnesium hydroxide causes it to be precipitated before calcium hydroxide, and a smaller concentration of hydroxyl is necessary to precipitate the former than the latter. Furthermore, as long as magnesium ions are present in the solution to any extent the concentration of the hydroxyl ions cannot increase very much, as the latter are attacked and precipitated by the former. As soon, however, as the magnesium ions are practically all removed from the solution, the concentration of the hydroxyl ions can then increase to a value sufficient to begin to precipitate the calcium ions present.

Now this increase in the concentration of the hydroxyl ions is quite sufficient, if it can be measured, to furnish an endpoint for the titration of magnesium in the presence of calcium. Instead, however, of measuring the hydroxyl-ion concentration, we may just as well measure that of the hydrogen ions, which is connected with the former by the relation derived from the ionization of water, that

$$[H^+]\ [OH^-] = \text{constant}$$

where the value of the constant is approximately 10^{-14} at 20°, and the brackets denote the concentration of the enclosed ions. An increase in $[OH^-]$ through a power of ten would thus be accompanied by a decrease in $[H^+]$ likewise through a power of ten.

The concentration of the hydrogen ion (or hydrion) can be easily measured by means of the hydrogen electrode. The use of the hydrogen electrode in titration was first suggested by Böttger[1] in connection with the ordinary neutralization of acids and bases. So far as we are aware it has not been used in a reaction of the type to which it is here applied. Furthermore, the use of a potentiometer to determine the e. m. f. of the electrode, and the calculation thereby involved, have made any electrometric method seem to the analyst too impractical to be anything more than an interesting curiosity. To avoid this difficulty we have made use of a voltmeter instead of a potentiometer, as Sand[2] has done in his apparatus for separation of the metals by means of graded potential. A rather laborious and time-consuming task to the analyst is thus made quite rapid and simple. It is not necessary, for this purpose even, to calculate the hydrion concentration from the e. m. f., but merely to plot the latter against the alkali added.

APPARATUS

The hydrogen electrode devised for this purpose is shown in Fig. 1. A platinum foil 8 x 25 mm. is welded to a short piece of platinum wire, which is in turn fused to a stiff copper wire. The latter is thrust into a glass tube just wide enough to receive it, which is fused around the platinum wire just above the foil. The copper wire is fastened in the tube at the top with marine glue. This electrode is surrounded by a slightly wider tube having a side arm near the top for the admission of hydrogen, and a bell-

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[1] Zeit. phys. Chem., *24*, 253 (1897).

[2] J. Chem. Soc., *91*, 374 (1907).

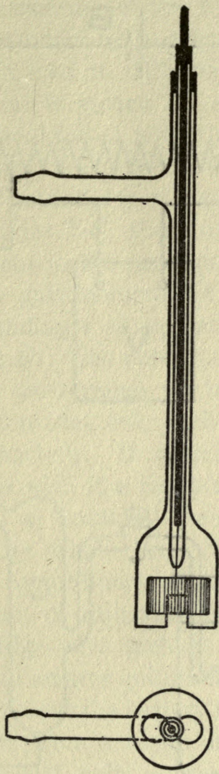

FIGURE 1

shaped enlargement at the bottom to protect the electrode and to confine the hydrogen which must bathe the upper half of the foil. A wide notch is cut in the bottom of the bell to allow the liquid to rise enough to cover the lower half of the foil. After adjusting the inner tube carrying the electrode to the proper height it is fastened to the outer by means of marine glue. The platinum foil has been previously bent into an S-shape so as to pass into the bell. This arrangement of the foil exposes a sufficient line of contact between solution — platinum — hydrogen to prevent the electrode from becoming unsaturated by the currents likely to be taken from it. Before use the electrode must be covered with

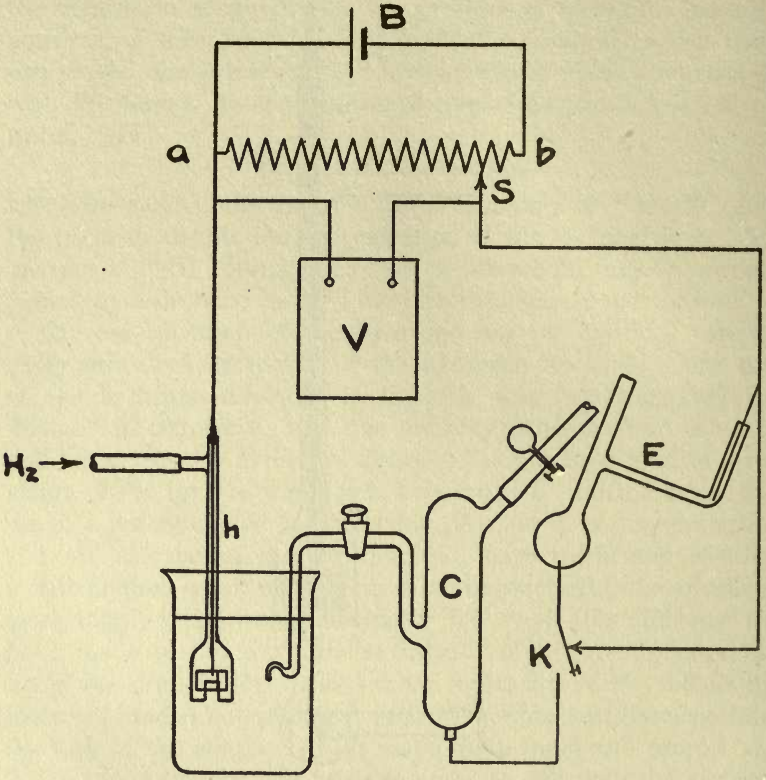

FIGURE 2

platinum black by the usual process.[1] This platinizing should be repeated after some dozens of titrations in order to secure the most satisfactory readings.

The arrangement of the rest of the apparatus is shown in Fig. 2. C is a calomel electrode which furnishes a constant potential to compare with the hydrogen electrode *h*. The latter and the siphon from the former dip into the solution to be titrated contained in the beaker. The potential of the cell thus formed from

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[1] For this as well as other information concerning the principles and use of the various pieces of apparatus described later, see works on physical-chemistry, such as Ostwald-Luther, Physiko-Chemische Messungen; or Findlay, Practical Physical Chemistry.

the two electrodes is a measure of the hydrion concentration in the solution, and is determined by balancing against it an exactly equal potential which is read to 0.01 volt on the voltmeter, *V*. This adjustable potential is gotten by shunting off a variable proportion, *a-s*, of the total fall of potential given by the battery, *B*, through the resistance, *a-b*. When the resistance *a-s* is adjusted so that the fall of potential from *a* to *s* is equal to the e. m. f. of the combined electrodes *h-C*, then, on pressing the key, *K*, there is no flow of current in the corresponding circuit, as shown by the electrometer or galvanometer at *E*. The measurement consists, therefore, in sliding *s* along until, on pressing the key, there is no deflection at *E*. The potential is then read at *V*.

Since the potentials used range up to one volt the battery *B* may be any fairly constant cell, such as a storage, dry, salammoniac, or gravity battery. If a lead accumulator is used it is better to put in series with it a resistance approximately equal to *a-b*, so that the fall of potential through the latter shall be about one volt, and its whole length may be utilized. The resistance *a-b* may be an ordinary sliding rheostat of sufficient number of turns to admit of adjustment of the voltmeter to 0.01 volt. An ordinary bridge wire such as is used in Wheatstone bridge measurements will answer quite well, although its resistance should be sufficient to prevent the battery from too rapid discharge.

The voltmeter should have a range of at least one volt, and should be readable to 0.01 volt, a greater accuracy not being necessary for this purpose.

The Lippmann electrometer is less expensive and in some respects more satisfactory as a zero indicator at *E* than a galvanometer, although the former may require some attention to keep in order. It has the advantage that it is practically a static instrument, thus not discharging the hydrogen electrode, and allowing the stopcock (not greased) of the calomel electrode to remain closed during measurements, and therefore preventing the solution in the beaker from diffusing into the siphon-arm of the electrode. As noted in the figure, the electrometer must be short-circuited between each observation by suitable connection at the key.

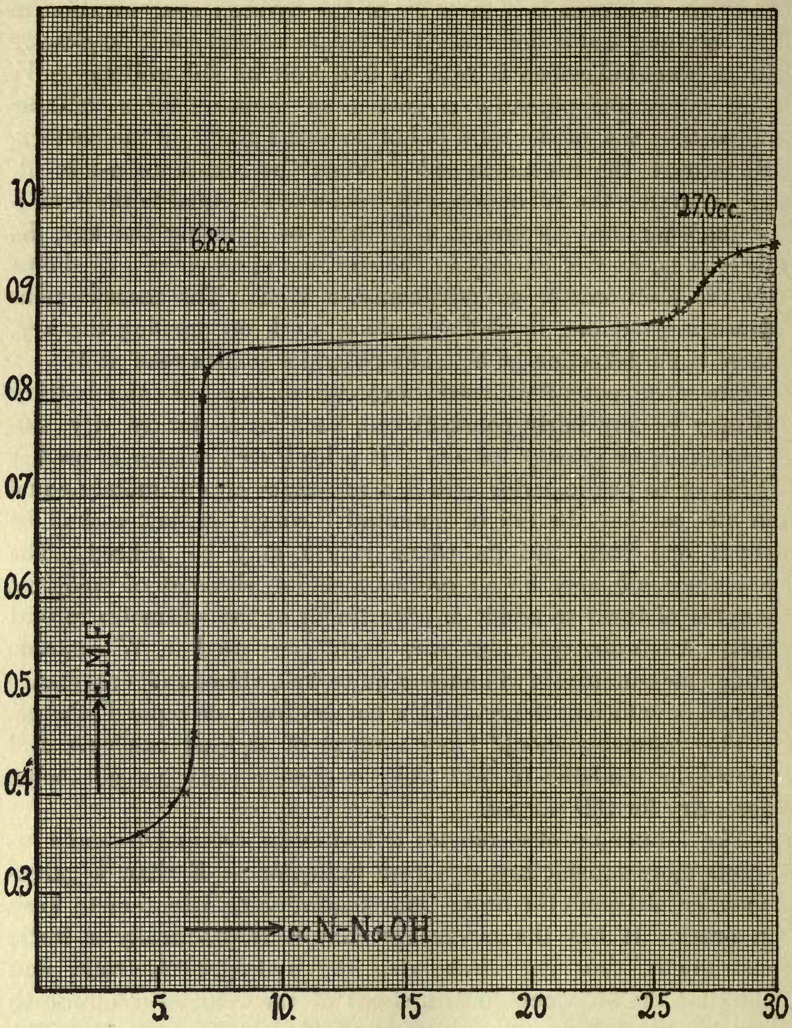

FIGURE 3

MANIPULATION

The apparatus being assembled as just described, the hydrogen electrode is placed in a beaker of water and hydrogen passed in so that the platinum will become saturated with the gas and it will be all ready for use as soon as the sample is prepared. The hydrogen should be washed, say through alkaline permanganate, but not dried. From ten to fifteen minutes should suffice to saturate the electrode with the hydrogen, although the time varies somewhat with the character of the platinum-black deposit.

The sample of limestone is now weighed out, the quantity depending upon the magnesia content and the accuracy desired. The accuracy with which the endpoint of the titration can be determined is about 0.02 cc., using normal alkali, which corresponds to 0.004 gr. MgO, so that a sample containing about 0.4 gram MgO, and requiring 20 cc. for its precipitation, could have its magnesia content determined with an accuracy of 0.01 of itself. Greater accuracy is, of course, offset by slightly greater time, so that the amount of sample must be determined according to the conditions.

The sample having been weighed out (with an accuracy of one per cent of itself), it is transferred to a small round-bottomed flask, sufficient hydrochloric acid added to effect its solution, and the last traces of carbon dioxide expelled by boiling for a few moments under reduced pressure by attaching to a filter pump, a safety trap being inserted. As soon as solution is complete and all the carbon dioxide expelled, the contents of the flask are washed out into a beaker for titration. The gangue need not be removed as it does not interfere with the titration.

The hydrogen electrode and the siphon of the calomel electrode are next inserted into the solution and the titration begun. A moment is necessary for the readings to become constant, due to the momentary contact of the hydrogen electrode with the air. The normal alkali (which must be free from carbonate by the presence of a small amount of barium hydroxide) is added, at first several cc. at a time until the e. m. f. begins to increase. The readings of e. m. f. should be plotted directly as taken on cross-section paper. The course of a typical curve is given in Fig. 3. As soon as the free hydrochloric acid is neutralized, the e. m. f. rises rapidly, due to the rapid increase in the hydroxyl ion concentration. Any iron present is precipitated along this portion of the curve. As soon as the hydroxyl ion concentration is sufficient to precipitate magnesium ions, the latter remove the former as fast as added, so that the e. m. f. remains nearly constant, as shown by the curve. When the magnesium is practically all precipitated a further rise in potential is observed. The point of inflection of this portion of the curve, along which readings should be made every 0.2 cc., is taken as the endpoint of the reaction.

RESULTS

The results obtained are given in Tables I and II. Those in Table I represent the first quantitative experiments made, so it is evident that no special experience is necessary beyond an understanding of the manipulation. The first four analyses in Table II were done simultaneously. Each sample was weighed out and its solution started, successively, so that by the time the fourth was done the first was ready for titration. The time required, two and one-half hours, includes the entire time from the weighing of the samples to the final calculation of the results. The next two determinations were made with larger samples, and no great effort for speed was put forth.

The time might be still further reduced by determining the beginning of the precipitation of the magnesium by having phenolphthalein present, and using the e. m. f. only to give the endpoint. Phenolphthalein changes color at a hydroxyl-ion concentration just a little less than that required to precipitate magnesium hydroxide, so that its change could be taken as the beginning with a slight time-saving. The rise at the end is too gradual for any indicator to give a sharp change in color, so that the point of inflection of the curve must remain as the endpoint. The work had to be interrupted before any data could be secured to confirm this suggestion, although in the above analyses methyl-orange was used to ascertain when to begin readings of the e. m. f. This indicator changes at a hydrion concentration represented by the bottom of the curve, just as it is about to rise. No readings need therefore be taken till methyl-orange has changed color. The preliminary neutralization of the excess of acid used in dissolving the sample is thus quickly effected.

The ease and speed with which magnesium can be determined in the presence of calcium by the method here outlined will, we hope, cause it to prove of service to the large number of chemists who are confronted by this task.

It may be stated, in conclusion, that other data are being obtained in this laboratory which promise to make the apparatus here described a valuable addition to the laboratory of the analyst for the solution of a variety of analytical problems.

TABLE I

Wt. Sample.	cc. N-NaOH.	Wt. MgO.	%MgO
1.297	12.1	0.242	18.7
1.297	12.2	0.244	18.8
	Gravimetric	18.75	

TABLE II

Wt. Sample	cc. N-NaOH	Wt. MgO	%MgO	Time.
0.524	5.4	0.109	20.8	2½ hours
0.535	5.4	0.109	20.4	
0.471	4.8	0.097	20.6	
0.485	5.1	0.103	21.2	
2.048	20.7	0.418	20.4	2 hours
2.012	20.1	0.406	20.2	
		Mean	20.6	
		Gravimetric	20.82	

VOLATILITY OF ARSENOUS CHLORID

BY J. I. D. HINDS
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In the qualitative analysis of the Copper-Arsenic Group we are always cautioned against boiling the solution for fear of losing arsenous ion. In studying a new method for precipitating the ions of the group, an account of which is given in the Journal of the American Chemical Society, 34,811, I found it desirable to concentrate the solution and was, therefore, led to investigate the quantitative loss of arsenous chlorid in the process. I was surprised to find that the loss was quite small and that it was a *function of the quantity of arsenic present*, as well as of the *acid concentration of the solution.* The rate of loss being very much less than that of the concentration, the boiling could in no case lead to failure in detecting the arsenic. In boiling a solution half away, the arsenic concentration is practically doubled, since the loss is generally less than one thousandth of the quantity present. I found that during the evaporation the arsenic loss varied somewhat with the rapidity of the boiling and the size of the distilling flask. No attempt was, therefore, made to determine quantities with very great accuracy. Still, all things considered, the results were quite remarkable.

I prepared 3 N, 1 N, 0.1 N, and 0.01 N solutions of a sodium arsenite which I found by analysis to be practically pure $NaAsO_2$, the normal solution containing 25 grams arsenic to the liter. From these by dilution I obtained any desired concentration. The hydrochloric acid concentration was varied from 0.2 N to 2 N. In most of the operations the solution was normal since this was the concentration which I desired to use in the new method of analysis.

The solutions were boiled in a 200 cc. distilling flask and the distillates collected in 50 cc. cylinders. Fragments of pumice were used to prevent bumping. Great care was necessary here because the tiniest drop thrown over contained more arsenic than the whole distillate. As a further precaution, the flask was closed with a cork through which passed a closed glass tube which extended the full length of the neck of the flask and almost filled it. Generally 50 cc. of the solution was used and the distillate was made up with water to 50 cc. for ready comparison. In the fractional distillations 100 cc. were used and the distillate was collected in 10 cc. portions. The concentration of the distillate was determined by making it 0.1 N in HCl (2 drops to each 10 cc.), passing hydrogen sulphide and comparing the cloud with that of the test solutions of known concentrations.

The test solutions were made by diluting the 0.01 N solution in 50 cc. portions made 0.1N in HCl (10 drops of the acid to 10 cc. and then passing hydrogen sulphide. The mixture was transferred to 25 cc. test tubes and the comparisons were made after the manner of nesslerizing. These solutions ranged from 0.00001 N to 0.005 N in arsenic, the first being the limit of perceptible cloud or color and the last furnishing so heavy a precipitate that comparison was difficult.

SERIES 1

Solutions of various concentrations were made containing 5 cc. hydrochloric acid and made up to 50 cc. so that they were about normal in HCl. Actually the acid was a little weak and the concentrations were somewhat below normal. The solutions were distilled half away, the distillate with 10 drops of hydrochloric acid made 50 cc. treated with hydrogen sulphide, and then compared with the test solutions. The results are given in Table 1.

TABLE 1

Acid concentration at the beginning N, at the close 2 N. Concentration of the distillate before dilution 0.0006 N in HCl.

As Conc.	Grams of As in the 50 cc.	As conc. of distillate.	Grams of As in distil.	Frac. of As lost.
0.1 N	0.125	0.00020	N 0.00025	0.0020
0.2	0.25	0.00025	0.00032	0.0013
0.3	0.375	0.00030	0.000375	0.0010
0.4	0.5	0.00035	0.000433	0.0009
0.5	0.625	0.00040	0.0005	0.0008
0.6	0.750	0.00043	0.00054	0.0007
0.7	0.875	0.00047	0.00058	0.0007
0.8	1.0	0.00050	0.00063	0.0006
1.0	1.125	0.00055	0.00068	0.0006

It will be observed here that as the concentration increases the quantity of arsenic lost increases, while the fraction lost diminishes. The actual loss is inconsiderable, while the fraction lost varies from 0.002 to 0.0006, being for all concentrations above 0.3 N less than 0.001.

SERIES 2

In this series the solutions were made 2 N in HCl, each 50 cc. containing 10 cc. hydrochloric acid. At the end of the distillation the residue was a little below 4 N.

TABLE 2

As Conc.	Grams of As in the 50 cc.	As conc of distillate.	Grams of As in distil.	Frac. of As lost.
0.1 N	0.125	0.0006 N	0.00075	0.006
0.2	0.25	0.0010	0.00125	0.005
0.3	0.375	0.0015	0.00187	0.005
0.4	0.5	0.0020	0.0025	0.005
0.5	0.625	0.0025	0.00313	0.005
0.6	0.750	0.0030	0.00375	0.005
0.7	0.875	0.0035	0.00433	0.005
0.8	1.0	0.004	0.005	0.005
0.9	1.125	0.004	0.005	0.004
1.0	1.25	0.004	0.005	0.004

In this series the fraction of arsenic lost is almost constant, being about one two-hundredth. The acid concentration, however, is never so high as this in the course of an analysis.

SERIES 4 AND 5

In these series the concentration of the arsenic was constant while that of the acid was varied.

SERIES 3 TABLE 3

Arsenic Concentration 0.3 N

Acid conc.	Conc. of dist.	Frac. lost
0.2 N	0.00006N	0.0002
0.4	0.00008	0.0003
0.6	0.00015	0.0005
0.8	0.00020	0.0007
1.0	0.00030	0.0010
1.2	0.00040	0.0013

SERIES 4 TABLE 4

Arsenic Concentration 0.8 N

Acid conc.	Conc. of dist.	Frac. of As lost.
0.2 N	0.00009 N	0.0001
0.4	0.00015	0.0002
0.6	0.00025	0.0003
0.8	0.0004	0.0005
1.0	0.0005	0.0006
1.2	0.0006	0.0008

SERIES 3 TABLE 3

Arsenic Concentration 0.3 N

Acid conc.	Conc. of dist.	Frac. lost
1.4	0.00048	0.0016
1.6	0.0006	0.002
1.8	0.0007	0.003
2.0	0.0015	0.005

SERIES 4 TABLE 4

Arsenic Concentration 0.8 N

Acid conc.	Conc. of dist.	Frac. of As lost
1.4	0.0008	0.001
1.6	0.0016	0.002
1.8	0.0025	0.003
2.0	0.004	0.005

Note that as the acid concentration increases the arsenic concentration of the distillate and also the fraction of arsenic lost increase. When the acid concentration is below 1 N, the fraction of arsenic lost is less than 0.001.

Several hundreds of these determinations were made and the average results are collected in the following two tables.

TABLE 5

Arsenic concentration of the distillate when the solution is boiled half away and the distillate brought to the original volume.

Acid	Arsenic Concentrations					
conc.	0.1 N	0.3 N	0.5 N	0.8 N	1.0 N	1.5 N
0.2 N	0.00004 N	0.00006 N	0.00007 N	0.00009 N	0.0001 N	0.0002
0.4	0.00007	0.00008	0.00009	0.00015	0.0002	0.0003
0.6	0.00010	0.00015	0.0002	0.00025	0.0003	0.0004
0.8	0.00015	0.00020	0.0003	0.0004	0.0004	0.0005
1.0	0.00020	0.00030	0.0004	0.0005	0.0006	0.0006
1.2	0.00025	0.00040	0.0005	0.0006	0.0007	0.0008
1.4	0.0003	0.00048	0.0006	0.0008	0.001	0.0014
1.6	0.0004	0.0006	0.0010	0.0016	0.002	0.003
1.8	0.0005	0.0009	0.0015	0.0025	0.003	0.004
2.0	0.0006	0.0015	0.0025	0.004	0.004	0.005

TABLE 6

Fraction of the arsenic lost when the solution is boiled half away.

Acid	Arsenic Concentrations					
conc.	0.1 N	0.3 N	0.5 N	0.8 N	1.0 N	1.5 N
0.2 N	0.0004	0.0002	0.0001	0.0001	0.0001	0.0001
0.4	0.0007	0.0003	0.0002	0.0002	0.0002	0.0002
0.6	0.0010	0.0005	0.0004	0.0003	0.0003	0.0003
0.8	0.0015	0.0007	0.0006	0.0005	0.0004	0.0003
1.0	0.0020	0.0010	0.0008	0.0006	0.0006	0.0004
1.2	0.0025	0.0014	0.0010	0.0008	0.0007	0.0005
1.4	0.003	0.0016	0.0012	0.001	0.001	0.0009
1.6	0.004	0.002	0.002	0.002	0.002	0.0020
1.8	0.005	0.003	0.003	0.003	0.003	0.0026
2.0	0.006	0.005	0.005	0.004	0.004	0.0033

From this last table it appears that when the concentration of the acid is below 1.2 N and that of the arsenic above 0.1 N, the fraction of the arsenic lost on boiling the solution half away is less than 0.001. It further appears that when the concentration of the acid is above that of the arsenic, the fraction of arsenic lost approaches a constant.

Series 3 and 4

Series 3 and 4 were made to ascertain the gradation of loss of arsenic during the boiling. One hundred cubic centimeters of a solution 0.5 N in arsenic and for Series 3 normal, for Series 4 two normal, in HCl were boiled and the distillates collected in 10 cc. portions. These portions, made 0.1 N in acid and treated with hydrogen sulphide, were compared with the test solutions. The results are given in Tables 7 and 8.

TABLE 7

100 cc. 0.5 N in As and N in HCl

	Conc. of dist.	Frac. of As lost
1 st 10 cc.	0.0003 N	0.00006
2 nd	0.0004	0.00008
3 rd	0.0006	0.00012
4 th	0.0009	0.00018
5 th	0.0015	0.00030
Total frac. lost		0.00074

TABLE 8

100 cc. 0.5 N in As and 2 N in HCl

	Conc. of dist.	Frac. of As lost
1 st 10 cc.	0.0010 N	0.00020
2 nd	0.0016	0.00032
3 rd	0.0024	0.00048
4 th	0.0060	0.00120
5 th	0.0090	0.00180
Total frac. lost		0.004

The total loss of arsenic here agrees fairly well with the figures in Table 6. The rapid increase of loss in the successive portions is due to the increasing concentration both of the arsenic and the acid.

This investigation leads to the following conclusions:

1. That the quantity of arsenous ion lost on boiling its hydrochloric acid solution is a function of the concentration both of the arsenic and of the acid.

2. That when the concentration of the acid exceeds that of the arsenic, the fraction of the arsenic lost on boiling approaches a constant value.

3. That with the concentrations usually employed in qualitative analysis the loss of arsenic on boiling the solution even half away is generally less than one thousandth of the quantity present.

SOME TESTS ON A NEW CALORIMETER BOMB

By Richard H. Jesse, Jr.
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In connection with the description of the new alloy bomb of nickel-copper-chromium[1] it may be of interest to report briefly the results of a series of experiments on the combustion of two standard substances, cane sugar and benzoic acid. These experiments were undertaken not only for the purpose of standardization but also to test the behavior of the instrument under actual working conditions.

The principal features of difference between this bomb and other types are: (1) the substitution of an alloy, very resistant to the action of acids, for the usual platinum, gold, or enamel lining; (2) the use of a well protected rubber gasket for sealing the bomb instead of a gasket of lead; (3) the replacement of the ordinary steel needle-valve by a seated valve bearing a rubber gasket. For one who has spent much physical and mental effort in trying to seal completely bombs fitted with needle valves and gaskets of lead and gold, a very short experience is sufficient proof of the superiority of the present method of sealing in so far as speed and ease of manipulation are concerned. Former experience in this laboratory has offered evidence that these features do not cause a decrease in the accuracy desired for commercial fuel analysis. It has remained, however, to prove that they will answer the purposes of investigations where the highest attainable accuracy is desired.

A series of semi-quantitative corrosion tests in which specimens of the alloy were exposed at ordinary temperatures and for varying lengths of time to the action of 4N sulphuric and nitric acids and mixtures of the two have indicated that the amounts of alloy which would dissolve in the time of a determination are

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[1] This bomb has been recently devised by Professor S. W. Parr, of this laboratory. A full description will be found in a paper presented by Professor Parr before section I of this Congress.

negligible. To test the corrosion under working conditions the washings from eight runs, which had been titrated in the usual manner for nitric acid with potassium hydroxide, were combined and analysed for copper and nickel. The copper was precipitated by hydrogen sulphide in acid solution and was weighed as cuprous sulphide; the nickel was determined by the dimethylglyoxime method. In the eight determinations 1.6 milligrams of copper and 6.2 milligrams of nickel were dissolved. In a single determination therefore we have the solution of 0.2 mg. Cu and 0.8 mg. Ni. This quantity of the metal nitrates would have a heat of formation of approximately 1.8 calories[1].

Since in these experiments the total amount of heat measured in a run was 9500 calories, about 0.02% of the rise was due to the solution of the alloy. This is a quantity which cannot be detected with certainty even in the very best calorimetric work. This particular bomb was the first successful casting. Since the work was begun there have been slight modifications in the composition of the alloy which have probably increased its acid resistance. Quantitative evidence on this point is, however, lacking as yet. In coal calorimetry sulphuric acid will be present in addition to the nitric acid. The corrosion tests already mentioned show that the mixture of these two acids is not much more active than nitric acid alone.

There is only indirect proof to show that the use of rubber gaskets is without effect on the accuracy of the bomb. The construction of the instrument is such that the rubber is well protected. The portion of the gasket which comes in contact with the gases in the bomb is a ring about 1/1000 inch in width and to reach this the hot gases have to pass through a very narrow space with massive metal on each side, so that they would almost certainly be cooled below the danger point. In these experiments there was absolutely no smell of burnt rubber in the bomb after a combustion. The constancy of the results given below is further proof that the rubber has no harmful effect, because it is hardly conceivable that if the rubber were burnt at all it should be burnt in such constant amount each time.

[1] Thomsen's results in Landalt-Börnstein.
$Ni+2N+6O+Aq=Ni\ (NO_3)_2\ Aq+113{,}200$ cal.
$Cu+2N+6O+6H_2O=Cu\ (NO_3)_2,\ 6H_2O+92{,}900$ cal.

The method of adiabatic calorimetry[1] devised by W. T. Richards was used for these combustions.

The principle of the method is that the calorimeter is surrounded on all sides and on top by a bath of caustic soda, the temperature of which is at all times kept the same as that of the calorimeter. By running in sulphuric acid in measured amounts the temperature of the bath can be readily changed so that it conforms to that of the calorimeter even during the first rapid rise. This method has already proved itself capable of extreme accuracy. The mercury thermometer used was of the Beckmann type and was calibrated by the Bureau of Standards. The results with it were very satisfactory. Three different samples of sugar were used. They were supplied at different times during the past three years by the Bureau of Standards. Two samples of benzoic acid were burnt, one from the Bureau of Standards and one that had been carefully purified in this laboratory. The experiment marked No. 10 was on this sample. The agreement is all that could be desired.

CANE SUGAR

No.	Weight Substance in Air Gram.	Observed Rise Cor. for bore, protruding thread and stirring	Correction for iron wire burnt	Correction for HNO_3 formed	Corrected Rise	Rise per gram substance	Deviation from mean %
1	2.4994	2.909°	–0.008°	–0.003°	2.898+°	1.1596°	+0.05
2	2.5018	2.908	–0.006	–0.004	2.898+	1.1585	–0.05
3	2.4987	2.910	–0.008	–0.004	2.898–	1.1597	+0.06
4	2.5004	2.909	–0.006	–0.004	2.899–	1.1593	+0.02
5	2.5035	2.911	–0.008	–0.003	2.900	1.1583	–0.07
6	2.2743	2.646	–0.007	–0.003	2.636	1.1590	±0.00

Average rise per gram sugar (weighed in air) = 1.1591

Average rise per gram sugar (weighed in vacuum) = 1.1584

BENZOIC ACID

7	1.5089	2.812°	–0.007°	–0.003°	2.802°	1.8570°	+0.02%
8	1.5390	2.870	–0.008	–0.004	2.858	1.8570	+0.02
9	1.5059	2.809	–0.008	–0.004	2.797	1.8574	+0.04
10	1.4467	2.698	–0.008	–0.003	2.687	1.8572	+0.03
11	1.5635	2.913	–0.008	–0.003	2.902	1.8561	–0.04
12	1.5630	2.912	–0.007	–0.004	2.901	1.8560	–0.04
13	1.6584	3.090	–0.008	–0.004	3.078	1.8560	–0.04

Average rise per gram benzoic acid (weighed in air) = 1.8567

Average rise per gram benzoic acid (weighed in vacuum) = 1.8552

All the experiments fell within the temperature range 21-25°C.

[1] Proc. Amer. Acad., *42*, 573, (1907); Z. physik Chem., *59*, 532; J. Am. Chem. Soc., *31*, 268, (1909).

Since the temperature rise measured was about 3°, it follows that the mean temperature of any experiment did not differ from that of any other by more than 1°. This is worthy of mention because in this neighborhood the heat capacity of water changes by about 0.02% per degree. However, since the metal portions of the system have a larger temperature coefficient of opposite sign, the effect of the changing heat capacity of water is at least partially neutralized.

The internal agreement of the two series on sugar and benzoic acid indicates that the new bomb can be safely used for work involving the highest accuracy. The greatest deviation from the mean is 7 parts per 10,000 in the case of sugar and 4 parts in the case of benzoic acid. This is probably as close an agreement as can be expected from a mercury thermometer and, indeed, it compares very favorably with the best work with electrical thermometers.

The results described in this paper are not absolute, but are purely relative. Therefore, it is interesting to compare the ratio of sugar and benzoic acid. The ratio resulting from this series (vacuum weights) is 1.6014. A similar comparison of a very high order of accuracy has been made by Emil Fischer and Wrede[1]. They have made two series of determinations on benzoic acid. The ratio from their first and most concordant series is $\frac{26.478\text{Kj}}{16.545\text{Kj}} = 1.6003$; that from the average of the two series is $\frac{26.472}{16.545} = 1.6000$; while the ration for their three highest determinations of benzoic acid is 1.6008. The differences between these ratios and that found in this paper are respectively 0.07%, 0.09% and 0.035%. The value of the ratio found by the Bureau of Standards is 1.6016[2]. The agreement here is even more satisfactory; in fact, it is identical within the possible experimental accuracy. In spite of the concordance of their ratios the absolute values assigned by Fischer and Wrede and the Bureau differ by a quarter of a per cent. The reason for this discrepancy is not apparent at present.

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[1] Sitzber. K. Acad. Berlin, *19*, *20*, *21*, 687, (1904); Z. physik, Chem., *53*, 161, (1903); *69*, 218, (1909); *75*, 81, (1910).

[2] Private communication from Dr. W. F. Hillebrand.

SUR UNE METHODE GENERALE DE DOSAGE DE L'ACIDE TARTRIQUE EN PRESENCE DE METAUX CAPABLES DE DONNER DES EMETIQUES

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Tous les procédés de dosage de l'acide tartrique utilisés jusqu'à ces derniers temps consistent à précipiter celui-ci à l'état de tartrate acide de potassium en milieu éthéro-alcoolique et à titrer acidimétriquement ce précipité.

Mais plusieurs reproches doivent être adressées à ces méthodes.

Tout d'abord la réaction qui leur sert de base est une réaction réversible et comme telle incomplete. L'acide tartrique en présence d'un sel de potassium donne en effet la réaction.

$$CO_2H\ (CHOH)_2-CO_2H+RK \leftrightarrows CO_2H\ (CHOH)_2\ CO_2K+R-H.$$

Il s'établit entre ces quatre corps un équilibre dépendant à la fois de la dilution, de la nature de l'acide R H mis en liberté, de la température, etc.

Si au lieu d'acide tartrique, on emploie du bitartrate de sodium, la réaction est à peu prés complete, mais dans la pratique, cette circonstance n'est jamais réalisée, car les produits naturels renferment toujours d'autres substances capables de déplacer partiellement l'acide tartrique.

D'autre part, l'acide tartrique peut-être entrainé à l'état de tartrate neutre insoluble dans le milieu éthéro-alcoolique, en particulier à l'état de sel de chaux, de magnésie, etc. et des lors il échappera au dosage acidimétrique.

De plus certains acides, tels que l'acide malique peuvent,dans des liquides complexes, donner naissance à des sels acides peu solubles qui se précipitent en même temps que le bitartrate de potassium et qui sont comptés comme acide tartrique lors du dosage acidimétrique.

Enfin la présence de certains métaux, tels que le fer, l'alumine, l'antimoine, etc. qui forment avec l'acide tartrique des émétiques, fausse totalement les résultats.

Ces différentes causes d'erreur font qu'un même opérateur trouve des nombres différant entre eux de 0 gr.2 ou 0 gr.3, alors que la quantité d'acide tartrique à doser n'est le plus souvent que de 3 à 4 grammes dans les produits naturels, (vins) soit une erreur de 6 à 8% qui peut d'ailleurs être doublée quand il s'agit d'opérateurs différents.

C'est en vue de rémédier à ce manque de précision que l'un de nous a proposé il y a quelque temps[1] une nouvelle méthode basée sur la précipitation de l'acide tartrique à l'état de racémate de chaux: $(C_4H_4O_6)_2$ Ca, $8H_2O$.

Tandis en effet que le tartrate droit de chaux ne précipite qu' incompletement, le racémate est un sel presque rigoureusement insoluble dans l'eau, dans l'acide acétique étendu, la solution de tartrate et les sels ammoniacaux. Mais il se dissout aisément dans les acides minéraux même étendus.

Si donc a une solution contenant un tartrate alcalin ou de l'acide tartrique droit, le seul qui se rencontre dans les produits naturels, on ajoute du tartrate d'ammoniaque gauche en excès, puis de l'acétate de chaux, tout l'acide tartrique droit sera précipité *intégralement* à l'état de racémate de chaux à la condition qu'il ne subsiste pas dans la liqueur d'acide minéral libre.

L'expérience ayant montré que ce premier précipité n'est pas pur car il entrainé avec lui une certaine quantité de tartrate gauche de chaux, il est nécessaire de rédissoudre le précipité dans l'acide chlorhydrique faible puis de le précipiter par addition d'un excès d'acétate de soude.

Le précipité recueilli sur filtre et lavé, est évalué volumétriquement en milieu sulfurique à l'aide d'une solution de permanganade potasse titrée elle-même à l'aide d'une solution connue d'acide tartrique pur.

(Le nombre obtenu pour l'acide tartrique contenu dans le racémate, doit bien entendu être divisé par 2, puisque le racémate

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[1] A. Kling, Bulletin Soc. Chim. T. 7 (4° série) p. 569.

renfeme une quantité d'acide tartrique gauche égale à la quantité d'acide tartrique droit préexistante dans la liqueur.)

Cette méthode donne des resultats excellents, à la seule condition que la liqueur dans laquelle se fait la précipitation ne renferme pas de métaux capables de fournir des émétiques avec l'acide tartrique. On sait que ce sont les métaux donnant des sesquioxydes de la forme M_2O_3 qui sont particulierement aptes à fournir avec l'acide tartrique des *complexes* dans lesquels l'oxyde et l'acide sont dissimulés. Il en résulte que la présence de fer, d'alumine, d'antimoine sera particulierement gênante et en effet des que la dose de ceux-ci depasse 0 gr. 4 à 0 gr. 5 0/00 la méthode décrite donne des résultats notablement trop faibles.

Or ily a un grand interêt à pouvoir effectuer correctement ce dosage même en présence des métaux gênants, car certains produits naturels: tartres, lies, etc., renferment des doses notables de fer ou d'alumine.

Nous avons été assez heureux pour étendre la méthode précipitée au cas ou la liqueur renferme des éléments gênants, et à la rendre générale, alors que les anciennes méthodes sont totalement inapplicables dans ce cas.

Principe de la Méthode

Nous avons pensé à engager les métaux gênants dans une combinaison suffisamment stable dans le milieu de précipitation pour que l'acide tartrique soit libéré et puisse précipiter complètement à l'état de racémate. L'acide citrique nous a semblé tout indiqué, car lui-même donne avec ces métaux des combinaisons complexes.

L'expérience a bien verifié ces considérations théoriques et l'adjonction d'acide citrique à la solution libéré complètement l'acide tartrique qui des lors précipite *intégralement* à l'état de racémate de chaux. A la vérité des essais nous ont montré que l'acide citrique lui-même avait l'inconvénient d'augmenter l'acidité de la liqueur et par là même la solubilité du racémate, c'est pourquoi nous lui avons substitué le citrate biammonique qui, tout comme l'acide, se combine aux métaux gênants pour donner des complexes et libéré l'acide tartrique.

Tout d'abord nous avons tenu à nous assurer à nouveau que l'acide citrique ne gênait pas la précipitation du racémate même à dose assez élevée, bien que l'un de nous l'ait déjà constaté par quelques essais succints au cours du travail précedent.

Voici les résultats obtenus:

N° des essais	Teneur en acide citrique	Nombre obtenu	Nombre théorique
1	0	0 gr. 198	0 gr. 195
2	0 gr. 200	0 gr. 197	0 gr. 195
3	1 gr. 000	0 gr. 196	0 gr. 195
4	2 gr. 000	0 gr. 187	0 gr. 195

On constate donc que des doses d'acide citrique atteignant plus de cinq fois le poids d'acide tartrique à doser ne gênent en rien la précipitation du racémate et qu'un fléchissement des résultats ne s'accuse que pour des doses d'acide citrique décuplés du poids d'acide tartrique.

En outre le citrate d'ammoniaque ajouté à la solution tartrique présente la propriété avantageusee de diminuer sensiblement la proportion de tartrate gauche de chaux entrainé dans le précipité du racémate lors de la premiere précipitation. C'est là un résultat avantageux, car dans le cas d'un précipité de racémate charge en tartrate gauche, même en le redissolvant et le reprécipitant on obtient des nombres parfois un peu forts.

Cet entrainement de tartrate gauche de chaux est mis en évidence par l'expérience ci-dessous:

Aprés 12 heures de précipitation:

Teneur en citrate d'ammoniaque	Acide tartrique	
	Trouvé	Calculé
0	0 gr. 208	0 gr. 204
0 gr. 500	0 gr. 2046	0 gr. 204

D'ailleurs nous avons vérifié directement que le citrate augmentait la précision des résultats par suite d'un moindre entrainement de tartrate gauche, et non par suite de compensation d'erreurs de sens inverse. Acet effet, le racémate provenant des premieres précipitations a été dissous dans une solution saturée de molybdate d'ammoniaque, (qui, comme on le sait, exalte considérablement le pouvoir rotatoire de l'acide tartrique) or dans le cas ou il a été obtenu en présence de citrate d'ammoniaque il devie beaucoup moins à gauché la lumière polarisée que dans le cas contraire. (La déviation diminue du 1–3 environ.)

Nous avons esayé également de diminuer l'entrainement de tartrate gauche de chaux en réduisant la dose de tartrate gauche d'ammoniaque indiquee dans la précedente note[1] mais ce procédé n'est recommandable que dans le cas où il n'y a pas de métaux gênants car dans ce cas, même en présence du citrate d'ammoniaque il est nécessaire d'avoir un excés de tartrate gauche pour que la précipitation soit complète.

Il est à remarquer que le citrate retarde la précipitation du racèmate, aussi est-il nécessaire dans le cas où il est présent d'attendre 3 à 6 heures pour avoir une précipitation totale.

Enfin dans le cas ou la liqueur renferme en outre des doses notables de métaux gênants, la précipitation est encore ralentie et il est nécessaire cette fois d'attendre 12 heures (une nuit) avant de jeter sur filtre.

De tout ceci nous concluons que la présence d'un citrate ne gêne pas la précipitation et qu'en diminuant l'entrainement du tartrate gauche par le racémate il augmente même la precision des résultats. Aussi proposons nous de modifier légerement la premiere méthode et d'ajouter *dans tous les cas* de dosage d'acide tartrique une certaine quantité de citrate d'ammoniaque avant de précipitér le racémate.

Nous exposerons plus loin avec détails cette nouvelle technique.

Dosage de l'Acide Tartrique en Présence de fer et d'Alumine.

En l'absence de citrate des doses même faibles d'alumine ou de fer influencent considérablement les résultats du dosage de l'acide tartrique par quelle que méthode que ce soit, ainsi que le fait ressortir le tableau suivant.

		Acide tartrique par litre		
	Al_2O_3 par litre	Méthode au racemate[2]	Méthode officielle	Théorie
Solution d'acide tartrique . .	0,01	3,96		3,97
(id)	0,10	3,23		3,97
Solution de tartrate de Na .	0,00	3,18	3,00	3,20
(id)	0,08	2,96	2,88	3,20

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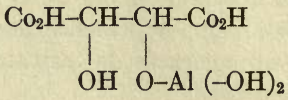
[1] Loc. cit.

[2] sans addition de citrate.

Mais des que l'on met de l'acide citrique ou mieux du citrate d'ammoniaque, il est possible d'avoir une précipitation intégrale du racémate même en présence de dose d'alumine atteignant 40% du poids d'acide tartrique, c'est à dire bien supérieure à la quantité nécessaire pour former le complexe:



$$\mathrm{Co_2H{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\underset{\displaystyle O{-}Al\,({-}OH)_2}{\underset{|}{CH}}{-}Co_2H}$$

dans lequel Al_2O_3 ne représente que 33% du poids d'acide tartrique.

Voici en effet les résultats obtenus.

		Acide tartrique	
Al_2O_3	Citrate d'ammoniaque	Trouvé	Théorie
0	0	0,199	0,195
0 gr. 0032	0	0,197	0,195
0 gr. 0158	0	0,179	0,195
0 gr. 079	0	0,103	0,195
0 gr. 079	0 gr. 500	0,198	0,195
0 gr. 085	0 gr. 700	0,204	0,204

En présence de fer nous avons obtenus des résultats analogues.

		Acide tartrique	
F_2O_3	Citrate d'ammoniaque	Trouvé	Théorie
0 gr. 086	0	0 gr. 138	0 gr. 1945
0 gr. 069	0 gr. 700	0 gr. 2088	0 gr. 2076
0 gr. 086	0 gr. 700	0 gr. 2076	0 gr. 2076
0	0 gr. 700	0 gr. 2058	0 gr. 204

La présence d'alumine et surtout de fer retarde considérablement la précipitation du racémate et il est nécessaire d'attendre 12 heures (une nuit) pour que la précipitation soit complete.

Nous avons cherché quelle était la teneur maximum en Al_2O_3 ou Fe_2O_3 pour laquelle le dosage était encore exact.

Voici les résultats:

		Acide tartrique	
	Citrate d'ammoniaque	Trouvé	Théorie
Fe_2O_3 0 g. 1296	0 g. 750	0,204	0,2076
Al_2O_3 0, 1264	0 g. 750	0,2004	0,2076

Conclusions

L'adjonction de citrate d'ammoniaque permet d'obtenir une précipitation complete de l'acide tartrique à l'état de racémate pour des teneurs en oxydes anhydres pouvant atteindre 50% environ du poids d'acide tartrique, mais à partir de 60% l'erreur atteint 2% environ dans le cas du fer et 3,5% dans le cas de l'alumine.

Neanmoins on peut parvenir à doser l'acide tartrique en présence de grandes quantites de fer, d'alumine, grâce à une méthode que nous décrirons plus loin.

Dosage en Présence de Cuivre et d'Antimoine.

Nous avons appliqué cette même méthode au cas du cuivre et de l'antimoine, en particulier au dosage de l'acide tartrique dans les émétiques d'antimoine.

Dans le cas du cuivre nous avons obtenu les résultats suivants:

		Acide tartrique	
CuO	Citrate d'ammoniaque	Trouvé	Théorie
0,058	0	0,2006	0,2041
0,058	0,700	0,2053	0,2041

Le premier essai de ce tableau montrè que le cuivre *en solution acide* apporte peu de trouble au dosage, même en l'absence de citrate, ce qui s'explique aisément en considérant que l'acide tartrique ne donne de complexes véritables qu'en milieu alcalin. Au contraire le complexe que donne l'antimoine, tout comme ceux de fer et d'alumine, sont assez stables en milieu acétique ce qui rend impossible la précipitation intégrale du racémate sans adjonction de citrate.

La méthode a été essayée dans le cas de l'antimoine avec de l'émétique pur, préalablement desséche à 100° de facon à lui faire perdre sa ½ molécule d'eau de cristallisation.

Le tableau ci-contre rend compte des résultats:

Poids d'émétique		Citrate d'ammoniaque	Acide tartrique	
			Trouvé	Calculé
Emétique No. 1 0 gr. 400	non	0	0,1212	0,1813
Emétique No. 2 0 gr. 400	desseché	0,700	0,183	0,181
Emétique No. 1 0 gr. 400	seché à 100°	0,700	0,188	0,186
Emétique No. 2 0 gr. 400		0,700	0,1845	0,186

Dosage en Présence de Doses Massives de Métaux Gênants

On a vu plus haut que par l'introduction d'une quantite suffisante de citrate d'ammoniaque on peut arriver à doser correctement l'acide tartrique en présence d'oxyde de fer et d'aluminium à la condition que les oxydes ne depassent pas la teneur de 50 à 60% (par rapport à l'acide tartrique à doser), mais qu'au de là de ces limites le procédé était à nouveau en défaut.

Aussi nous sommes nous préoccupés de rendre la méthode tout à fait genérale en l'étendant au cas où les métaux gênant la précipitation se trouvent en dose massive par rapport à l'acide tartrique.

Nous y sommes parvenus en précipitant la majeure partie des métaux gênants à l'aide de réactions s'effectuant en milieu acide par un acide mineral (Hcl), car dans ce milieu le complexe est detruit et le metal peut précipiter intégralement sans entraîner d'acide tartrique.

1°—Cas de l'Alumine

Nous avons précipite la plus grande partie de celle-ci à l'état d'alun d'ammoniaque en solution lelégerement chlorhydrique; a cet effet la solution renfermant l'alumine et l'acide tartrique est additionné de sulfate d'ammoniaque en quantite plus que suffisante pour former l'alun: $(SO_4)_3\ Al_2,\ SO_4\ Am_2$. On ajoute quelques gouttes de Hcl à 22° B. et on concentre à petit volume (25 à $30^{cc.}$) puis la liqueur est additionnée de son volume d'alcool à 95°; on obtient ainsi une cristallisation d'alun d'ammoniaque que l'on sépare par filtration sur un petit entonnoir Büchner. Les cristaux sont lavés soigneusement avec de l'alcool à 55-60° puis le filtrat est evaporé de facon à chasser la majeure partie de l'alcool. Dans cette derniere liqueur étendue d'eau en quantité convenable le racémate est enfin précipité, aprés addition de citrate d'ammoniaque (en vue d'éliminer l'action gênante des petites quantités d'alumine qui ont échappé à la précipitation à l'état d'alun).

On s'est assuré que l'alun d'ammoniaque ainsi précipité n'entraînait pas d'acide tartrique car, dissous dans l'eau, il ne réduit pas le permanganate à l'ébullition en milieu sulfurique.

Voici le résultat de nos essais:

		Acide tartrique	
Al_2O_3	Citrate d'ammoniaque	Trouvé	Théorie
0 gr. 600	0 gr. 700	0,2046	0,2076
0 gr. 600	0 gr. 700	0,2052	0,2076

2°—*Cas du Fer*

Nous avons éliminé la majeure partie du fer à l'état de sulfure ferreux (par H_2S) en milieu acetique. La solution contenant le sel ferrique (Fe cl_3) est additionnée d'acétate de soude et de quelques gouttes d'acide acétique, puis dans la solution chaude on fait passer un courant de H_2S. Le précipité de sulfure de fer est filtré, la liqueur est portée à l'ébullition pour chasser H_2S et apres neutralisation partielle de l'acide acétique par NH_3 le racémate est précipité suivant la méthode générale.

Résultats des essais:

		Acide tartrique	
Fe_2O_3	Citrate d'ammoniaque	Trouvé	Théorie
0,432	0 g. 500	0,2052	0,2076
0,432	0 g. 500	0,2064	0,2076

3°—*Cas, du Cuivre et de l'Antimoine*

Le cuivre et l'antimoine sont éliminés par H_2S en solution chlorhydrique. Aprés séparation du sulfure, la liqueur est portée à l'ébullition pour chasser H_2S, puis neutralisée par NH_3, et le racémate est précipité en présence de citrate d'ammoniaque.

Les deux tableaux suivants résument nos expériences:

SO_4Cu 5 aq.	Citrate d'ammoniaque	Acide tartrique Trouvé	Théorie
0 g. 500	0 g. 500	0,2058	0,2076
0 g. 500	0 g. 500	0,2058	0,2076

Sb Cl_3	Citrate d'ammoniaque	Acide tartrique Trouvé	Théorie
0 g. 500	0 g. 500	0,2064	0,2076
0 g. 500	0 g. 500	0,2064	0,2076

Pratique de la Méthode Definitivement Adoptee pour le Dosage de l'Acide Tartrique a l'Etat de Racémate de Chaux.

L'étude qui précede nous ayant prouvé qu'à tous les points de vue l'addition de citrate d'ammoniaque aux solutions tartriques était trés avantageuse, nous avons modifié légerement le procedé publié par l'un de nous et nous nous sommes arrêtés pour effectuer le dosage de cet acide, au mode opératoire suivant:

Solutions Employees

A.—Une solution de citrate biammonique renfermant 50 grammes de citrate au litre.

B.—Une solution de tartrate gauche d'ammoniaque pur rigoureusement exempt de tartrate droit[1] contenant 20 grammes de tartrate par litre à laquelle on ajoute 5 à 6^{cc} de formol pour assurer la conservation.

C.—Solution acétique d'acétate de chaux obtenu en dissolvant 16 grammes de carbonate de chaux chimiquement pur dans 120^{cc} d'acide acétique cristallisable et en completant à un litre.

D.—Une solution de HCl renfermant 40 grammes d'acide à 22 B. par litre.

E.—Une solution renfermant: 5 grammes de CO_3Ca dissous dans 20 grammes d'acide acétique, et 100 grammes d'acétate de soude par litre.

F.—Une solution de Mno_4 K à 16 grammes environ par litre.

Cette derniére solution est titrée par rapport à une solution

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[1] Pour sa préparation.—Voir pour plus de détails le Bull. Soc. chim., 1910, T. 7., p. 571.

d'acide tartrique pur de titre connu (determiné volumétriquement à l'aide d'une solution KoH $\frac{N)}{10}$.

Pour effectuer un dosage d'acide tartrique, qu'il y ait ou non en présence des métaux gênants, on ajoute à la solution tartrique ramenée à un volume de 150^{cc} environ 10 à 15^{cc} de la solution A (Citrate d'ammoniaque) puis successivement 25^{cc} de la solution B. et 20^{cc} de la solution C.

On mélange avec un agitateur et on abandonne quelques heures; la durée de ce repos doit atteindre 12 heures dans le cas où la liqueur renferme des quantites appréciables de métaux gênants. (Fe. Al. SI.)

Ce temps écoulé le précipité est jeté sur filtre lavé à l'eau froide, puis le filtre est perce et le précipité entrainé à l'aide d'un jet de pissette dans un vase à précipiter. On ajoute 20^{cc} à la solution chlorhydrique D. avec laquelle on lave le filtre. La dissolution du racémate terminée on étend à 150^{cc} et on additionne le liquide de 40 à 50^{cc} de solution E, aprés avoir amené la liqueur vers 80° au bain-marie on l'abandonne au refroidissement quelques heures, puis le précipité est jeté sur filtre lavé et dissous sur le filtre même à l'aide d'une solution chaude d'acide sulfurique à 10% en volume.[1] Cette solution est recueillie dans une capsule de porcelaine, elle est portée à l'ébullition et titrée en faisant tomber goutte à goutte le Mno_4K tout en agitant et en continuant à faire bouillir. Le nombre obtenu pour l'acide tartrique contenu dans le racémate, divisé par 2, fournit celui qui correspond à l'acide tartrique droit, contenu dans la solution analysée.

APPLICATIONS QUI ONT ETE FAITES DE CE PROCEDE

I. Cas des Tartres et des Lies

La méthode de précipitation de l'acide tartrique à l'état de racémate de chaux en présence de citrate d'ammoniaque s'applique trés bien au dosage de cet acide dans les tartres et dans les lies

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[1] La teneur en So_4H_2 influençant le dosage au permanganate il est indispensable de titrer la solution F. de Mno_4K., puis le racémate, à l'aide de cette solution F, dans un milieu contenant a peu prés toujours la même teneur en So_4H_2; l'emploi d'acide sulfurique à 10% en volume est en particulier trés commode.

qui renferment des quantités de fer, d'alumine non gênantes grâce au citrate d'ammoniaque.

A cet effet on dissout dans l'eau chaude légerement acidulée par quelques gouttes de Hcl la quantité de tartre ou de lies que l'on suppose renfermer approximativement 0 gr. 200 d'acide tartrique (de 0 gr. 300 pour les tartres riches à 2 gr. 000 pour les lies). La liqueur aprés refroidissement complete est filtrée, ramenée à 150^{cc} on ajoute 10 à 15^{cc} d'une solution de citrate d'ammoniaque on neutralise la plus grande partie de l'acide chlorhydrique par, NH_3, puis on additionne la liqueur d'acétate de soude[1] et on précipité le racémate suivant le méthode générale.

Voici les résultats que nous avons obtenu avec un tartre commercial.

Poids	Citrate d'ammoniaque	Acide tartrique %
0 gr. 303	0	67,1
0 gr. 252	0	66,6
0 gr. 300	0 gr. 500	68,6

Le même tartre précipité par l'alcool 95°, puis titré par $KoH\frac{N}{10}$ (Méthode Berthelot et de Fleurieu) nous a donné: Acide tartrique %: 61, 0.

Nous avons dose l'acide tartrique dans une lie renfermant 6, 48% de cendres minérales.

La méthode au racémate-citrate nous a donné 10, 3% d'acide tartrique, tandis que la méthode de précipitation du bitartrate de potasse par l'alcool ne nous en a donné que 6, 75%.

Afin de voir l'influence des substances minérales que renfermait cette lie sur la précipitation du racémate, nous avons dissous les cendres provenant de 2 grammes de lie dans de l'eau acétique et la solution obtenue a été a joutée à une quantité connue d'acide tartrique, puis celui-ci a été précipité à l'état de racémate en présence et en l'absence de citrate.

Voici les résultats:

	Acide tartrique	
	Trouvé	Théorie
Présence de citrate..................	0,2088	0,2076
Absence de citrate..................	0,1980	0,2076

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[1] Il peut arriver qu'à ce moment il se produise un léger louche dû à la précipitation d'alumine; il n'y a pas lieu de s'en préoccuper, on ajoute une nouvelle quantité de citrate d'ammoniaque et on continue le dosage.

Nous nous sommes assures, indirectement il est vrai, que les substances organiques que les lies renferment, n'avaient pas d' influence sensible sur la précipitation du racémate; a cet effet 1 gramme de lie renfermant 10,3% d'acide tartrique a été additionné de 0 gr. 1038 d'acide tartrique pur, or le dosage de l'acide tartrique total nous a donné 0 gr. 210 au lieu du nombre théorique 0,2064, somme de l'acide tartrique pur et de l'acide trouvé préalablement dans la lie.

II. Cas des Vins. Cidres. Poires.

Nous rappellerons seulement pour mémoire les résultats déjà publiés par l'un de nous.

La méthode au racémate permet le dosage rigoureux d l'acide tartrique dans les vins naturels ou plâtres[1]; un vin synthétique a été analysé par la méthode au racémate et par la méthode officielle ainsi qu'une partie de ce vin préalablement plâtré.

Les résultats ont été les suivants:

	Acide tartrique par litre		
	Méthode au racémate	Méthode officielle	Théorie
Vin non plâtré..........	2 gr. 01	2 gr. 18	2 gr. 025
(id)...............	2 gr. 04	2 gr. 07	(id)
Vin plâtré.............	2 gr. 05	1 gr. 80	(id)

Cette méthode a donné également de trés bons résultats dans le dosage de l'acide tartrique dans les cidres, poirés et Minaigres[2], ainsi qu'il résulte des analyses suivantes effectuées sur des produits synthétiques.

	Acide tartrique par litre		
	Méthode au racémate	Méthode officielle	Théorie
Cidre N°. 1....................	3,98		4,02
Cidre N°. 2....................	3,17	2,69	3,22
Vinaigre......................	1,50		1,52

En résumé la méthode au racémate pour le dosage de l'acide tartrique se présente comme une méthode générale applicable aussi bien dans le cas du dosage de l'acide dans les sels métalliques que dans le cas de produits trés complexes tels que les boissons fermentées, les tartres et les lies.

[1] A. Kling.—Dosage de l'acide tartrique dans les Vins (Bull. de chimie T. 7, p. 569).

[2] A. Kling et L. Gobert.—Dosage de l'acide tartrique dans les cidres epoirés. (Ann. de falsif, T. 4, p. 185.)

APPLICATION DE LA METHODE DE DOSAGE DE L'ACIDE TARTRIQUE A L'ETAT DE RACEMATE DE CHAUX, AUX CAS DES SOLUTIONS D'ETHERS TARTRIQUES

PAR M. ANDRE KLING, *Directeur du Laboratoire Municipal de la Ville de Paris et*

E. GELIN, *Chimiste Controleur au Laboratoire Municipal de la Ville de Paris*

A l'occasion d'un travail actuellement en cours nous avons eu à nous préoccuper de déterminer less quantités respectives d'acide libre et combiné dans des solutions hydroalcooliques, contenant à la fois de l'acide tartrique et de l'éther éthyltartrique.

L'un de nous ayant institué un mode de dosage de l'acide tartrique par précipitation à l'état de racémate de chaux, nous avions tout d'abord essayé d'imaginer un procédé analogue pour précipiter l'acide éthyltartrique. A cet effet, nous avions préparé de l'acide éthyltartrique gauche dans l'espoir qu'en l'ajoutant à l'acide éthyltartrique droit, il se formerait un racémique éthyltartrique, précipité à l'état de sel alcalino-terreux. Mais nous avons dû renoncer à ce mode opératoire qui ne nous a pas donné satisfaction.

Nous nous sommes alors rabattus sur la metode consistant à doser l'acide tartrique existant soit à l'état d'acide libre, soit à l'état de sel alcalin par formation du racémate de chaux suivant la metode publiée antérieurement, puis à saponifier l'éther éthyltartrique et à doser sous forme de racémate l'acide tartrique droit total.

Partant de ce principe que le procédé au racémate s'applique rigoureusement au cas d'acide tartrique libre ou à l'état de tartrate alcalin, il importait de se rendre compte tout d'abord s'il en était encore de même dans le cas de la présence simultanée d'acide libre ou de tartrate alcalin et d'éthers tartriques.

On pouvait craindre, en effet, qu'au des opérations relatives au dosage de l'acide, une certaine quantité des éthers ne subît la saponification et que, de ce fait, une nouvelle quantité d'acide libéré ne vint s'ajouter à celle primitivement contenue dans la liqueur.

Les divers essais que nous avons effectués à l'aide de solutions tartriques (rendues acides par l'acide acétique) additionnées de quantités variables d'éthers tartriques (acide éthyltartrique et tartrate neutre d'éthyle) nous ont prouvé que nos craintes n'étaient pas fondées et que, dans le cas de solutions acides contenant un mélange d'acide tartrique et d'éther tartrique la méthode au racémate permettait de précipiter exclusivement l'acide tartrique qui y était contenu à l'état libre ou à l'état de sels alcalins.

Il y avait également lieu de se demander si par saponification, en solution trés faiblement alcalin, (par la soude, la potasse ou la chaux) et étendue, l'acide éthyltartrique et le tartrate neutre d'éthyl régénéraient sans altération tout l'acide tartrique auquel l'alcool était combiné dans ces éthers.

Pour le vérifier, nous avons pris des poids connus d'acide tartrique pur, nous les avons dissous dans l'alcool à 96° et par chauffage en tubes scèllés vers 150° pendant 48 heures, nous avons déterminé l'éthérification partielle du mélange. Aprés refroidissement des solutions ainsi obtenues, nous avons ouvert les tubes scèllés et traité le contenu au réfrigérant ascendant par un petit excès de potasse ou de soude, et ayant acédifié les liqueurs résultant par l'acide acétique, nous avons dosé l'acide tartrique à l'état de racémate.

Nous avons obtenus les résultats suivants:

Acide tartrique théorie	Acide tartrique dosé
5,15	5,12
6,36	6,35
7,55	7,49
8,71	8,65

Ces résultats prouvent que par saponification dans les conditions ci-dessus indiquées, la totalité de l'acide tartrique existant à l'état d'éthers se trouve régénérée.

Application de la Methode

Nous rappellerons d'abord brièvement la technique du dosage de l'acide tartrique droit.

Prélever un volume de la solution à analyser tel qu'il contienne environ 0 gr. I à 0 gr. 2 d'acide tartrique, l'étendre d'eau à $150^{cm.3}$ ajouter $25^{cm.3}$ de la solution de tartrate gauche d'ammoniaque à 20 gr. 1 et $20^{cc.}$ de la solution d'acétate de chaux acétique. Laisser reposer ½ heure, filtrer, laver le racémate sur filtre à l'eau froide; crever le filtre et faire passer le racémate au moyen d'un jet de pissette dans un vase à précipiter. Laver le filtre avec $20^{cc.}$ de la solution chlorhydrique à 40 g. l. d'acide à 22° B^{é}. Le racémate se dissout dans HCl. Etendre à $150^{cc.}$ avec de l'eau et ajouter 40 à $50^{cc.}$ de la solution acétique d'acétate de soude et de chaux. Aprés ébullition, laisser refroidir et filtrer le racémate de chaux. Dissoudre ce racémate sur le filtre même au moyen d'une solution bouillante d'acide sulfurique à 10%. Titrer cette solution sulfurique de racémate de chaux avec une solution de permanganate de potasse à 16 g. l. que l'on aura étalonnée elle même en la faisant tomber goutte à goutte dans une solution sulfurique d'acide tartrique connue maintenue à l'ébullition comme pour un dosage d'acide oxalique.[1]

Pour faire application de cette méthode au cas de la présence simultanée dans une solution d'acide tartrique ou de tartrate et d'éthers tartriques, nous avons commencé par faire de semblables mélanges.

A cet effet, nous avons éthérifié en tubes scèllés, par chauffage durant 48 heures à 150° degrés, des solutions alcooliques d'acide tartrique. On sait que dans ces conditions la solution alcoolique partiellement éthérifiée contient: de l'acide tartrique libre, de l'acide éthyltartrique et du tartrate neutre d'éthyle dans les proportions variables suivant les conditions dans lesquelles l'éthérification a été conduite.

Afin de calculer ces proportions nous avons opéré de la facon suivante:

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[1] Il importe pour obtenir des résultats rigoureux de faire le titrage du permanganate et le dosage du racêmate en opêrant dans des liquides ayant la même concentration sulfurique. L'expêrience montre en effet que le volume de permanganate à ajouter pour oxyder une même quantitê d'acide tartrique, varie un peu avec la concentration de la liqueur en acide sulfurique.

Désignons par:
a la quantité d'acide tartrique total introduite
x la quantité d'acide tartrique libre dans le mélange
y la quantité d'acide tartrique engagé à l'état d'acide éthyltartrique.
z la quantité d'acide tartrique transformé en éther tartrique neutre.

Nous pouvons d'aprés ce qui a été exposé au paragraphe précèdent doser l'acide libre en le précipitant à l'état de racémate. Soit *C* la proportion % d'acide libre ainsi déterminée.

Un[1] titrage acidimétrique effectué à l'aide de la potasse $\frac{N}{10}$ dont les résultats seront exprimés en acide tartrique permet de déterminer l'acidité totale *b* due 1°, à l'acide tartrique libre et 2° à celui combiné sous forme d'acide éthyltartrique, [l'acidité de ce dernier $C_2H_5\,CO_2-(CHOH)_2-CO_2H$ étant la moitie de celle de l'acide $CO_2H-(CHOH)_2\ CO_2H$].

Or les valeurs a, b, c, x, y, z, ci-dessus désignées sont reliées entre elles par le système d'équations suivant:

$$(1)\qquad a=x+y+z$$

$$(2)\qquad b=x+\frac{y}{2}$$

$$(3)\qquad c=x=$$

En résolvant ce système on obtient:

$$x=c$$
$$y=2\,(b-c)$$
$$z=a-2b+c$$

On voit qu'en principe, la méthode dont nous avons fait usage permet dans des mélanges où n'entrent que de l'acide tartrique et ses éthers éthyliques de déterminer à la fois les proportions d'acide libre, d'acide éthyltartrique et d'éther neutre.

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[1] Ce titrage par la potasse $\frac{N}{10}$ dont être fait trés rapidement et à trés basse température, vers zero degré pour eviter que la potasse ajoutée ne saponifie les éthers tartriques existant dans le mélange.

Nous l'avons appliquée à des mélanges de ce genre et nous avons obtenu les résultats suivants:

1° *Mélange*

35 gr. 617 solution tartrique à 150 g. l.
54 gr. 854 alcool absolu

Aprés chauffage en tube scèllé, il fut trouvé:

$a=5,15$ $x=1,60\%$
$b=2,22$ d'où $y=1,24\%$
$c=1,60$ $z=2,31\%$

Acide tartrique introduit 5,15%
Acide tartrique total retrouvé. 5,12%

2° *Mélange*

45 gr. 183 solution tartrique à 150 g. l.
47 gr. 520 alcool absolu

Aprés chauffage en tube scèllé il fut trouvé:

$a=6,36$ $x=1,99\%$
$b=3,24$ d'où $y=2,50\%$
$c=1,99$ $z=1,87\%$

Acide tartrique total introduit....6,36%
Acide tartrique total retrouvé....6,35%

3° *Mélange*

54 gr. 780 solution tartrique à 150 g. l.
40 gr. 268 alcool absolu

Aprés chauffage en tube scèllé il fut trouvé:

$a=7,55$ $x=2,62$
$b=4,55$ d'où $y=3,86$
$c=2,62$ $z=1,07$

Acide tartrique total introduit....7,55%
Acide tartrique total retrouvé......7,49%

4° *Mélange*

65 gr. 086 solution tartrique à 150 g. l.
32 gr. 596 alcool absolu

Aprés chauffage en tube scèllé il fut trouvé:

$a=8,71$ $x=4,22$
$b=6,18$ d'où $y=3,92$
$c=4,22$ $z=0,57$

Acide tartrique total introduit....8,71%
Acide tartrique total retrouvé....8,65%

Mais dans la pratique, des mélanges tels que ceux mentionnés ci-dessus ne se présentent qu'exceptionnellement. Le plus souvent, comme dans le cas des vins et autres liquides fermentés, on se trouve en présence de solutions contenant: acide tartrique libre, tartrates acide et neutre, éthers tartriques et autres substances à caractère acide plus ou moins accusé. En pareille occurence, il ne peut plus être question, à l'aide des seules données: acide tartrique total, acide tartrique libre, acidité totale de résoudre le problème ainsi que nous l'avons fait dans le cas simple, et d'établir quelles sont les diverses proportions d'acide tartrique sous ses diverses formes. Dans ces cas ce qu'il est possible d'effectuer, c'est la détermination des proportions d'acide tartrique libre ou combiné à l'état de sel, et de l'acide existant à l'état d'éther (acide ou neutre.)

Pour cela on commencera d'abord par un premier dosage direct en formant le racémate pour déterminer l'acide tartrique existant à l'état libre et à l'etat de sel alcalin. Puis aprés une saponification, par un nouveau dosage à l'état de racémate on dosera l'acide tartrique total. La différence entre les deux résultats obtenus donnera la proportion d'acide tartrique existant à l'état d'éthers.

(*Contribution from the Chemical Laboratory of Allegheny College*)

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE CALCIUM GROUP

By Richard Edwin Lee and F. L. Mickle

INTRODUCTION: OUTLINE OF THE INVESTIGATION

Although it is well known that many of the methods which are generally used in qualitative analysis need revision, apparently very little time has been devoted to the systematic study of their relative effectiveness. It would seem, therefore, that any investigation which comprehended a detailed study of qualitative methods with particular reference to their accuracy in detecting small amounts of the elements in the presence of large amounts of any or all of the other elements, and for the purpose of developing and formulating more reliable procedures, would be of considerable value to the analytical chemist.

The investigation reported in this paper was undertaken not for the purpose of making an experimental survey of all the qualitative methods, but of only those which are most frequently used in precipitating and separating the metals of the Calcium Group, namely, barium, strontium and calcium.

It was hoped that the result of such an examination would render possible the selection of the best of the proposed methods and enable the formulation of the conditions best adapted to securing the desired end. As the work progressed, and larger discrepancies among the recommended procedures than had been anticipated were noted, it became obvious that although some methods ought to be revised, others ought to be rejected and new ones substituted, if possible.

The results of the investigation are reported in the order of their dependence. For convenience in presenting data, the paper has been divided into three parts: "Precipitation of the Group," "Analysis of the Group," and "Summary." Under each of the first two parts there is first presented a "General Discussion" in which the reasons for rejecting certain processes, and adopting others, are given. This is followed by a record of the "Test Experiments" which were performed to test the accuracy of a given process. Next there is presented the "Procedure and Notes" in which the various details of the adopted procedure are submitted and briefly discussed.

The abbreviations used in the cross references may be explained as follows: G. D. is used for General Discussion; P. for Procedure; N. for Notes; T. E. for Test Experiments.

The authors take this opportunity of expressing their appreciation of the assistance extended by Mr. Walter Fegley who cooperated with them in carrying out the experimental details of the investigation.

PART I. PRECIPITATION OF THE GROUP

(a) General Discussion (b) Test Experiments (c) Procedure

General Discussion

With respect to the original precipitation of the elements of this group, schemes of qualitative analysis differ as to whether magnesium should be precipitated separately or with this group.

Among the objections offered to the precipitation of magnesium with the Calcium Group is the fact that the concentration of the carbonate ions requisite for the complete precipitation of magnesium as a double ammonium magnesium carbonate [$MgCO_3.(NH_4)_2CO_3.4H_2O$], is so great that there is danger of precipitating lithium carbonate at the same time. Moreover, the analysis of the group is made more complex.

The majority of authors[1] prefer a separate precipitation for

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[1] Those in Group I suggest a separate precipitation of magnesium; those in Group II precipitate magnesium with the Calcium Group.

Group I: Qual. Anal.- Bailey and Cady, Qual. Anal.- Böttger, Wm., Qual. Anal.- Dennis and Whittelsey, Qual. Chem. Anal.- Eliot and Storer, Qual. Chem. Anal.- Fresenius, C. R., Qual. Anal.- Gooch and Walker, Qual. Chem. Anal.- Hinds, J. D., Qual. Chem. Anal.- Jones, C., Qual. Anal.- Morgan, W. C., Qual. Chem. Anal.- Newth, Qual. Chem. Anal.- Noyes, A. A., Qual. Anal.- Noyes, Wm. A., Qual. Chem. Anal.- Scott, W. W., Qual. Chem. Anal.- Tower O. F., Qual. Anal.- Treadwell-Hall, Qual. Anal.- Long, J. H., Anal. Chem.-Menschutkin, N. (trans. by Locke), Qual. Chem. Anal.- Perkin, F. M.

Group II : Qual. Chem. Anal.- Noyes, Bray and Spear.

magnesium. The objections offered to this procedure are due to the difficulties encountered in securing a complete precipitation of barium, strontium and calcium without precipitating some magnesium, but these difficulties may in a large measure be overcome by a proper regulation of the conditions under which precipitation is effected.

It has seemed advisable, therefore, to adopt the method of precipitating magnesium separate from the Calcium Group.

The next problem to be solved was the determination of the most reliable group precipitant. A study of many of the procedures recommended showed that whereas practically all of the authors propose precipitation of the group by ammonium carbonate in the presence of ammonium chloride and ammonium hydroxide, the directions vary greatly as to the *concentration of*, and *the quantity to be used* of these reagents. See footnote[1] for comparative study of procedures adopted by various authors.

Again, confusion was found to exist in regard to the optimum temperature for precipitating the group in order to accomplish its

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[1] Authors in Group I suggest the addition of NH_4OH until the solution is just alkaline; those in Group II fail to provide for the use of NH_4OH; those in Group III advise the addition of this reagent but do not give directions concerning the amount to be used.

Group I: Bailey and Cady, Böttger, Wm., Hinds, J., Hill, A. E., Newth, G. S., Scott, W. W., Long, J. H., Menschutkin, N. (transl.). Group II: Tower, O. F., Perkin, F. M. Group III: Dennis and Whittelsey, Fresenius, C. R., Jones, C., Noyes, Wm. A., Treadwell-Hall.

Authors in Group I do not recommend the use of NH_4Cl; those in Group II suggest the addition of NH_4Cl but do not specify the amount; those in Group III advise the addition of a definite amount of NH_4Cl.

Group I: Böttger, Wm., Jones, C., Treadwell-Hall, Analytical Chemistry, Vol. I, Pg. 55, Par. 2 ("In the presence of considerable ammonium chloride and only small amounts of ammonium carbonate a precipitate of calcium often fails to form"), Perkin, F. M.

Group II: Bailey and Cady, Dennis and Whittelsey, Fresenius, C. R., Hinds, J. I. D., Newth, G. S., Noyes, W. A., Tower, O. F., Long, J. H., Hill, A. E.

Group III: Scott, W. W.

Authors in Group I advise the addition of a stated amount of $(NH_4)_2CO_3$ as the group precipitant; those in Group II direct its addition in slight excess or so long as a precipitate continues to form; those in Group III specify a large excess.

Group I: Scott, W. W., Hill, A. E.

Group II: Böttger, Wm., Dennis and Whittelsey, Fresenius, C. R., Jones, C., Newth, G. S., Noyes, W. A., Tower, O. F., Long, J. H., Perkin, F. M.

Group III: Bailey and Cady, Hinds, J. I. D., Treadwell-Hall.

complete separation from the other groups. Some authors[1] give directions for precipitating from boiling solutions; some from solutions slightly warm; and others, precipitate from *cold* solutions. It is obvious that although the various authors have a common aim, namely, the complete precipitation of the group, the greatest discrepancy exists as to the directions for securing this result.

The work as conducted in this laboratory indicates that precipitation is most satisfactorily accomplished by the method outlined in Procedure I.

The method of precipitating the group with ammonium carbonate containing a definite concentration of CO_3 ions, from a *cold, slightly alkaline* solution to which 10-15 cc. of ammonium chloride have been added (providing this reagent is not already present as the result of the precipitation of previous groups) gives an approximately complete precipitation of barium, strontium, and calcium as carbonates and prevents the precipitation of magnesium. This practically eliminates all difficulties attendant upon the separation of this group, and is, therefore, satisfactory as a method.

Test Experiments and References

Series I.—*Difficulties Encountered in Attempting to Precipitate Magnesium with the Calcium Group.*

After a few trial experiments in an attempt to follow the procedure of precipitating magnesium with the Calcium Group, this method was rejected on the grounds that it possessed no advantages over the method of precipitating magnesium alone, and that it made the analysis of the group more complex.

Series II.—*Determination of the Most Advantageous Concentration of CO_3 Ions in the Precipitant.*

After making a considerable number of exploratory tests, it was concluded that the group precipitant should be prepared in the following manner: Dissolve 200 gm. of $(NH_4)_2CO_3$ in 500 cc. of

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[1] Authors in Group I precipitate at boiling temperature; those in Group II direct that the solution be gently warmed; those in Group III precipitate from cold solutions; those in Group IV precipitate from cold solutions and then gently warm the mixture. Group I: Baily and Cady, Böttger, Wm., Scott, W. W., Tower, O. F., Perkin, F. M., Treadwell-Hall. Group II: Fresenius, C. R., Newth, G. S., Menschutkin, N. (trans. by Locke). Group III: Noyes and Bray. Group IV: Dennis and Whittelsey, Hill, A. E., Jones, C., Long, J. H., Noyes, W. A.

strong NH_4OH (sp. gr. 0.90) and dilute to a liter with distilled water.

Series III.—*Completeness of Separation of Magnesium from the Members of the Calcium Group as Secured by the Method Outlined in Procedure I.*

In the following series of experiments the amount of the metal in the form of the chloride was dissolved in distilled water and diluted to 10 cc. The solution was then made slightly alkaline with (5N) NH_4OH, and 10-15 cc. (5N) NH_4Cl were added. Precipitation in every case was carried out in the *cold* by the addition of an excess of $(NH_4)_2CO_3$.

A. *Magnesium*

0.10 gm. Mg [8.22 cc. (1N) $MgCl_2.6H_2O$] failed to give a precipitate in 8 minutes.

0.12 gm. Mg [4.92 cc. (2N) $MgCl_2.6H_2O$] gave no precipitate at first but a slight precipitate formed in from 3-10 minutes according to the amount of NH_4Cl added.

0.13 gm. Mg [5.34 cc (2N) $MgCl_2. 6H_2O$] gave no precipitate at once but a distinct precipitate formed after 5-6 minutes.

0.15 gm. Mg [6.17 cc. (2N) $MgCl_2. 6H_2O$] gave no precipitate immediately but a distinct precipitate after 3 minutes.

0.20 gm. Mg [8.22 cc. (2N) $MgCl_2. 6H_2O$] gave a precipitate at once.

These test experiments with Mg as $MgCl_2. 6H_2O$ show that this metal, unless present in a greater quantity than 0.13-15gm. will not interfere with the precipitation of this group of metals. The presence of this large quantity would occur only rarely. The foregoing series of experiments, however, indicates that the procedure should not be interrupted at this point as a precipitate forms more readily on standing.

B. *The Calcium Group*

1. *Barium.*

0.001 gm. Ba (1.45 cc. N/100 $BaCl_2. 2H_2O$) gave no precipitate on standing for 10 minutes.

0.002 gm. Ba (1.45 cc. N/50 sol.), no precipitate separated on standing for 10 minutes.

0.003 gm. Ba (0.43 cc. N/10 sol.), a distinct precipitate separated after 1-2 minutes.

2. *Strontium.*

0.001 gm. Sr (2.28 cc. N/100 $SrCl_2 . 6H_2O$) gave no precipitate on standing for 10 minutes.

0.002 gm. Sr (2.28 cc. N/50 sol.), no precipitate separated on standing for 10 minutes.

0.003 gm. Sr (0.70 cc. N/10 sol.), a distinct precipitate separated in 1-2 minutes.

3. *Calcium.*

0.001 gm. Ca (4.99 cc. N/100 $CaCl_2 . H_2O$) gave no precipitate on standing for 10 minutes.

0.002 gm. Ca (4.99 cc. N/50 sol.), no precipitate separated but the solution became turbid after standing for a few minutes.

0.003 gm. Ca (1.50 cc. N/10 sol.), a distinct precipitate was obtained after 1-2 minutes.

This series of test experiments shows that quantities as small as 0.003 gm. of either Ba, Sr, or Ca are precipitated in 1-2 minutes. By the method outlined, therefore, the precipitation of these metals is practically complete.

Series IV.—*The Determination of the Amount of Ammonium Hydroxide to be used in Precipitating the Group.*

All the experimental work relating to the precipitation of the group showed that the solution should be made just slightly alkaline prior to adding the group precipitant. Too large an excess has a tendency to precipitate some of the metals as hydroxides.

Series V.—*The Effect of the Presence of Varying Amounts of Ammonium Chloride on the Separation of Magnesium from the Members of the Calcium Group.*

In the following series of experiments the amount of the metal in the form of the chloride was dissolved in distilled water and diluted to 10 cc. The solution was then made slightly alkaline with (5N) NH_4OH, and an excess of $(NH_4)_2CO_3$ added. Precipitation in every case was made from *cold* solutions.

A. *Effect upon Magnesium*

1. *In the presence of 5 cc. of 5N NH_4Cl.*

0.03 gm. Mg (2.47 cc. 1N $MgCl_2$. $6H_2O$) gave no precipitate on standing 10 minutes.

0.04 gm. Mg (3.29 cc. of sol.) gave a slight precipitate after 10 minutes.

0.05 gm. Mg (4.11 cc. of sol.) gave a very slight precipitate immediately.

0.06 gm. Mg (4.92 cc. of sol.) gave a heavy precipitate at once.

2. *In the Presence of 10 cc. of 5N NH_4Cl.*

0.10 gm. Mg (8.22 cc. 1N $MgCl_2$. $6H_2O$) failed to give a precipitate on standing 8 minutes.

0.12 gm. Mg (4.93 cc. 2N sol.) gave a slight precipitate on standing 3 minutes.

0.15 gm. Mg (6.17 cc. of 2N sol.) gave no precipitate at once but a distinct precipitate in 3 minutes.

0.20 gm. Mg (8.22 cc. of 2N sol.) gave a heavy precipitate at once.

3. *In the Presence of 15 cc. of 5N NH_4Cl.*

0.12 gm. Mg (4.93 cc. of 2N $MgCl_2$. $6H_2O$) gave no precipitate at once but a slight precipitate after 9 minutes. (After this precipitate had stood for 10 minutes, it could not be distinguished with regard to size from the one in the experiment in which the same amount of Mg was present but to which only 10 cc. 5N NH_4Cl were added.)

0.13 gm. Mg (5.34 cc. of 2N sol.) gave no precipitate at first but a distinct precipitate separated after 6 minutes. (Results obtained in this test experiment were practically identical with those in the experiment in which the same amount of Mg was used but 10 cc. of 5N NH_4Cl were present.)

4. *In the Presence of 20 cc. of 5N NH_4Cl.*

0.12 gm Mg (4.93 cc. of 2N $MgCl_2$. $6H_2O$) gave no precipitate at first but a small precipitate separated after 10 minutes. (Results with 0.12 gm. Mg were practically identical when using either 10, 15, or 20 cc. of 5N NH_4Cl.)

These experiments show that when working with a solution diluted to 10 cc. the addition of an equal volume of 5N NH_4Cl is effective in holding in solution 0.15 gm. Mg, whereas the addition of but 5 cc. 5N NH_4Cl is effective in holding in solution but 0.04 gm. Mg. The addition of either 10, 15, or 20 cc. of 5N NH_4Cl gave practically identical results. (Cf. P. I.)

B. *Effect upon Barium, Strontium, and Calcium*

1. *In the presence of no* NH_4Cl.

0.001 gm. each of Ba, Sr, and Ca, as chlorides gave no precipitate on standing for 10 minutes.

0.002 gm. each of the three metals, as chlorides gave no precipitate in 10 minutes. However, the solution containing the Ca became slightly turbid.

0.003 gm. of either one of the three metals as chlorides gave a distinct precipitate after 3 minutes.

0.005 gm. of either one of the three metals as chlorides yielded a heavy precipitate at once.

2. *In the Presence of 10 cc. of 5N* NH_4Cl.

0.002 gm. of either Ba, Sr, or Ca, as chlorides, gave no precipitate on standing for 10 minutes.

0.003 gm. of either Ba, Sr, or Ca, as chlorides, gave a distinct precipitate after 1 minute.

The results of this portion of the investigation tend to show, therefore, that the precipitation of the members of the Calcium Group is unaffected by the addition of 5N NH_4Cl in quantities up to and including an equal volume.

Series VI.—*The Effect of Temperature on the Separation of Magnesium from the Calcium Group.*

In the following series of experiments the specified amount of the metal in the form of the chloride was dissolved in distilled water and diluted to 10 cc. The solution was made slightly alkaline with 5N NH_4OH, and 10-15 cc. of 5N NH_4Cl were added. Precipitation was then effected by the addition of an excess of the special reagent $(NH_4)_2CO_3$. (Cf. T. E., Series II.)

A. *Magnesium*

1. *Precipitation at Boiling Temperature.*

0.06 gm. Mg (4.92 cc. of 1N $MgCl_2$. $6H_2O$) gave no precipitate.

0.07 gm. Mg (5.75 cc. of 1N sol.) gave a distinct precipitate which dissolved after the solution was boiled for 2.5 minutes, with frequent shaking.

0.10 gm. Mg (8.22 cc of 1N sol.) gave a heavy precipitate which did not appreciably dissolve when heated for 30 minutes at a temperature of 75°-80° C. The precipitate dissolved, however, after being boiled vigorously, with frequent shaking, for 3.5 minutes.

0.12 gm. Mg (9.86 cc. of 1N sol.) gave a heavy precipitate which would not dissolve when heated at a temperature of 75°-80° C. The precipitate dissolved, however, after being boiled hard, with frequent shaking, for 4-5 minutes. Several duplicates of this test were made.

2. *Precipitation in the Cold.*

0.07 gm. Mg (5.75 cc. of 1N $MgCl_2$. $6H_2O$) gave no precipitate on standing for 30 minutes. *A slight precipitate separated, however, when the temperature of the solution was raised to 90-100° C.*

0.10 gm. Mg (8.22 cc. of 1N sol.) gave no precipitate on standing for 8 minutes. However, when the solution was brought just to boiling, a heavy precipitate separated which dissolved only after being boiled *hard* for 3-4 minutes.

0.12 gm. Mg (4.93 cc. of 2N sol.) gave no precipitate at first. A slight precipitate formed after 3 minutes. A heavy precipitate separated at once if the solution was warmed.

0.15 gm. Mg (6.17 cc. of 2N sol.) gave no precipitate at first, but a distinct precipitate separated after 3 minutes.

0.20 gm. Mg (8.22 cc of 2N sol.) gave a large precipitate at once.

Conclusions: The foregoing set of test experiments with equal volumes of solutions containing various amounts of Mg, as the chloride, at boiling temperatures and in the cold, shows conclusively that the Mg is precipitated far more readily at boiling temperatures or even on being warmed than in the cold. This conclusion is directly opposite to the one reached by practically all of the authors who were consulted. In the cold, it was not difficult to keep 0.12 gm.-0.15 gm. Mg in solution, but on boiling or warming the solution either before or after the addition of the precipitant, a distinct precipitate was obtained when working with quantities of Mg as small as 0.07 gm. Even slight precipitates of Mg failed to dissolve when heated for 30 minutes at from 70-80° C. Precipitates kept at a temperature just below the boiling-point for 3-5 minutes did not appear to dissolve. Furthermore, these experiments show that precipitates of Mg dissolved only after being boiled vigorously, with frequent shaking, for 4-6 minutes; at the end of this time the precipitate dissolved suddenly, presumably as the result of hydrolytic action.

B. *The Calcium Group*

Sets of test experiments with small amounts each of Ba, Sr, and Ca, in the form of chlorides, were conducted under conditions similar to those of the experiments with Mg. Although it was found that the precipitates were slightly heavier in warm solutions, yet it was easily possible to detect 0.003 gm. of any of these elements in the cold. As this was also the smallest amount that could be detected when the solutions were warmed or boiled, either before or after the addition of the precipitant, the conclusion is that temperature has no disturbing effect on the precipitation of these three metals as outlined in the adopted procedure. (Cf. P. I.)

Conclusions: This series of experiments indicates that in order to secure the most favorable conditions for the complete separation of Mg from the Calcium Group, the solution should be kept *cold* throughout the precipitation of the group.

PART I. PRECIPITATION OF THE GROUP

Adopted Procedure, and Notes

Procedure I.—To the cold solution, which should have a volume of approximately 10 cc., add an equal volume of 5N NH_4Cl solution, and then 5 cc. in excess (providing this reagent is not already present), and sufficient 5N NH_4OH to make the solution alkaline. To this mixture (cold) add an equal volume of $(NH_4)_2CO_3$ solution (special reagent[1]) and then 3-5 cc. in excess. Shake the mixture for one minute. Filter, and test the filtrate for traces of Ba, Sr, and Ca by the addition of a few drops of the precipitant. Wash the

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[1] See T. E., Series II for the method used in preparing this reagent.

precipitate into the tip of the filter with cold, distilled water to which a little $(NH_4)_2CO_3$ reagent has been added. The filtrate may contain Mg ions and ions of the metals of Group VI. For the analysis of the group precipitate see Procedure II.

Note 1.—If the previous groups have been sought, the filtrate from Group IV may be colored by the presence of $(NH_4)_2S$ or some of the members of the previous groups soluble in that reagent, or in NH_4OH. If so, a few drops of $HC_2H_3O_2$ should be added and the solution boiled until the H_2S formed by the decomposition of the $(NH_4)_2S$ has been expelled and the solution rendered colorless. The solution is then concentrated to approximately 10 cc., and any residue filtered off and rejected before proceeding with the analysis.

2.—Providing the previous groups have been sought, the proper concentration of NH_4Cl will ordinarily be present in the solution. (See T. E., Series V.)

3.—Avoid a large excess of NH_4OH in making the solution alkaline. (See T. E., Series IV.)

4.—It is important that the solution be maintained cold throughout the precipitation of the group. (Compare T. E., Series VI.)

PART II. ANALYSIS OF THE GROUP

(a) General Discussion.
(b) Test Experiments and References.
(c) Adopted Procedure and Notes.

General Discussion

In separating barium from the other members of the Calcium Group, it seemed advisable to follow the well-known and almost universal method of precipitating it as barium chromate. This procedure is based upon the order of rapidly increasing solubilities of the chromates of barium, strontium, and calcium. Barium chromate is practically insoluble in water (0.0038 gm. to the liter), thus differing from strontium chromate which is moderately soluble (1.2 gm. to the liter), and calcium chromate which is quite soluble. All of these chromates are soluble in the strong mineral acids, but barium chromate alone is only slightly soluble in acetic acid, while the chromates of strontium and calcium are easily soluble in that reagent. In order, therefore, to finally effect a complete separation of barium from strontium and calcium, hydrochloric or nitric acid must not be used in place of acetic acid to dissolve the group precipitate, for only in the presence of the acetate ion or the anion of a similar weak acid is the precipitation of barium practically complete.

Although the precipitation of barium as a chromate seems to be the established method, this scheme of analysis appears to differ from the majority of them in the choice of the precipitant. That is, the precipitation of barium as barium chromate is usually effected by the use of a solution of the *dichromate* of potassium instead of the *chromate* of that metal, the use of which is recommended in this paper. The explanation of the formation of a chromate when the dichromate reagent is used is based upon the fact that the dichromate ion reacts with water forming chromate ions;

$$Cr_2\overset{=}{O_7} + H_2O = 2Cr\overset{=}{O_4} + 2\overset{+}{H}.$$

The usual procedure, when viewed from the standpoints of the mass law and of ion effects, rests upon the theory which takes into account that acetic acid is but slightly dissociated, and that yellow, alkaline chromate solutions are transformed into red dichromates when made only slightly acidic.

That potassium dichromate, however, is not entirely satisfactory as a precipitant for barium is admitted by some of the analysts who adhere to the use of it. For example, Böttger who uses this reagent, says: "Apparently potassium chromate would furnish a more efficient means of separating the barium ion, since its solutions contain only chromate ion. It would also precipitate strontium ion, however, and hence is not used as a reagent for Ba.[1]"

By an inspection of the test experiments which follow, it may be seen that the difficulties attendant on the use of potassium chromate have been overcome in an entirely satisfactory manner by the methods proposed in this paper. When working with 0.003 gram of barium, which appears to be the smallest quantity of that substance which can be detected by the most accurate methods of group precipitation, conclusive confirmatory tests were easily obtained. (Compare T. E., Series VII.)

[1] Böttger, W., *The Principles of Qualitative Analysis*, par. 97, pg. 115.

The accuracy with which barium may be separated from strontium and calcium by the use of potassium chromate was further evidenced by the fact that in experiments where a saturated solution of barium chloride was used, the tests for strontium and calcium were not interfered with in the slightest degree. (See T. E., Series VIII.) On the other hand, the presence of a large concentration of strontium and calcium ions caused no confusion in confirming barium. (See T. E., Series XII, and Series XIV.)

The comparatively recent work of Caron and Raquet[1] practically confirms our conclusions with regard to the choice of reagents. They found in their study of different reagents with respect to their accuracy in detecting and removing barium from strontium salts that one part of barium may be detected in the presence of one hundred and fifty parts of strontium by the use of potassium dichromate and that one part of barium in the presence of fifteen thousand parts of strontium may be detected by the use of potassium chromate. (See T. E., Series VIII.)

The method followed in securing the separation of strontium from calcium departs markedly from the customary procedure. The method is based upon the difference in solubility of strontium chromate and calcium chromate in mixtures of water and ethyl alcohol. Only one or two schemes of analysis were found in which this principle was utilized in effecting the separation, and in these, results were obtained only after the carrying out of a long and circuitous procedure. The details of the adopted procedure are given in Procedures IV and V. The experimental data concerning the delicacy of the test relative to strontium proved that quantities as small as 0.003 gram may be confirmed easily. The results of the experiments with saturated solutions of strontium chloride (T. E., Series XII) indicate that the tests for either barium or calcium are not rendered less accurate by the presence of a large concentration of strontium ions.

The procedure outlined in this paper provides for the precipitation of calcium as an oxalate from an alkaline solution, and for its confirmation as calcium sulphate in the presence of a relatively large quantity of ethyl alcohol. Calcium oxalate is practically insoluble in water (0.006 gm. per liter at 20° C.) or in alkaline

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[1] Bul. soc. Chim., *3-4*, 483-93 (1908); Chem. Abstracts, *2*, 1940 (1908)

solution. It is converted into calcium sulphate which is insoluble in alcohol, by sulphuric acid. A set of test experiments (T. E., Series XIII) supplied conclusive proof that quantities of calcium as small as 0.003 gram may readily be confirmed. The results obtained from another set of test experiments indicate that the tests for barium and strontium are not interfered with by the presence of relatively large quantities of barium and strontium (T. E., Series XIV).

Test Experiments and References

Series VII.—*The Precipitation of Barium as Barium Chromate. The Delicacy of the Test.*

After making several exploratory tests the following experiment was performed: 0.003 gm. of Ba (0.45 cc. N/10 $BaCl_2 . 2H_2O$) which is the least quantity of this metal that can be precipitated by the group precipitant, was treated according to Procedure II. A distinct yellow precipitate of $BaCrO_4$ separated at once. Attempts to further confirm this test by dissolving the precipitate in 2 cc. of conc. HCl (sp. gr. 1.12) and reprecipitating the Ba as $BaSO_4$ by the use of a saturated solution of $CaSO_4$, were not always successful. The Ba was easily confirmed, however, by the flame test.

In a similar experiment in which 0.005 gm. of Ba (0.72 cc. N/10 $BaCl_2 . 2H_2O$) was used, the Ba was readily confirmed as $BaSO_4$.

Series VIII.—*Solubility of Barium, Strontium, and Calcium Chromates in Water and in Mixtures of Water and Acetic Acid. Effect of Temperature on Solubility.*

1 part of $BaCrO_4$ is soluble in 263,160 parts of H_2O at 18°—Kohlrausch and Rose, *Z. phys. Chem.*, *12*, 241.

1 part of $SrCrO_4$ is soluble in 840 parts of H_2O.—Meschezerski, *Z. anal. Chem.*, *21*, 399.

1 part of $CaCrO_4$ is soluble in 34 parts of H_2O.—Schwarz, *Dingl.*, *198*, 159.

1 part of $BaCrO_4$ is soluble in 3670 parts of 5% $HC_2H_3O_2$.

1 part of $BaCrO_4$ is soluble in 1986 parts of 10% $HC_2H_3O_2$.—Schweitzer, by Fresenius, *Z. anal. Chem.*, *29*, 414.

$BaCrO_4$ is practically insoluble in 4N $HC_2H_3O_2$ at 100°.—Test experiments by the authors.

1 part of $SrCrO_4$ is soluble in 63.7 parts of 1% $HC_2H_3O_2$.—Fresenius.

$SrCrO_4$ is readily soluble in 4N $HC_2H_3O_2$ at 100.—Test experiments by the authors.

$CaCrO_4$ is very easily soluble in warm 4N $HC_2H_3O_2$.

Considerable difficulty was experienced in determining the concentration of acid best adapted to securing the complete separation of barium. The results obtained from a long series of qualitative tests and a number of quantitative determinations prove that the use of 4N $HC_2H_3O_2$ as directed in P. II effects a practically complete separation of Ba from Ca and Sr.

Series IX.—*Effect of the Presence of HCl or HNO_3 on the Separation of Barium.*

The group precipitate must not be dissolved in a strong acid like HCl or HNO_3 as the presence of small quantities of these acids prevents the complete precipitation of Ba as $BaCrO_4$. As the carbonates of the metals of this group are soluble in warm 4N $HC_2H_3O_2$ no difficulty is encountered.

Series X.—*The Separation of Barium from Strontium and Calcium.*

The following experiments were performed in order to ascertain the accuracy with which the separation of variable amounts of Ba from variable amounts of Sr and Ca may be effected.

A solution containing 200 mgm. of Ba (10 cc. 2N $BaCl_2 . 2H_2O$—a saturated solution) was treated according to P. I, II, III, IV, and VI. Perfect blanks were obtained in the tests for Sr and Ca.

A solution containing 3 mgm. of Ba as $BaCl_2$, 500 mgm. of Sr as $SrCl_2$, and 200 mgm. of Ca as $CaCl_2$ was diluted to 10 cc. and treated according to P. I, II, and III. This experiment was repeated several times. Although it was possible to confirm the Ba in each experiment by the flame test, the attempts to reprecipitate and confirm it as $BaSO_4$ were not always successful.

The accuracy with which Ba may be separated from Sr (the only metal likely to interfere with the test) by the use of the reagent K_2CrO_4 is indicated by the work of H. Caron and D. Raquet, *Bull. soc. chim., 3-4,* 483-93. The effects of different reagents were studied with respect to their accuracy in detecting and removing Ba from Sr salts. The results are best shown by the following table.

Reagents	Parts Ba which may be detected	Parts Ba which may be detected in proportion to the amt. of Sr present
H_2SiF_6.......	1/2,500	1/15
$SrSO_4$	1/30,000	1/50
*$K_2Cr_2O_7$	1/100,000	1/150
*K_2CrO_4	1/2,500,000	1/15000

Series XI.—*The Solubility of Strontium Chromate and Calcium Chromate in Water and in Mixtures of Water and Alcohol.*

For the solubility of $SrCrO_4$, and $CaCrO_4$ in H_2O, see the preceding series of test experiments.

100 gms. of ethyl alcohol (29%) at 15° dissolves 0.0132 gm. of $SrCrO_4$;

100 gms. of ethyl alcohol (53%) at 15° dissolves 0.002 gm. of $SrCrO_4$;

100 cc. of ethyl alcohol (29%) at 15° dissolves 1.206 gm. of $CaCrO_4$;

100 cc. of ethyl alcohol (53%) at 15° dissolves 0.88 gm. of $CaCrO_4$.—Fresenius, *Z. anal. Chem., 30*, 672 (1891).

According to Mylius and Wrochem.—*Wiss. Abh. p. t. Reichsanstalt, 3*, 462 (1900) (*cf.* Seidell, *Solubilities*, pg. 90)—the solubility of $CaCrO_4$ decreases with rising temperature; on the other hand, the solubility of $SrCrO_4$ increases with rising temperature. Therefore, the separation is most satisfactorily accomplished at the usual temperature of the laboratory. W. Fresenius and Rupert, however, suggest 70° as the optimum temperature at which to conduct the separation.

Series XII.—*The Separation of Strontium and Calcium as Chromates by a Mixture of Water and Alcohol.*

W. Fresenius and Rupert were probably the first investigators to suggest this method as of possible use in qualitative analysis. Caron and Raquet, *Bull. soc. chim*, (3), *35*, 1060-1070 (1906), have also suggested a similar method. Although the principle of the method proposed in this paper is very similar to that of the preceding writers, the procedure is quite different.

After a careful examination of the tables relating to the solubility of the chromates of Sr and Ca in mixtures of water and alcohol, a series of test experiments were undertaken in the effort to ascertain the volume of alcohol to be added to the filtrate from the Ba separation in order to precipitate Sr alone. The results of these tests showed that the addition of an equal volume of ethyl alcohol (95%) to the filtrate previously made slightly alkaline effected a practically complete precipitation of Sr, but did not throw $CaCrO_4$ or K_2CrO_4 out of solution.

Series XIII.—*The Precipitation of Strontium as Strontium Chromate. The Delicacy of the Test.*

A solution containing 0.003 gm. of Sr (0.70 cc. N/10 $SrCl_2$. $6H_2O$) was diluted to 10 cc. and tested according to P. I, II, IV, and V. A comparatively heavy, yellow, precipitate was obtained and identified as $SrCrO_4$.

Series XIV.—*The Completeness of the Separation of Strontium from Barium and from Calcium.*

A solution containing 900 mgm. of Sr (10.26 cc. 2N $SrCl_2.6H_2O$—a saturated solution) was tested for Ba and Ca according to the procedures recommended in this paper. A perfect blank was obtained for Ba; but a slight turbidity appeared in the test for Ca. It was impossible, however, to confirm the Ca by the use of H_2SO_4.

The previous experiment was repeated several times with similar results.

A solution containing 800 mgm. of Sr when tested as in the preceding cases, gave perfect blanks for both Ba and Ca.

The conclusions drawn from this series of experiments are as follows: (a) The presence of a large concentration of Sr ions does not interfere with the tests for Ba and Ca. (b) A slight turbidity in the case of the test for Ca ought never to be confused with the white, readily-forming precipitate of $CaSO_4$. Moreover, the confirmatory test for Ca as $CaSO_4$ eliminates the likelihood of the Ca test being interfered with by Sr ions.

Series XV.—*The Precipitation of Calcium as Calcium Oxalate and Its Confirmation as Calcium Sulphate. The Delicacy of the Test.*

Calcium oxalate, $Ca(COO)_2$ H_2O, is very difficultly soluble in H_2O, but readily soluble in a mixture of one volume of concentrated H_2SO_4 and three volumes of H_2O. The Ca may be precipitated almost quantitatively from the acid solution by the addition of two or three volumes of alcohol.

According to Richards, McCaffrey, and Bisbee—*Z. anorg. Chem.*, *28*, 85 (1901) (*cf.* Seidell, *Solubilities*, 95), 100 cc. of H_2O at 95° dissolve 0.0014 gm. of CaC_2O_4.

It was found that the precipitation of Ca was more accurate and rapid when the precipitant, 1N $(NH_4)_2C_2O_2$, is added to a hot solution than when it is added to a cold solution. Furthermore, the precipitate is in a better condition for rapid filtration. If Ca is present in a solution, the precipitate usually forms at once.

The accuracy of the proposed method was determined by testing a solution containing 0.003 gm. of Ca (1.50 cc. N/10 $CaCl_2$. H_2O) according to P. I, II, IV, and VI. The precipitate which formed *at once* was heavy and easily confirmed by the use of H_2SO_4 and alcohol.

Series XVI.—*The Completeness of the Separation of Calcium from Barium and Strontium.*

With a view to ascertaining if a large concentration of Ca ions interferes with the tests for Ba and Sr, a solution containing 800 mgm. of Ca (10 cc. 4N $CaCl_2$. H_2O—practically a saturated solution) was examined according to the procedures adopted. Perfect blanks were obtained for both Ba and Sr.

Series XVII.—*Relative to the Accuracy and General Utility of the Proposed Methods.*

More than 100 students doing work in this laboratory in Qualitative Analysis during the past two years have used the methods proposed in this paper, and apparently have encountered no difficulties in following the procedures. Unknown mixtures particularly difficult of analysis have been given to the students in order to test the accuracy and utility of the methods. The instructor in charge of the work reports an unusually small percentage of failures. This is probably due to the fact that a moderate change in the conditions of precipitation does not greatly alter the accuracy of the methods.

Adopted Procedure and Notes

Procedure II.—The group precipitate (P. I.) consists of $BaCO_3$, $SrCO_3$, and $CaCO_3$. If the precipitate is small, dissolve it on the filter by pouring repeatedly through the filter 10-20 cc. of *hot* 4N $HC_2H_3O_2$, and wash the filter with 5 cc. of water. (If the precipitate is large, transfer it to a beaker, dissolve in the least quantity of hot 4N $HC_2H_3O_2$, and add 5 cc. of water.) Make the solution *slightly* alkaline with NH_4OH, then add 5-6 cc. of 4N $HC_2H_3O_2$. Heat to boiling, add 1N K_2CrO_4 solution (10-15 cc. are usually sufficient), a few drops at a time, until precipitation is complete, shake thoroughly, then boil the mixture for 1 minute. Filter, even though the solution shows no evidence of the presence of a precipitate. Remove the filtrate, and wash the precipitate thoroughly with cold water. A pale yellow precipitate indicates the presence of Ba. For the confirmation of the precipitate, see P. III; for the subsequent treatment of the filtrate, see P. IV.

Notes—1. All the carbonates of this group are soluble in hot 4N acetic acid. In order to effect a complete separation of Ba from Sr and Ca, HCl or HNO_3 must not be used in place of the acetic acid, for only in the presence of the acetate ion or the anion of a similar weak acid is the precipitation of Ba practically complete.

2. Although the acetic acid is added to prevent the precipitation of $SrCrO_4$ a large excess is to be avoided as sufficient $BaCrO_4$ may be dissolved to interfere with the tests for Sr and Ca.

3. It is advisable to precipitate at boiling temperature for two reasons: (a) The separation of Ba is more rapid and complete. (b) The precipitate is thrown down in a form less likely to run through the filter paper. Continued boiling, however, may result in the precipitation of $SrCrO_4$ owing to the volatilization of acetic acid.

4. The addition of the K_2CrO_4 solution, *drop by drop*, prevents the occlusion of Sr and Ca. An excess of the reagent imparts a yellow color to the solution, thereby indicating that the precipitation is complete.

5. The precipitate should be washed thoroughly to remove any traces of Sr or Ca which if allowed to remain might interfere with the flame test for Ba.

Procedure III.—To confirm the presence of Ba, dissolve the K_2CrO_4 precipitate obtained in P. I. in conc. HCl (sp. gr. 1.12). Divide the solution into two unequal portions. To the larger portion, add an equal volume of a saturated solution of $CaSO_4$. A white precipitate, $BaSO_4$, confirms Ba. Evaporate the smaller portion of the HCl solution to a few drops. Dip a clean platinum wire into the concentrated solution and then introduce the wire into a colorless flame. A green flame confirms Ba.

Notes—1. The SO_4 ion combines with the Ba ion to form $BaSO_4$ which is one of the least soluble salts of Ba. One part of this salt requires for its solution 385,000 parts of water. Even in concentrated acids, it is but very slightly soluble.

2. The conc. HCl solution may be tested for Ba by means of the spectroscope. With this instrument, compounds of Ba show numerous yellowish-green lines, one of which is very near to the position of one of the Ca lines, and a less distinct greenish-blue line.

Procedure IV.—The filtrate from P. II contains Sr, Ca, K, CrO_4, H, and $C_2H_3O_2$ ions. Add 5N NH_4OH until the filtrate is *just* alkaline; this point is indicated when the color of the solution changes from a reddish-brown to a yellow,—then add 5 cc. more of the reagent. To the solution add slowly with frequent shaking, an equal volume of 95% ethyl alcohol. Allow the mixture to stand for several minutes, then filter if a precipitate forms. Do not wash the precipitate. Use suction if filtration is slow. For the further identification of the precipitate, follow P. V; for the subsequent treatment of the filtrate, see P. VI.

Notes—1. For a discussion of the separation of Sr and Ca as chromates by a mixture of water and alcohol, see T. E. and References, Series XI, XII, XIII and XIV.

Procedure V.—The yellow precipitate obtained in P. IV indicates the presence of Sr. To confirm it, wash the precipitate *once* with a small quantity of water; transfer it to a small beaker and dissolve in the least quantity of conc. HNO_3. Evaporate the solution to a few drops. Test on a platinum wire in a colorless flame. A transient crimson flame confirms Sr.

Notes—1. The method outlined in P. IV is so reliable that if a precipitate forms on the addition of the alcohol, it seldom needs to be confirmed by the flame test. If desirable, however, it may be further confirmed by use of the spectroscope. Compounds of Sr give several orange and red lines, and a brilliant blue line.

2. For the delicacy of the test for Sr as $SrCrO_4$, see T. E. Series XIII.

Procedure VI.—The filtrate from P. IV contains $CaCrO_4$ and traces of $SrCrO_4$.

To remove any traces of Sr, add 5 cc. of 1N K_2CrO_4 solution, and 10-20 cc. of 95% alcohol; filter, and reject any precipitate.

To the filtrate add twice its volume of water, heat to boiling, and add slowly to the boiling solution 35-40 cc. of 1N $(NH_4)_2C_2O_4$ solution. If Ca is present, a white precipitate usually forms *at once.* Stir the solution and let it stand for several minutes. A white precipitate, CaC_2O_4, indicates Ca. Filter, wash the precipitate, transfer it to a small beaker and dissolve in the least quantity of a mixture of 1 volume of conc. H_2SO_4 (sp. gr. 1.84) and 3 volumes of distilled water. Add to the solution an equal volume of 95% alcohol, then 2-5 cc. more. A white precipitate, $CaSO_4$, confirms Ca.

Notes—1. For a discussion of the tests for Ca, see T. E., Series XV and XVI.

2. The flame and spectroscopic tests for Ca are valuable. Ca compounds color the flame yellowish-red. The spectrum shows a sharp orange line and a blue line.

PART III. SUMMARY

1. Attention has been directed to the well-known facts that the methods which are generally used in qualitative analysis have received but little systematic study, and are in need of revision.

2. A comparison of a large number of methods for the precipitation and analysis of the Calcium Group, as outlined by the respective authors, has been made, and the discrepancies and inaccuracies of the procedure noted.

3. A method has been formulated by which the members of the Calcium Group may be separated, in the presence of magnesium, by means of a "special reagent," from a solution containing all of the metals or acid radicals. The difficulties encountered in securing a complete precipitation of barium, strontium and calcium without precipitating some magnesium have been overcome by a proper regulation of the conditions under which precipitation is effected. By a series of test experiments it has been shown that a quantity as small as .003 gm. of either one of the metals may be readily detected and that a large concentration of Mg ions does not interfere with the tests.

4. In the second part of the paper which deals with the subsequent analysis of the group precipitate, the proposed methods have been shown to be entirely adequate for confirming even lesser amounts, i.e., less than .003 gm. of any of the metals of the group.

5. The accuracy and general utility of the proposed methods have been proven as shown by Series XVII of the Test Experiments.

Authors' Note. Since the completion of this paper the attention of the authors has been called to the work of Curtman and Frankel[1]. In the summary of their work, they state that the test for barium is unreliable because of the failure of the reagent ammonium carbonate to detect as small a quantity as 10 mgms. of the metal in the presence of ammonium salts. They propose to substitute a new method, and announce that they will publish such method in the near future. The authors of this paper would confirm the above in regard to the inaccuracy of the usual methods employed in precipitating the group, but call attention to the fact that by the method set forth in this paper, 2 mgm. of barium can be detected, and 3 mgm. can be confirmed.

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[1] A study of the Factors Influencing the Systematic Qualitative Determination of Barium—Curtman and Frankel, J. Amer. Chem. Soc., *33*, 724 (1911).

THE INFLUENCE OF LEAD ON THE FERROCYANIDE TITRATION OF ZINC

By Victor Lenher and C. C. Meloche
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Of all the volumetric methods for the determination of zinc in ores, the procedure as outlined in the "Modified Waring Method"[1] is by far the most satisfactory for complex ores. The principal service which this method renders is the removal of all of the heavy metals which interfere with the ferrocyanide titration. In many zinc ores, notably those from the Mississippi Valley, the heavy metals which thus interfere are absent, hence the separations called for in this method can be materially simplified.

While it is universally acknowledged that iron must not be present in the ferrocyanide titration for zinc, the influence of lead has been a much mooted question. Beringer[2] gives quantitative data to show that lead gives a higher result. Seaman[3] gives data to show the bad influence of lead. Stone[4] is of the opinion that lead alone need not be separated, but that if lead be present the solution must be quite strongly acid. Miller[5] indicates conditions which allow for the presence of lead.

With this brief resumé of the various statements as to the effect of lead on the ferrocyanide titration for zinc, attention should be directed to the ferrocyanide method for lead itself, as described by its originator Low[6]. In this method the titration of lead acetate is carried out in a solution containing about 2½ per cent free acetic acid. While Low does not in his latest description of the method specifically state that free mineral acids should not be present, yet from the procedure as outlined, namely, solution of lead carbonate in dilute acetic acid, it is inferred

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[1] Jr. Amer. Chem. Soc., *29*, 265 (1907).

[2] Beringer, Text Book of Assaying.

[3] Jr. Amer. Chem. Soc., *29*, 207.

[4] Jr. Amer. Chem. Soc., *17*, 475, 476 (1875).

[5] Miller, Quantitative Analysis for Mining Engineers.

[6] Jr. Amer. Chem. Soc., *15*, 550.

that free mineral acid would not be present. As a matter of fact, our experience with the method seems to show that free mineral acids must be absent in the ferrocyanide titration for lead. In other words, even a very small amount of free nitric or hydrochloric acid prevents the formation of lead ferrocyanide, which would render the method worthless.

Galletti[1], who devised the ferrocyanide titration for zinc, worked in acetic acid solution. He used no indicator to obtain the end-point. Fahlberg[2] later showed the efficiency of the method in hydrochloric acid solution, using uranium nitrate as an outside indicator, which is the method commonly used today.

A number of series of experiments have been made, the conditions being varied as to the character of the liquid titrated.

Lead acetate was titrated with potassium ferrocyanide in the diluted acetic acid solution as recommended by Low. The temperature of titration was 65° and the solution had a volume of 200 cc.

TABLE I

Pb Present gm.	HCl Present per cent	Pb Found gm.	
.1947	none	.1947	
.1947	.0125	.1947	
.1947	.025	.1947	
.1947	.125	.1921	Difference dependent to some extent on temperature
.1947	.125	.1867	
.1947	.25	.0000	
.1947	.75	.0000	

It is apparent that free hydrochloric acid present up to one-eighth of one per cent does not notably affect the lead determination, but when present in quantity as low as one per cent no lead ferrocyanide is precipitated and no lead is indicated.

Precisely the same order of results occurs when a chloride is added to the acetic acid solution.

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[1] Zt. Anal. Chem. *4*, 213.

[2] Ibid., *13*, 379.

TABLE II

Pb Present gm.	NH_4Cl Present gm.	Pb Found gm.
.1947	none	.1947
.1947	.1	.1951
.1947	.5	.1947
.1947	1.0	.1938
.1947	3.0	.035 – .088[1]
.1949	5.0	.0000

It is obvious that the presence of hydrochloric acid or small quantities of chlorides renders worthless the ferrocyanide titration for lead.

In the titration of lead by the ferrocyanide method, a solution of uranium acetate is by far the best indicator. The nitrate is unsuitable, inasmuch as it invariably contains free acid.

Mixtures of varying amounts of zinc and lead acetates were titrated in the presence of different amounts of hydrochloric acid and ammonium chloride.

TABLE III

Acetate solutions of lead and zinc titrated at 70° in a volume of 200 cc. in presence of 10 gms. NH_4Cl and 3 cc. HCl.

Zn Present gm.	Pb Present gm.	Zn Found gm.	Error gm.
.2000	.0000	.2000	....
.2000	.0431	.2010	+.0010
.1500	.0862	.1512	+.0012
.1000	.1292	.1005	+.0005
.0500	.1723	.0498	–.0002
.0000	.1758	.0005	+.0005

TABLE IV

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 gms. NH_4Cl and 6 cc. HCl.

Zinc Present gm.	Lead Present gm.	Zinc Found gm.	Error gm.
.2000	.0000	.2000	....
.2000	.0431	.2000	....
.1500	.0862	.1502	+.0002
.1000	.1292	.1005	+.0005
.0500	.1723	.0498	–.0002
.0000	.1723	.0005	+.0005

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[1] Results differing due to temperature change.

TABLE V

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 gms. NH_4Cl and 12 cc. HCl.

Zn Present gm.	Pb Present gm.	Zn Found gm.	Error gm.
.2000	.0000	.2000	....
.2000	.0431	.2005	+.0005
.1500	.0862	.1506	+.0006
.1000	.1292	.1003	+.0003
.0500	.1723	.0504	+.0004
.0000	.1723	....	....

A number of experiments were next made using solutions containing chlorides only.

TABLE VI

In this group of experiments the amount of hydrochloric acid present was varied. All of the solutions were titrated at 70°, had a volume of 200 cc. and contained 10 gms. NH_4Cl.

Zinc Present gm.	Lead Present gm.	Zinc Found gm.	Free HCl Present per cent	Error gm.
.1000	.1133	.1001	0.0	+.0001
.1000	.1133	.0999	.12	−.0001
.1000	.1133	.1002	.25	+.0002
.1000	.1133	.1002	.75	+.0002
.1000	.1133	.1000	1.00	.0000
.1000	.1133	.1001	1.25	+.0001
.1000	.1133	.0998	1.50	−.0002
.1000	.1133	.1001	2.25	+.0001
.1000	.1133	.1006	3.00	+.0006
.1000	.1133	.1004	6.00	+.0004
.1000	.1133	.0991	12.00	−.0009

With large amounts of free hydrochloric acid present, that is, from twelve to eighteen per cent, it is impossible to obtain a definite endpoint. When no free acid or as little as one-fourth per cent, is present, the true endpoint in the titration is a matter of considerable uncertainty. An apparent endpoint appears, but by continued stirring disappears. This false endpoint is due to the hydrosol form of the colloidal zinc ferrocyanide, which with insufficient free acid goes only slowly into the hydrogel form. The true endpoint is quickly reached with one and one-half per cent of free hydrochloric acid and is distinct up to as much as six per cent free acid.

From Table VI it is apparent in general in the presence of a material amount of free hydrochloric acid that the presence of lead would never be discovered in the ferrocyanide titration for zinc.

In the next experiments successively larger amounts of lead chloride have been added.

TABLE VII

Volume of solution 200 cc. Ten grams of ammonium chloride, and one and a half per cent free hydrochloric acid present. Titrations made at 70°.

Zinc Present gm.	Lead Present gm.	Zinc Found gm.	Error gm.
.1000	.2266	.1002	+.0002
	.3399	.1005	+.0005
	.4532	.1005	+.0005
	.5665	.1007	+.0007
	.6798	.1005	+.0005
	.7931	.1005	+.0005
	.9064	.1005	+.0005
	1.0197	.1010	+.0010
	1.117	.1003	+.0003
	2.234	.1003	+.0003
	3.352	.1005	+.0005
	3.724	.1003	+.0003

In our experience the quantity of ammonium chloride necessary to have present can be anywhere from one to twenty grams in a 200 cc. solution. When excessively large amounts are present, forty grams or more, the endpoint becomes indistinct.

Various indicators have been suggested from time to time to determine the endpoint in the ferrocyanide titration for zinc. Our experiments suggest that a 0.9% ammonium molybdate solution is the most delicate of the various indicators proposed, but that it is not widely applicable. Glacial acetic acid, 5% sodium tungstate, cobalt nitrate, hydrochloroplatinic acid, are fair indicators, but not as delicate as uranium nitrate or ammonium molybdate. Of all the indicators used, the 5% solution of uranium nitrate is very delicate and reliable.

CONCLUSIONS

In the ferrocyanide titration for zinc as commonly carried out, lead is without influence.

The ferrocyanide titration for lead should be carried out in acetic acid solution and the mineral acids must be absent.

In the technical examination of ores for zinc where lead and iron are the only heavy metals present to an appreciable extent, and such is the case with the Wisconsin zinc ores, it is unnecessary to remove the lead for the ferrocyanide titration for zinc. Half-gram samples of the ore can be dissolved in 10 cc. concentrated hydrochloric acid with the addition of a little nitric acid. To the solution after dilution, ammonium hydroxide is added and the ferric hydroxide and insoluble matter are removed by filtration. The precipitate is dissolved in dilute hydrochloric acid and reprecipitation by ammonia is effected, the filtrates being united. The solution should now be acidified with hydrochloric acid and when evaporated somewhat is ready to be titrated.

For titration the solution must be hot, it should have a volume of 200 cc., should contain 6–10 cc. concentrated hydrochloric acid and 10 grams of ammonium chloride. The ferrocyanide solution should be of such strength that 1 cc. = .005 gm. zinc, and the best indicator is a 5% solution of uranium nitrate.

A NEW COLORIMETRIC METHOD FOR TITANIUM

By Victor Lenher and W. G. Crawford

The estimation of titanium is commonly considered by chemists as one of the more troublesome determinations. The methods most widely used exemplify two distinctly different types of chemical action, namely, hydrolysis and colorimetric comparisons, With high percentages of titanium, the hydrolysis of the sulphate is one of the oldest gravimetric methods. The substitution by Gooch[1] and Chatard[2] of acetic acid solution for that of the sulphate affords a solution for hydrolysis which gives a far more satisfactory method of separation and precipitation than the older sulphate method. Baskerville's[3] method of hydrolysis in hydrochloric acid has been repeatedly tried out in this laboratory with titanium-bearing material carrying very low percentages up to pure rutile, and uniformly excellent results have been obtained as compared with the acetate method.

For low percentages of titanium the colorimetric method first proposed by Weller[4] is most generally applicable. The method is based on the yellow color produced when hydrogen peroxide is added to a sulphuric acid solution of titanium. This colorimetric method has found great applicability in the analysis of clays, silicate rocks and material of this general character low in titanium. The sensibility of the color to the presence of fluorides is so pronounced that this bleaching action on a titanium solution containing hydrogen peroxide has been proposed by Steiger[5] as a means of estimating fluorides.

Levy[6], in studying some color reactions of titanic, columbic, tantalic and stannic acids, found that certain organic compounds containing one or more phenol groups gave deep colorations with these acids. He worked in concentrated sulphuric acid solutions and observed that all of the colorations were destroyed by the

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[1] Chemical News, *52*, 55, 68 (1885).
[2] Amer. Chem. Jr., *13*, 106 (1891).
[3] Jr. Amer. Chem. Soc., *16*, 427 (1894).
[4] Berichte, 15, 2593 (1882). See also Fres. Zeit., *9*, 41, and *9*, 330.
[5] Jr. Amer. Chem. Soc., *30*, 219 (1907).
[6] Comptes rendus, *103*, 1075,1195.

addition of a small quantity of water, with the exception of those produced by stannic acid. From the results obtained he suggested a qualitative method for those acids and conversely a method for the detection of certain phenols.

Muller[1] has studied the colorimetric determination of titanium in aqueous solution by means of the color imparted by salicylic acid, and finds the detection of very small amounts of titanium is thus made possible.

In studying the double fluorides of columbium, titanium, tantalum and tungsten with various reagents in concentrated sulphuric acid, Hall and Smith[2] give a number of color reactions for titanium.

TABLE I

Morphine	Crimson
Codeine	No color
Brucine	Light red
Phenol	Brick red
a Naphthol	Green to green grown
B Naphthol	Coffee brown
Thymol	Garnet
Resorcin	Red brown
Hydrochinon	Crimson
Pyrocatechin	Chocolate
Pyrogallol	Dark red brown
Salicylic acid	Deep red
Meta oxybenzoic acid	Chrome yellow
Para oxybenzoic acid	Chrome yellow
Gallic acid	Brick red
Cinchonidine	No color
Apomorphine	Light red brown
Narceine	Brown
Bebeerine	Clear brown
Narcotine	Brown
Chromotropic acid	Deep red

Continuing this line of study a number of other substances have been studied with regard to their behavior with titanium in strong sulphuric acid solution with the following results:

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[1] Jr. Amer. Chem. Soc., *33*, 1506 (1910).
[2] Proc. Am. Phil. Soc., *44*, 196 (1905).

TABLE II

Reagent	Color produced in one minute	Color produced in 24 hours
Codeine	Light amethyst	Darker
Homatropine	Light red	Cherry
Hydrastine	Light pink	No change
Hyoscyamine	Dark brown	No change
Pelletierine	Light yellow	Pink
Physostigmine	Red	No change
Physostigmine salicylate	Rose yellow	No change
Piperine	Brown	Charred
Strophanthine	Light brown	No change
Aspidospermine	Red	No change
Avenin Legumin	Chocolate	No change
Belladonnine	Deep red	Chocolate
Bulbocapnine	No color	Pink
Colchicine	Yellow, then red	Reddish brown
Collidine	Light brown	No change
Cryptopine	Deep purple	Black
Chelidonine	Deep red	Purple
Chlorogenine	Yellow	Light brown
Conessine	Light yellow	Dark yellow
Colchicine	Yellow	No change
Cotarnine	Red	No change
Delphinine	Dark red	Darker
Duboisine	Pink	Light reddish brown
Erythrophleine	Light red	Darker
Ditamine	Pink	Red
Digitalein	Red	Darker
Emetine	Red	Deep red
Hydrocotarnine	Red	Black
Jaborine	Red	Dark red
Jervine	Brown	Dark green
Lepidine	Light yellow	No change
Pelletierine	Light red	No change
Pseudopelletierine	Light yellow	No change
Daturine	No color	Pink

No colors are caused by atropine, caffeine, cinchonidine, pilocarpine, cinconine, cocoaine, quinine, scopolamine, sparteine, arecoline, anagyrine, cocaethyline, cinchonamine, conhydrine, cysisine, gelseminine, ecgonine, gussospernine, hyoscine, choline, lobeline, tritopine, tropine, taxine, laudanosine, lycoctonine, oxyacanthine, oxysparteine, picoline, protopine, papaverine, quebrachine, sabadilline, sabadine, aporetin, either in one minute or on being allowed to stand twenty-four hours.

The colorations produced by many of the substances worked with are so much more intense than the hydrogen peroxide color that a number have been tested to ascertain whether the color is proportional to the amount of titanium present and not affected by an excess of the reagent.

Phenol and titanium in sulphuric acid solution give a deep red color in strong solution and a yellow red in dilute. A series of experiments were carefully carried out with phenol and titanium in concentrated sulphuric acid solution, and although a color developed with as small an amount of titanium dioxide as .00005 gm., in no case was it found possible to get a solution in which the color is proportional to the amount of titanium present.

A similar series of experiments carried out with hydroquinon and titanium in concentrated sulphuric acid showed that while it is possible to detect .0001 gm. of titanium dioxide by this method, hydroquinon is not a satisfactory reagent for the determination of titanium.

Chromotropic acid in concentrated sulphuric acid solution was similarly found to show the presence of .00001 gm. of titanium dioxide, but the color produced is not a function of the amount of titanium present.

Salicylic acid in concentrated sulphuric acid solution will indicate as small a quantity of titanium dioxide as .00001 gm.., but here again the color is not proportional to the amount of titanium present.

A number of alkaloids were likewise tested with titanium in sulphuric solution, and while a number of them showed intense color reactions, none were found in which the color produced is proportional to the amount of titanium present.

Thymol and titanium in concentrated sulphuric acid solution give a deep red coloration if sufficient titanium is present, while in dilute solution a reddish yellow color is developed. The color produced by the addition of a sulphuric acid solution of titanium is proportional to the amount of the latter present and can be made the basis of a colorimetric determination.

Thymol dissolves in concentrated sulphuric acid with a slightly yellow color, which rapidly intensifies as the amount of thymol is increased. This coloration can be avoided if the thymol is first dissolved in a little acetic acid in which thymol is very soluble, or in acetic acid containing ten per cent alcohol. Sulphuric acid can then be added without the formation of any color. The solution of thymol in sulphuric acid thus prepared is fairly stable and if kept out of bright light will not discolor, but if exposed to direct sunlight it will darken in a few hours.

The ratio of thymol to titanium can vary greatly, but it has been found best to have at least .006 gm. of thymol present to every .0001 gm. TiO_2.

Table III indicates results obtained in a Soleil-Duboscq colorimeter.

TABLE III

No.	TiO_2 Present mg.	TiO_2 Found mg.
1	.21	.20
2	.21	.19
3	.31	.30
4	.31	.294
5	.40	.405
6	.40	.37
7	.50	.50
8	.50	.52

Table IV represents results obtained on somewhat larger quantities of titanium with a Kennicott-Sargent colorimeter.

TABLE IV

No.	TiO_2 Present mg.	TiO_2 Found mg.
9	1.	.9
10	1.5	1.5
11	2.1	2.0
12	2.5	2.5

Four previously analyzed samples of bauxite in which the titanium content had been obtained by the Weller method, are compared in Table V with the thymol method. Samples of 0.3 gm. each were fused with potassium bisulphate for a half hour, after which the fusion was taken up in concentrated sulphuric acid.

TABLE V

No.	Weller's Method	Thymol Method	
13	3.3% TiO_2	3.7% TiO_2	3.4% TiO_2
14	1.93	2.2	2.1
15	2.20	2.15	2.28
16	2.97	2.83	2.95

EFFECT OF DILUTION

Levy noted, when water is added to a titanium solution colored by thymol, that the color fades and is essentially destroyed. The following experiments indicate the effect of the dilution of the acid on the apparent percentage of titanium. Five hundred cc. of a standard titanium dioxide solution was prepared with an excess of thymol present. Aliquot portions were taken and a known amount of water was added to each portion. These portions were cooled and diluted to 50 cc. by the addition of sulphuric acid, sp. gr. 1.84. These test solutions were compared in turn with a 25 cc. portion of the original solution, diluted to 500 cc. with sulphuric acid, sp. gr. 1.84. The addition of water has apparently no effect on the color until a concentration of 79.4% (sp. gr. 1.725) sulphuric acid has been reached, after which the color fades in a perfectly regular manner. It has been necessary in making this dilution study to cool the solutions to room temperature after the dilution of the acid, inasmuch as a warm solution is much lighter in color than one of the same strength a few degrees cooler.

TABLE VI

%H_2SO_4	Actual TiO_2 Present mg.	Apparent TiO_2 Present mg.	Apparent TiO_2 Present per cent
90.05	.625	.625	100
87.60	.625	.625	100
85.70	.625	.625	100
83.32	.625	.625	100
82.00	.625	.625	100
80.68	.625	.625	100

TABLE VI—*Concluded*

%H_2SO_4	Actual TiO_2 Present mg.	Apparent TiO_2 Present mg.	Apparent TiO_2 Present per cent
79.36	.625	.625	100
77.60	.625	.575	92
76.30	.625	.537	86
74.51	.625	.500	80
73.23	.625	.462	74
71.99	.625	.412	66
70.74	.625	.375	60
68.97	.625	.337	54
67.59	.625	.300	48

EFFECT OF TEMPERATURE

The fact that a titanium solution colored by thymol loses some of its color when heated and that on cooling the color returns, has been repeatedly observed. A series of experiments was therefore conducted to determine at how high a temperature such a solution could be heated without change of color. In each case the solution was heated to the temperature noted, after which it was cooled and compared with a sample of the original solution. It has been found that the color is not permanently changed until the solution is heated to 100°.

TABLE VII

No.	Room Temperature	Temperature of Heating	TiO_2 Present mg.	Apparent TiO_2 after Heating mg.	Apparent TiO_2 per cent
1	20°	30°	.625	.625	100
2	20	40	.625	.625	100
3	20	50	.625	.625	100
4	20	60	.625	.625	100
5	20	80	.625	.625	100
6	20	90	.625	.625	100
7	20	100	.625	.425	68
8	20	110	.625	.250	40
9	20	120	.625	.150	24

EFFECT OF FLUORINE

Inasmuch as fluorides exhibit the well known bleaching effect on the yellow color produced by the addition of hydrogen peroxide to a titanium solution, the action of hydrofluoric acid on the thymol titanium color was studied. Fluorides or hydrofluoric acid bleach the color. In this connection it should be noted that from the preliminary treatment of a titanium-bearing material in order to bring it into concentrated sulphuric acid solution, it is practically impossible for fluorides to be present.

TABLE VIII

No.	TiO_2 Present mg.	Fl_2 Present mg.	Apparent TiO_2 mg.	Apparent TiO_2 per cent
1	.625	.26	.588	95.6
2	.625	.52	.576	93.7
3	.625	.78	.448	72.2
4	.625	1.04	.388	62.2
5	.625	1.30	.338	54.1
6	.625	1.52	.301	48.9
7	.625	1.82	.276	44.2
8	.625	2.08	.250	40.1
9	.625	2.34	.213	34.1
10	.625	2.60	.187	30.0
11	.625	2.86	.150	24.0

EFFECT OF CHLORIDES, PHOSPHATES, TIN AND TUNGSTEN.

Solutions of various strengths containing hydrochloric acid, phosphoric acid and tin were systematically added to a thymol sulphuric acid solution and are apparently without any effect on the coloration. Tungstic acid, on the other hand, markedly affects the color in direct ration to the amount of tungsten present.

TABLE IX

No.	TiO_2 Present mg.	WO_3 Present mg.	Apparent TiO_2 mg.
1	2.2	.47	2.48
2	2.2	.94	2.75
3	2.2	1.41	3.01
4	2.2	1.88	3.250
5	2.2	2.35	3.50

Of the various organic bodies which produce distinctive colorations with titanium in concentrated sulphuric acid, thymol, phenol, hydroquinon, salicylic acid and chromotropic acid, are the most distinctive. For various reasons thymol produces the most satisfactory coloration which can be used for the detection and estimation of small amounts of titanium. The intensity of the coloration produced by thymol in sulphuric acid with titanium is at least twenty-five times as great as that produced in the hydrogen peroxide method; hence the method is applicable to smaller amounts of titanium than can be determined by the Weller method.

The method possesses certain advantages in simplicity and small number of operations. The actual time for the fusion, dilution and comparison is short. With a standard prepared the actual working time of the method is less than an hour. The only process requiring time is for the sulphuric acid to cool to room temperature and this can be facilitated by use of a constant temperature bath.

The sample of the titanium-bearing substance is usually most conveniently brought into solution by fusing with potassium acid sulphate. The fusion can be taken up in concentrated sulphuric acid, and after adding an excess of thymol in sulphuric acid, diluted to a definite volume and the color compared in a colorimeter with a standard titanium solution.

REFRACTOMETRY

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The first extensive use of the refractive index in analytical chemistry was in the examination of fats and oils and with these substances it was employed as a means of establishing purity, and in their mixtures, in connection with other constants, for the purpose of determining the composition of the sample. The instruments employed for this purpose were the oleo refractometer of Amagat and Jean, the Abbé and the Zeiss butyro refractometer.

Of recent years the principles of refractometry have been applied to other analytical purposes such as the quantitative determination of fat in milk, measuring the concentration of aqueous solutions, the determination of ethyl and methyl alcohol in mixtures containing both substances, the determination of alcohol and extract in beer, etc., by means of specific gravity and refraction of the sample, the detection of added water in milk from the refraction of the milk serum, the examination of blood and urine as well as for many other purposes.

The instruments most used are the Abbé which gives value of n_D from 1.3 to 1.7 to the fourth decimal; the Pulfrich, reading to the fifth decimal of ND and the Zeiss Butyro, Wollney milk fat and Zeiss immersion refractometers, the three latter possessing centesimal scales the average of the 0.1 of a scale division being .000037 in the immersion, .000068 in the butyro and .000089 in the milk fat refractometer. The centesimal scales are not proportioned to the values of the scale reading and for this reason the scale readings must be transferred into values of n for certain calculations; this is shown in the following table giving the value of n_D corresponding to each tenth division of the three instruments.

Scale Reading	Immersion Refractometer		Butyro Refractometer		Milk Fat Refractometer	
	^{n}D	Difference 10°	^{n}D	Difference 10°	^{n}D	Difference 10°
0	1.32736		1.4220		1.3332	
10	1.33126	.00390	1.4300	.0080	1.3436	0.0104
20	1.33513	.00387	1.4377	.0077	1.3537	0.0101
30	1.33896	.00373	1.4452	.0075	1.3636	0.0099
40	1.34275	.00379	1.4524	.0072	1.3730	0.0094
50	1.34650	.00375	1.4593	.0069	1.3821	0.0091
60	1.35021	.00371	1.4659	.0066	1.3909	0.0089
70	1.35388	.00367	1.4723	.0064	1.3993	0.0084
80	1.35750	.00362	1.4783	.0060	1.4072	0.0079
90	1.36109	.00359	1.4840	.0057	1.4148	0.0076
100	1.36464	.00355	1.4895	.0055	1.4220	0.0072

The refractive index like the specific gravity varies with the temperature, for with rising temperature the refraction and gravity both decrease. As a result of this phenomenon there have been numerous attempts made to devise an expression which will be independent of the temperature; of these expressions called specific refraction, those of Gladstone and Dale $\frac{n-1}{d}=K$ and of Lorenz and Lorentz $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}=K$ are the most extensively employed, particularly the latter. In these formulæ n = the refractive index, d the specific gravity and k is a constant. This holds true with the Lorenz and Lorentz formula for most aqueous solutions provided that the refraction and gravity are taken at the same temperature (in the case of the gravity it should be compared with water at 4°) and in many instances it is independent of the concentration. With many substances, however, such as certain organic liquids, and with glasses this relation does not hold.

The Lorenz and Lorentz formula has been modified as follows: $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$ where M = the molecular weight of the substance in question. This formula is extensively used in theoretical studies of solutions, for example Baxter in making studies upon solutions of halogen salts has determined the molecular refractions of the chlorides, bromides and iodides of potassium, sodium and lithium in various concentrations. In this work Baxter[1] states that "at present there is no wholly satisfactory general expression connecting change of index of refraction with changing density."

K. G. Falk[2] has devised the following expressions which he has applied to organic liquids, $\frac{n}{a}+\frac{t}{b}=1$ $\frac{d}{a^1}+\frac{t}{b^1}=1$ in which n, t and d represent the refraction, temperature, and gravity respectively and a, b, a^1 and b^1 are constants for any one substance within certain limits of temperature. Falk has substituted these values in the various formulæ for specific refraction, as a result of which he has reached the following conclusions: $\frac{n^2-1}{d}$ always decreases with increasing temperature, $\frac{N-1}{d}$ or $\frac{n_2^2-1}{n^2+2}$. $\frac{1}{d}$ may increase, decrease, or be constant with increasing temperature. Pulfrich has devised an expression for mixtures as follows: $\frac{N-Nv}{N}=\frac{\alpha\,(d-dv)}{d}$ where α = a constant, d = the density, $N = n-1$ for the mixture and Nv and dv the corresponding values calculated for the pure substances by the rule of mixtures (assuming no contraction). This formula has been elaborated by Hess[3] as follows: $\frac{N-Nv}{N}=qC$ in which C = the contraction and $q=\alpha, \beta$, or γ according as $N=n-1$, $\frac{n^2-1}{n^2+2}$ or n^2-1. $\frac{d-dv}{d}=C$, for $dv=d(1-C)$

For solutions B. Walter[4] and later Robertson[5] evolved the equation $\frac{n-n^1}{c}=A$ in which n = the refractive index of the solution, n^1 that of the solvent, c = the concentration and A = a constant. If n and n^1 are taken at the same temperature this equation holds for all temperatures. It has been shown by Chenéveau[6] that the equation is incorrect for some substances. The following examples

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[1] J. Am. Chem. Soc. 1911 *33*, 901.
[2] J. Am. Chem. Soc. 1909 *31*, 806-821.
[3] Hess. Wiener Berichte, 115 II a, 459-79, 1906.
[4] Wied. Ann. 1889 *38*, 107.
[5] J. Phys. Chem. 1909 *13*, 469.
[6] Ann. Chem. Phys. 1907 *12*, 384.

calculated for barium chloride solutions and sulphuric acid solutions from Wagner's table show in one case only a slight variation in the value of *A* and in the other a considerable variation.

Barium Chloride		Sulphuric Acid	
C. Grams per 100 cc.	$\frac{n-n^1}{c}$	C. Grams per 100 cc.	$\frac{n-n^1}{c}$
1.02	0.00128	1.022	0.00128
4.01	0.00127	5.030	0.00118
5.01	0.00126	10.018	0.00114
6.02	0.00125	15.022	0.00112
7.01	0.00124	20.033	0.00109
12.02	0.00123	25.032	0.00107
28.2	0.00122	29.496	0.00105

Robertson found the values of *A* very constant for protein solutions and the writer has found a similar condition in alcoholic camphor solutions, for instance for solutions of casein in dilute alkali the value of *A* is 0.00152, for concentrations above 0.5% and for camphor the value of *A* is 0.00106 for 5 grams per 100 cc., 0.00105 for 10 grams per 100 cc. and 0.00104 for 25 grams per 100 cc.

All these formulæ are of more or less value to one who is preparing a table or series of figures for use in analytical chemistry. A number of such tables have been prepared for this purpose and they will be described below or referred to in the bibliography.

In the examination of fats and oils we must consider the differences between the refractions of the oil in question and that of the possible adulterant, and where this is great enough the figure is of value. In the case of butter fat, the refraction is as valuable as the Reichert-Meissl number. Beef oleo refracts about five scale divisions higher than butter, consequently the presence of 6% of oleo would raise the refraction about 0.3 of a division, but oleomargarine seldom contains as little oleo as in this instance, and as a rule the amount present is more than 75%. One person can make five or six times as many refractions of butter fat in an hour as he can determine Reichert-Meissl numbers in a day. In the case of olive oil the usual adulterants are cottonseed, sesame, rape seed, corn, peanut, poppyseed or sunflower oil, and with the exception of peanut oil, all these oils give a scale reading of from 6 to 9 division on the scale of the butyro refractometer higher than that of olive oil. An adulteration of 5% is clearly indicated by the refraction in these cases and the only possible oil which could be present and result in giving a normal refraction is peanut oil if present in small quantities. If peanut oil is present in small amounts the iodine number and other constants are as liable to be normal for olive oil as the refractive index. Of course, the index of refraction should not be relied upon exclusively in the examination of oils any more than the iodine number or the saponification number, for it is possible to mix oils in such a manner that the mixed oils will refract like the oil to be imitated, but if a sample of alleged olive oil is found to contain cottonseed oil the refraction is as good as the iodine number to determine the quantities present, and if the refraction of the oil in question is wrong, the oil is impure.

The refractive index of the fatty acids has been and is determined in the analysis of fats, oils, and soaps. W. B. Smith[1] has shown that the relation between the refractive index of the oil and that of the fatty acids depends upon the percentage of acid in the glyceride, being nearly independent of the total refraction and the iodine value. The refractive index of the insoluble fatty acids of liquid oils should be close to the refractive index of the oils multiplied by 0.9938; the factor in the case of solid fats lies between 0.992 and 0.994 depending upon the composition of the fat.

In the examination of turpentine the index of refraction is very valuable. It is usual to submit the sample to fractional distillation and, after taking the specific gravity or refraction of the different fractions, to plot the figures obtained using the percent distilled as ordinates, and the constants of the fractions as abscissæ. Here it is much easier to obtain the refractive index by means of the Abbé refractometer, than the specific gravity. A further application of refraction to turpentine analysis is in the polymerization test as first shown by McCandless[2] and later by Herzfeld-Bohme[3] modified by Donk and Veitch.[4] The turpentine (5 cc.) is polymerized in a Babcock milk bottle with 20 cc. of 38N sulphuric acid. After no further heating of the bottle occurs it is warmed

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[1] J. Ind. & Eng. Chem. 1912 *4*, 36.
[2] J. Am. Chem. Soc. 1904 *26*, 981.
[3] Chem. Ztg. 1906 *30*, 631.
[4] Bur. Chem. U. S. D. A. Cir. 85.

to 60°, concentrated acid is added to nearly fill the neck and the bottle centrifuged to drive the unpolymerized oil into the calibrated neck where the volume is read. Some of the oil is then placed between the prisms of the Abbé refractometer and if the refraction is less than 1.51 we know that some foreign oil is present. Inasmuch as the quantity of oil may be only a few drops, no other quantitative figure could be obtained. The following chart shows the constants of a pure and adulterated sample of turpentine from which it is evident that the refraction figures are sufficient to establish the purity or impurity of the sample in question.

MIXTURES OF ORGANIC LIQUIDS

Beythien and Hennicke propose to use the refraction of a liquid as a means of determining the amount of the constituents of mixtures of two organic liquids, such as mixtures containing acetone, benzol, carbon, tetrachloride, etc., where no other method is available. The formula $x=\frac{100\,(n-n_2)}{n_1-n_2}$ is given where $x=$ the approximate percentage of the more highly refractive substance, $n=$ the observed refraction, $n_1=$ the refraction of the more highly refractive substance, and n_2 the refraction of the lower refracting substance. This formula does not take into consideration the possible contraction or expansion of the liquid due to the mixture, and two control mixtures are prepared one (A), having a greater percentage $=a$ and the other (B), having a less percentage $=b$ of the higher refracting substance. The refraction of these solutions is determined, and by substituting in the equation

$$x=b\frac{+(a-b)\,(n-n_b)}{n_a-n_b}$$

the exact value of x is determined. For mixtures of three components one must be determined by some other method and the others as above.

In the quantitative determination of alcohol the refractometer can be used to demonstrate the purity of the alcohol[1] and also to

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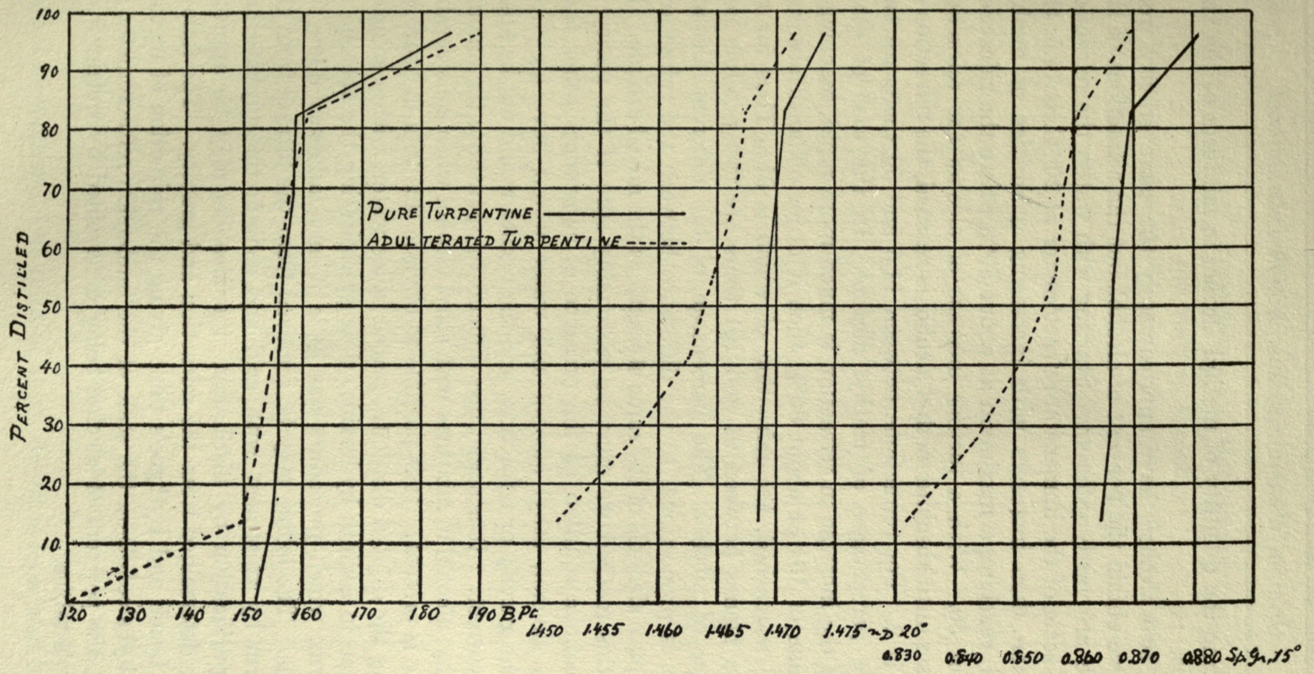
[1] This has proven of value in the prosecution of liquor cases in the Mass. courts. It is a well known principle of criminal law that the government must prove its case beyond a reasonable doubt. A chemist testifying for a defendant said that a determination of the specific gravity of a distillate from a sample of beer was insufficient to determine the percentage of alcohol, because it might have been wood alcohol. The determination of both the gravity and refraction of such distillates proves beyond doubt the percentage and kind of alcohol in the sample.



Physical properties of a sample of turpentine three years old subjected to fractional distillation before and after mixing with fifteen per cent of petroleum b. pt. 120-170.

determine the quantity of methyl alcohol in mixtures of the two alcohols.

The two alcohols have approximately the same gravity from which we obtain the per cent of alcohol, but the refractions of the alcohols are vastly different. Starting with water, the refraction on the scale of the immersion refractometer at 20° C. is 14.5; the refraction then increases with increasing quantities of methyl alcohol, reaching a maximum at about 50% where the refraction is about 50. With a further increase of alcohol the refraction decreases until absolute methyl alcohol is reached, the refraction of which is 2. For refractions between 14.5 and 50 there are two possible percentages of methyl alcohol. In the case of ethyl alcohol the increase in refraction is much more rapid, reaching a maximum of 101 at about 85%, then it drops off until absolute alcohol is reached, the refraction of which is 91. Thus for refraction figures between 91 and 101 there are two possible percentages of alcohol. The percentage of the different alcohols present is proportional to the difference between the refractions of the pure alcohols of the same strength as the mixed sample. In using this method we must be reasonably sure of the purity of the alcoholic solution as the presence of substances other than methyl alcohol, ethyl alcohol and water would have an effect upon the gravity or refraction, and the results would not be absolutely correct. It is sometimes difficult to quantitate the amount of methyl alcohol in mixtures with ethyl alcohol when considerable acetone is present. It is possible to obviate this to a measure by treating the diluted distillate, placed in ice water, with a solution of iodine in sodium hydroxide, thus precipitating the acetone as iodoform, which procedure has little if any influence upon the alcohols. The iodine may be removed from the filtrate from the iodoform by treatment with acid and sodium thiosulphate and after purification by distillation the alcohols may be approximately determined from the refraction and gravity. The following is Leach and Lythgoe's table giving the refraction of methyl and ethyl alcohols on the scale of the immersion refractometer at 20° C, the per cent of alcohol being determined by weight from Hehner's tables.

Scale Readings on Zeiss Immersion Refractometer at 20° C. Corresponding to Each Per Cent by Weight of Ethyl and Methyl Alcohols

Per cent alcohol by weight	Scale Readings		Per cent alcohol by weight	Scale Readings		Per cent alcohol by weight	Scale Readings		Per cent alcohol by weight	Scale Readings	
	Methyl alcohol	Ethyl alcohol		Methyl alcohol	Ethyl alcohol		Methyl alcohol	Ethyl alcohol		Methyl alcohol	Ethyl alcohol
0	14.5	14.5	30	32.8	69.0	60	37.9	96.2	90	16.1	98.6
1	14.8	16.0	31	33.5	70.4	61	37.5	96.7	91	14.9	98.3
2	15.4	17.6	32	34.1	71.7	62	37.0	97.1	92	13.7	97.8
3	16.0	19.1	33	34.7	73.1	63	36.5	97.5	93	12.4	97.2
4	16.6	20.7	34	35.2	74.4	64	36.0	98.0	94	11.0	96.4
5	17.2	22.3	35	35.8	75.8	65	35.5	98.3	95	9.6	95.7
6	17.8	24.1	36	36.3	76.9	66	35.0	98.7	96	8.2	94.9
7	18.4	25.9	37	36.8	78.0	67	34.5	99.1	97	6.7	94.0
8	19.0	27.8	38	37.3	79.1	68	34.0	99.4	98	5.1	93.0
9	19.6	29.6	39	37.7	80.2	69	33.5	99.7	99	3.5	92.0
10	20.2	31.4	40	38.1	81.3	70	33.0	100.0	100	2.0	91.0
11	20.8	33.2	41	38.4	82.3	71	32.3	100.2	..	..	..
12	21.4	35.0	42	38.8	83.3	72	31.7	100.4	..	..	..
13	22.0	36.9	43	39.2	84.2	73	31.1	100.6	..	..	..
14	22.6	38.7	44	39.3	85.2	74	30.4	100.8	..	..	..
15	23.2	40.5	45	39.4	86.2	75	29.7	101.0	..	..	..
16	23.9	42.5	46	39.5	87.0	76	29.0	101.0	..	..	..
17	24.5	44.5	47	39.6	87.8	77	28.3	100.9	..	..	..
18	25.2	46.5	48	39.7	88.7	78	27.6	100.9	..	..	..
19	25.8	48.5	49	39.8	89.5	79	26.8	100.8	..	..	..
20	26.5	50.5	50	39.8	90.3	80	26.0	100.7	..	..	..
21	27.1	52.4	51	39.7	91.1	81	25.1	100.6	..	..	..
22	27.8	54.3	52	39.6	91.8	82	24.3	100.5	..	..	..
23	28.4	56.3	53	39.6	92.4	83	23.6	100.4	..	..	..
24	29.1	58.2	54	39.5	93.0	84	22.8	100.3	..	..	..
25	29.7	60.1	55	39.4	93.6	85	21.8	100.1	..	..	..
26	30.3	61.9	56	39.2	94.1	86	20.8	99.8	..	..	..
27	30.9	63.7	57	39.0	94.7	87	19.7	99.5	..	..	..
28	31.6	65.5	58	38.6	95.2	88	18.6	99.2	..	..	..
29	32.2	67.2	59	38.3	95.7	89	17.3	98.9	..	..	..

The refractometer is useful in the examination of drugs as a means of corroborating other methods of analysis and as a qualitative test for the presence of wood alcohol. In the examination of spirit of peppermint or spirit of anise, the oil is separated by diluting the sample with water or some aqueous solutions in a calibrated tube, and its volume measured. We may remove the separated oil, dry it with calcium chloride and take its refraction together with the refraction of the tincture. If we know the per cent of alcohol present, the per cent of oil may be calculated from the refraction figures by the method previously described. It is not always necessary to know the per cent of alcohol to corroborate the other findings for if any quantity of oil is present we know the alcohol must be over 90% in strength in order to keep the oil in solution, and the refraction should correspond to that of an alcoholic solution containing the percentage of oil found by the other method.

In making examination of spirit of camphor by means of the polariscope there is a possibility that synthetic camphor may be present which would not influence polarized light, but would influence the refraction, thereby creating a discrepancy which would necessitate further work. The following table shows the value of the refraction in making a qualitative test for methyl alcohol in spirit of anise and spirit of camphor.

Anise oil 10 cc.	Ethyl Alcohol 95% 90 cc.	n_D 20° 1.3822
Anise oil 4 cc.	Ethyl Alcohol 95% 95 cc.	n_D 20° 1.3713
Anise oil 10 cc.	Ethyl Alcohol 80% 90 cc.	n_D 20° 1.3831
Anise oil 10 cc.	Methyl Alcohol 95% 90 cc.	n_D 20° 1.3525
Anise oil 10 cc.	Methyl Alcohol 95% 45 cc. Ethyl Alcohol 95% 45 cc.	n_D 20° 1.3673

Camphor 10 grams	Ethyl Alcohol 95%	to make 100 cc.	n_D 1.3747
Camphor 10 grams	Ethyl Alcohol 80%	to make 100 cc.	n_D 1.3755
Camphor 10 grams	Methyl Alcohol 95%	to make 100 cc.	n_D 1.3439
Camphor 10 grams	Methyl Alcohol 95% Ethyl Alcohol 95%	Equal quantities to make 100 cc.	n_D 1.3593

A perusal of the above shows that the presence of 1% of methyl alcohol in the alcohol present will lower the refraction by approximately 0.0003 and by dilution with water to 80% alcoholic strength (the highest refracting alcohol) the refraction is increased by 0.0009, therefore from the determination of the camphor by means of the polariscope and taking its refraction, or in the case of spirit of anise by determining the anise oil and the refraction of the spirit, the presence of 5% of methyl alcohol is clearly indicated by the reduction of the refraction below that which is expected. As a rule it is not possible to prepare for commercial use tinctures of essential oils with alcohol as weak as 80% on account of the cloudiness produced, and therefore the refraction of such tinctures would be liable to be normal in most instances. With camphor, however, tinctures can be and are commercially made with 80% alcohol, and such tinctures could be adulterated with 3% of methyl alcohol and escape detection by the determination of only the refraction and polarization of the sample. This slight amount of adulteration could be possible only by accident.

The immersion refractometer is primarily used in the examination of aqueous solutions, and for this purpose Bernard Wagner has published 79 tables giving readings on the scale of the instrument corresponding to the concentration of various aqueous solutions, expressed as grams per 100 cc. at 17.5° C. The accuracy of the determinations may best be illustrated by the following table:

Substance	Amount causing variation of 0.1 scale division mg. per 100 cc.	Highest concentration measurable on instrument Grams per 100 cc.	Max. error at highest concentration	Max. error at scale division 37⅓ max. concentration
HCl	17	15.55	0.11%	0.46%
H_2SO_4	35	32.21	0.11%	0.48%
HNO_3	31	28.54	0.11%	0.45%
KCl	30	27.89	0.11%	0.46%
$BaCl_2$	24	21.63	0.11%	0.48%
$CaCl_2$	31	28.34	0.11%	0.46%

As each 1/10 of a scale division is equivalent to a definite weight of substance per 100 cc. of solution it is evident that the percentage error must be greater with the lower concentrations and will decrease as the concentration rises. The maximum error in concentrations of approximately normal solutions is about four to five tenths of one per cent. This becomes less as the concentration increases and at the maximum concentration within the scale limits of the instruments it is reduced to about one-tenth of one per cent. Bernard Wagner[1] has computed tables showing the refractive indices on the scale of the immersion refractometer of seventy-six different substances in aqueous solutions for all concentrations within the range of the instrument. He has also devised methods for the determination of reducing sugars, calcium,

[1] Bernard Wagner. Dissertation Jena 1903.

Bernard Wagner. Tabellen zum Eintauchrefractometer. Sonderhausen 1907.

magnesium, and phosphates, using the refractometer as a means of determining the weight of the final product.

Sodium chloride and potassium chloride solutions possess different refracting power at the same concentration. In concentrations of 20 grams per 100 cc. NaCl gives a scale reading of 99.5 and KCl of the same concentration 80.75, the difference being 18.75 scale divisions. Upon this difference Wagner has based a method of estimating the per cent of KCl and NaCl in mixtures. The mixed chlorides are weighed, sufficient water is added to produce a solution equivalent to 20 grams per 100 cc., the refraction of which is then determined, and the percentage of sodium and potassium chloride is calculated or is obtained from the table; 0.1 scale division equals 0.53% of either constituent. This of course is not as accurate as the separation, but may be used as a check before precipitating with platinum if greater accuracy is desired.

The immersion refractometer may be used to determine the concentration of sugar solutions up to 23% (Wagner's tables) but for sugar solutions such as syrup, maple syrup, molasses, etc., with concentrations of 60%-65% the Abbé refractometer is to be used, employing the table of Geerlig (Inter. Sugar Journal, *10* pp., 69–70).

In sugar solutions of high purity such as cane table syrup, the refractometric method of determining solids is as accurate as that of drying at 100°, and of course can be done more conveniently and quickly. The following table of A. H. Bryan[1] shows the difference between gravimetric and refractometric methods.

Substance	Number of Samples	Difference between Gravimetric and Refractometric Methods
Maple syrup	13	−1.34 to +0.72
Cane table syrup	10	−0.79 to +0.62
Cane molasses	17	−1.53 to +0.59
Beet molasses	15	−1.83 to −0.07
Honey	24	−2.52 to +0.91
Glucose	2	−0.27 to +0.27

Sugar solutions have a gravity and refraction greater than water, but aqueous solutions of alcohol possess a gravity less, and a re-

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[1] J. Am. Chem. Soc. *28*, 1443, 1908.

fraction greater than the solvent. If we determine the refraction and the gravity of a fermenting solution we find as the fermentation proceeds the gravity is reduced more than the refraction, and for this reason it is possible to determine the alcohol and solids in beer from the specific gravity and refraction. This is accomplished by the circular revolving rule of Ackermann; the rule is rotated until the arrow mark in one scale coincides with the specific gravity of the beer. There are two scales of refraction: the figure coinciding with the refraction found on one scale is the per cent of solids, and on the other scale is the per cent of alcohol. The results obtained are very accurate. Frank-Kamenctzky has devised a slide rule for the determination of alcohol and extract in potato mash based upon a similar principle.

Robertson determines the percentage of casein in milk as follows: 50 cc. of milk are diluted to 250 cc. and 75 cc. N/10 acetic acid slowly added with constant stirring. The precipitate is filtered, washed, allowed to drain one hour, transferred with the filter to a dry beaker and 100 cc. N/10 sodium hydroxide (n_D 20° 1.33444) added. After complete solution it is filtered and the refraction determined by means of a Pulfrich refractometer at 20°. The results are calculated as follows:

$$\text{Grams of casein in 50 cc. milk} = \frac{n - 1.33444}{0.00152},$$ where n = the refractive index of the final solution.

The detection of added water in milk by the refractive index of the milk serum is largely a question dealing with the composition of milk. It depends upon the fact that the most variable constituents of milk are the fat and the casein and by removing these, the serum obtained is of more constant composition than the milk. Villiers and Bertault[1] prepared the serum by boiling one volume of 1% acetic acid with two volumes of milk, cooling, filtering, and they then measured the refraction by means of the oleorefractometer. From the figure so obtained they subtracted one-third of the difference between the refraction values of the dilute acid and distilled water and then multiplied the difference by one and one-half, thus giving the value for undiluted milk.

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[1] Bull. Soc. Chim. 1898 *19*, 305.

Matthes and Muller[1] first used the immersion refractometer for this purpose, preparing the serum by allowing the milk to sour spontaneously.

Leach and Lythgoe[2] prepared the serum by heating the milk with two per cent of twenty-five per cent acetic acid and determined the refraction by means of the immersion refractometer.

Ackermann[3] prepared the serum by heating 30 cc. of the milk with 0.25 cc. of calcium chloride solution (sp. gr. 1.1375) in a boiling water bath for fifteen minutes, cooling and decanting the liquid, the refraction of which was then determined.

Baier and Neumann[4] use a citric acid and asaprol solution, which is mixed cold with an equal volume of the milk and the refraction of the clear filtered serum obtained by means of the milk fat refractometer.

Lythgoe[5] mixes one volume of copper sulphate solution (72.5 grams per liter) with four volumes of milk and determines the refraction of the filtrate by means of the immersion refractometer.

All of these methods are of value, and all have their disadvantages. If the sample of milk is sour when received, the Ackermann method is the only one applicable, but if the sample is sweet this method is somewhat slow, especially in cold weather. The asaprol citric acid method has been criticized on account of the difficulty of procuring pure asaprol, and the consequent difficulty of making the precipitating solutions of the same concentration. It has been further critized because the serum is diluted by the reagent. This criticism also applies, but in a less degree to the copper method. The calcium chloride and acetic acid methods both require heat and considerable time in the preparation of the serum, while the asaprol and copper sera are prepared quickly at the room temperature.

The refraction of milk serum depends upon its concentration, and if the concentration is known, the refraction or the gravity can be calculated. Weigner and Yakuwa[6] have shown that the value

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[1] Z. Off. Chem. 1903 *9*, 173.
[2] J. Am. Chem. Soc. 1904 *26*, 1195.
[3] Z. Nahr-Genussm. 1907 *13*, 186.
[4] Ibid 1907 *13*, 369.
[5] Report Mass. State Board of Health. 1908-594.
[6] Milchwirtsch. Zentr. 1909 *5*, 473.

of $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ for refractive indices at 17.6° C and specific gravity at 15/15 for the calcium chloride serum is 0.2056, and if *n* and *d* are taken at the same temperature the value is 0.2058. Watering of the serum has but little effect upon the specific refraction of the serum. Bull[1] has stated that the determination of both the gravity and refraction of the acetic serum is advisable for the detection of watered milk. The writer has recently calculated the specific refraction of milk serum prepared by the acetic acid method from some determinations made about five years ago from 105 samples of milk of known purity, the results of which are given below.

	Number of Samples	Solids %	Fat %	Acetic Acid Serum			
				Scale Reading 20°	n_D 20°	Sp. Gr. 15/15°	$\frac{N^2-1}{N^2+2}\cdot\frac{1}{d}$
Highest		15.38	5.95	45.9	1.34496	1.0333	0.20576
Lowest		14.02	4.20	42.9	1.34384	1.0306	0.20524
Average	12	14.45	4.92	44.7	1.34452	1.0319	0.20558
Highest		13.85	4.70	45.6	1.34485	1.0322	0.20576
Lowest		13.01	3.33	40.5	1.34294	1.0282	0.20541
Average	33	13.42	4.30	43.2	1.34396	1.0302	0.20554
Highest		12.97	4.40	44.2	1.34433	1.0314	0.20572
Lowest		12.00	3.10	40.6	1.34298	1.0280	0.20540
Average	33	12.44	3.73	42.8	1.34380	1.0301	0.20554
Highest		11.97	3.60	42.9	1.34384	1.0307	0.20572
Lowest		10.56	2.60	39.0	1.34237	1.0266	0.20545
Average	27	11.42	3.28	41.0	1.34313	1.0290	0.20553
Average	105	13.39	4.37	42.9	1.34384	1.0302	0.20554

Subsequent determinations upon a smaller number of whole and watered milk samples give a value of 0.20551. The average value of the specific refraction where the gravity and refraction were taken at the same temperature was 0.20592.

For the copper serum the specific refraction (gravity and refraction determined at the same temperature) was found to be 0.20526 and for the sour serum 0.20607.

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[1] J. Ind. & Eng. Chem. 1911 *3*, 44.

The relation between the solids and refraction of the serum prepared by both the copper and acetic acid methods is very constant, and the value of A in the formula suggested by Walter and by Robertson ($n - n' = a\ c$), is 0.00158.

Using the above constants and calculating from the lowest refraction found for several hundred samples of milk of known purity examined in the laboratory of the Massachusetts State Board of Health, the following figures are obtained representing the lowest possible values for pure milk.

Acetic acid serum	lowest refraction	20°	39.0
	lowest gravity	$\frac{20°}{4°}$	1.0244
	lowest solids per cent		5.94
Copper serum	lowest refraction	20°	36.0
	lowest gravity	20°/4°	1.0245
	lowest solids per cent		5.22
Sour serum	lowest refraction	20°	38.3
	lowest gravity	20°/4°	1.0229

The table on page 311 shows the figures obtained from a sample of milk systematically watered.

Naumann[1] has devised a method for the refractometric determination of the fat in milk which has been modified by Baier and Neumann.[2] This method consists in coagulating the milk with acetic acid, adding water, — saturated ether, shaking in a shaking machine, adding a glycerine, — potassium hydroxide copper solution, shaking again, centrifuging and taking the refraction of the ether solution of the fat from which the per cent of fat is calculated by means of tables. The quantities of milk and reagents used are different in the two methods, and consequently the tables differ. Baier and Neumann report a variation between the refractometric method and the Adams method in twenty-two instances of from +0.12 to −0.16, the mean being −0; between the refractometric and Gerber method in eighty instances of from +0.04 to −0.07, the mean being −0.013; and between the refractometric and Gottlieb method of from +0.08 to −0.11, the mean being −0.024.

[1] Milch Ztg. 1900 *29*, 50.
[2] Z. Nahr-Genussm 1907 *13*, 369.

Added Water %	Total solids %	Fat %	Ash %	ACETIC SERUM					COPPER SERUM					SOUR SERUM			
				Re-fraction 20°	Sp. gr. $\frac{20°}{4°}$	Solids %	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	$\frac{n-n^1}{C}$	Re-fraction 20°	Sp. gr. $\frac{20°}{4°}$	Solids %	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	$\frac{n-n^1}{C}$	Re-fraction 20	Sp. gr. $\frac{20°}{4°}$	Ash %	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$
0	12.19	3.60	0.71	41.4	1.0269	6.49	0.20589	0.00159	37.3	1.0261	5.61	0.20523	0.00153	39.9	1.0254	0.740	0.20588
10	10.97	3.24	0.64	38.6	1.0241	5.89	0.20589	0.00157	35.4	1.0243	5.15	0.20518	0.00156	37.5	1.0224	0.666	0.20601
20	9.75	2.88	0.57	35.6	1.0208	5.16	0.20592	0.00157	33.5	1.0223	4.62	0.20518	0.00158	34.7	1.0197	0.572	0.20597
30	8.53	2.50	0.50	33.0	1.0181	4.45	0.20592	0.00160	31.5	1.0204	4.14	0.20516	0.00158	32.0	1.0169	0.520	0.20597
40	7.31	2.16	0.43	30.1	1.0151	3.85	0.20594	0.00156	29.5	1.0118	3.65	0.20507	0.00158	29.4	1.0142	0.428	0.20597

Baier and Neumann[1] have also applied the refractometer to the determination of lactose in milk as follows: Treat 5 cc. of the milk with 5 drops of 4% calcium chloride solution, stopper the flask and place in boiling water for ten minutes, cool and place a few drops of the serum upon the prisms of the milk fat refractometer, and from the scale reading the per cent of sugar is determined by means of the table.

The refractive index may be used indirectly to determine a component of a substance. Zwick[2] uses the immersion refractometer for the determination of tannin by taking the refraction of the solution before and after precipitating with hide powder. The difference between the two readings is multiplied by the proper factor. Sager[3] and Falciola and Corridi[4], however, find that the factors given are either too slight or too variable for the determination of tannins or detection of adulteration. R. E. Remington[5] suggests the use of the immersion refractometer for the determination of the solids in cider vinegar. The reading of the vinegar on the scale of the immersion refractometer is determined, from which is subtracted the scale reading due to the acetic acid present, obtained from Wagner's table, and the difference divided by 3.9 gives the per cent of solids in the sample. Results show variations of from −0.18 to −0.24 in samples containing from 1.68% to 5.01% solids, and from 4.10% to 5.17% acetic acid. In all cases of wide variation, other analytical figures showed that the samples may have been adulterated. He makes no mention, however, of the influence of any alcohol that may have been present.

Hanus and Chocensky[6] have suggested the use of the immersion refractometer for the determination of caffein. They show that there is a loss of caffein during drying at 85° and a still greater loss in drying at 100°. To avoid this source of error they dissolve the caffein obtained in the usual way, in water, measure the volume and the refractive index at 17.6° (on the scale of the immersion refractometer) of the solution. The amount of caffein is then

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[1] Z. Nahr-Genussm 1907 *13*, 369.
[2] Chem. Ztg. *32*, 405.
[3] Ledertechm. Rundschau 1909, 27.
[4] Collegium 1910, 21.
[5] Bull. N. Dakota Agr. Exp. Sta. March, 1912.
[6] Z. Nahr-Genussm 1906 *11*, 313.

found by means of the formula $X = \frac{y-15}{5}$, where X = caffein as grams per 100 cc., y = the scale reading of the caffein solution and 15 is the reading of water at the same temperature.

The advantages of refractometry as applied to analytical chemistry may be briefly summarized as follows:

It is possible to obtain the refractive index when the specimen is too small for other quantitative measurement.

For routine work the refractive index is more quickly obtained than any other physical or chemical constant.[1] For the quantitative determination of methyl alcohol it is indispensable. For the determination of substances which may lose weight in drying, such as sugar, it is advantageous and time saving. It is helpful in checking results found by other methods and under certain conditions, as with beer, separations are unnecessary to secure quantitative results. It is also of value in obtaining the quantities of mixtures which cannot be separated, and as a rapid means of determination when the separation may be difficult.

The future of refractometry cannot, of course, be prophesied. Judging from the increase in the literature year by year, it is a subject of much study from which has been and can be derived data of considerable value. It seems probable that methods for the quantitative determination of fat in such substances as cocoa, coffee, spices, etc., in a manner similar to those for fat in milk are both feasible and desirable. There is a possibility that precipitation reactions similar to that described for tannins may be applicable where the refractive index is determined before and after precipitating, and from the difference, the precipitated substance may be calculated.

One difficulty in the manufacture of tinctures is the control of the alcohol content, which will vary according to the moisture in the drugs used. This may be solved by the use of the specific gravity and refractive index of the tinctures in a manner similar to that used in breweries and distilleries.

The instruments to be employed depend upon the character of

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[1] The chemist of a large soap factory told me that his Abbé refractometer paid for itself in one week by saving time in the determination of the concentration of glycerine.

the work. For the usual laboratory the Abbé and immersion refractometers are sufficient.

Two tables of value of $\frac{n^2-1}{n^2+2}$ follow, one for each value of *n* from 1.300 to 1.879, the other for each scale division of the immersion, butyro and milk fat refractometers. In preparing the first table the fractions were calculated for values of *n* from 1.30 to 1.80, using Vega's seven place logarithm tables. As the values of *n* increased, the differences between the corresponding values of $\frac{n^2-1}{n^2+2}$ decreased by a nearly constant quantity, and by means of this quantity the figures corresponding to the third decimal of *n* were calculated. By interpolation in the table it is possible to obtain correct values of $\frac{n^2-1}{n^2+2}$ of five figures corresponding to values of *n* to the fifth decimal place. The values corresponding to the scale readings of the immersion refractometer were calculated for each scale division up to 52 and from 53 to 105 were interpolated from values calculated every five scale divisions. The values corresponding to the other scales were obtained from the first table of specific refraction.

I wish to express my thanks to Dr. P. G. Nutting of the Bureau of Standards, Washington, D. C. who has kindly looked over this paper and verified the physical formulæ.

VALUES OF $\frac{N^2-1}{N^2+2}$ FOR VALUES OF N FROM 1.300 TO 1.879

N	3d Decimal of N.																			
	.000	Diff	.001	Diff	.002	Diff	.003	Diff	.004	Diff	.005	Diff	.006	Diff	.007	Diff	.008	Diff	.009	Diff
1.30	.186992	573	.187565	572	.188137	572	.188709	572	.189281	571	.189852	571	.190423	570	.190993	570	.191563	570	.192133	569
1.31	.192702	569	.193271	569	.193840	568	.194408	568	.194976	568	.195544	567	.196111	567	.196678	566	.197244	566	.197810	565
1.32	.198375	569	.198940	565	.199505	565	.200070	564	.200634	564	.201198	564	.201762	563	.202325	563	.202888	562	.203450	562
1.33	.204012	561	.304573	561	.205134	561	.205695	560	.206255	560	.206815	560	.207475	560	.207935	559	.208494	559	.209053	558
1.34	.209611	558	.210169	557	.210726	557	.211283	557	.211840	556	.212396	556	.212952	556	.213508	555	.214063	555	.214618	555
1.35	.215173	554	.215727	554	.216281	554	.216835	553	.217388	553	.217941	552	.218493	552	.219045	551	.219596	551	.220147	551
1.36	.220698	550	.221248	550	.221798	550	.222348	549	.222897	549	.223446	549	.223995	548	.224543	548	.225091	548	.225639	547
1.37	.226186	547	.226733	546	.227279	546	.227825	545	.228370	545	.228915	545	.229460	544	.230004	544	.230548	544	.247229	544
1.38	.231636	543	.232179	543	.232722	542	.233264	542	.233806	542	.234348	541	.234889	541	.235430	540	.235970	540	.236510	539
1.39	.237049	539	.237588	539	.238127	538	.238665	538	.239203	538	.239741	537	.240278	537	.240815	537	.241352	536	.241888	535
1.40	.242423	535	.242958	535	.243493	535	.244028	534	.244562	534	.245096	534	.245630	533	.246163	533	.246696	533	.247229	533
1.41	.247762	532	.248294	532	.248826	531	.249357	531	.249888	530	.250418	530	.250948	529	.251477	529	.252006	528	.252534	528
1.42	.253062	528	.253590	527	.254117	527	.254644	527	.255171	526	.255697	526	.256223	526	.256749	526	.257275	525	.257800	525
1.43	.258325	524	.258849	524	.259373	524	.259897	523	.260420	523	.260943	522	.261465	522	.261987	522	.262509	521	.263030	521
1.44	.263551	521	.264072	520	.264592	520	.265112	519	.265631	519	.266150	519	.266669	518	.267187	518	.267705	517	.268222	517
1.45	.268739	517	.269256	516	.269772	516	.270288	516	.270804	515	.271319	515	.271834	514	.272348	514	.272862	514	.273376	513
1.46	.273889	513	.274402	513	.274914	512	.275526	512	.275938	512	.276450	511	.276961	511	.277472	510	.277982	510	.278492	510
1.47	.279002	509	.279511	509	.280020	509	.280529	508	.281037	508	.281545	507	.282052	507	.282559	507	.283066	506	.283572	506
1.48	.284078	506	.284584	505	.285089	505	.285594	504	.286098	504	.286602	504	.287106	503	.287609	503	.288112	503	.288615	502
1.49	.289117	502	.289619	502	.290121	501	.290622	501	.291123	500	.291623	500	.292123	499	.292622	499	.293121	499	.293620	498
1.50	.294118	498	.294616	498	.295114	497	.295611	497	.296108	497	.296605	496	.297101	496	.297597	495	.298092	495	.298587	495
1.51	.299082	494	.299576	494	.300070	494	.300564	493	.301057	493	.301550	492	.302042	492	.302534	492	.303026	491	.303517	491
1.52	.304008	491	.304499	490	.304989	490	.305479	490	.305969	489	.306458	489	.306947	489	.307436	488	.307924	488	.308412	487
1.53	.308899	487	.309386	487	.309873	486	.310359	486	.310845	486	.311331	485	.311816	485	.312301	484	.312785	484	.313269	484
1.54	.313753	483	.314236	483	.314719	482	.315201	482	.315683	482	.316165	482	.316647	481	.317128	481	.317609	480	.318089	480
1.55	.318569	480	.319049	479	.319528	479	.320007	478	.320485	478	.320963	478	.321441	478	.321919	477	.322396	477	.322873	476
1.56	.523349	476	.323825	476	.324301	475	.324776	475	.325251	475	.325726	474	.326200	474	.326674	473	.327147	473	.327620	473

VALUES OF $\frac{N^2-1}{N^2+2}$ FOR VALUES OF N FROM 1.300 TO 1.879

N	3d Decimal of N.																			
	.000	Diff	.001	Diff	.002	Diff	.003	Diff	.004	Diff	.005	Diff	.006	Diff	.007	Diff	.008	Diff	.009	Diff
1.57	.327093	472	.328565	472	.329037	472	.329509	471	.329980	471	.330451	471	.330922	470	.331392	470	.331862	469	.332331	469
1.58	.332800	469	.333269	468	.333737	468	.334205	468	.334673	467	.335140	467	.335607	466	.336073	466	.336539	466	.337005	465
1.59	.337470	465	.337935	465	.338400	464	.338864	464	.339328	464	.339792	463	.340255	463	.340718	463	.341181	462	.341643	462
1.60	.342105	462	.342567	461	.343028	461	.343489	460	.343949	460	.344409	460	.344869	459	.345328	459	.345787	459	.346246	458
1.61	.346704	458	.347162	458	.347620	457	.348077	457	.348534	457	.348991	456	.349447	456	.349903	455	.350358	455	.350813	455
1.62	.351268	454	.351722	454	.352176	454	.352630	453	.353083	453	.353536	452	.353988	452	.354440	452	.354892	451	.355343	451
1.63	.345794	451	.356245	450	.356695	450	.357145	450	.357595	449	.358044	449	.358493	449	.358942	448	.359390	448	.359838	448
1.64	.360286	447	.360733	447	.361180	447	.361627	446	.362073	446	.362519	445	.362964	445	.363409	445	.363854	444	.364298	444
1.65	.364742	444	.365186	444	.365630	443	.366073	443	.366516	442	.366958	442	.367400	442	.367842	441	.368283	441	.368724	441
1.66	.369165	440	.369605	440	.370045	440	.370485	439	.370924	439	.371363	438	.371801	438	.372239	438	.372677	437	.373114	437
1.67	.373551	437	.373988	436	.374424	436	.374860	436	.375296	435	.375731	435	.376166	435	.376601	434	.377035	434	.377469	434
1.68	.377903	433	.378336	433	.378769	433	.379202	432	.479634	432	.480066	432	.480498	431	.480929	431	.481360	430	.481790	430
1.69	.482220	430	.382650	429	.387079	429	.383508	429	.383937	428	.384365	428	.384793	428	.385221	428	.385649	427	.386076	427
1.70	.386503	426	.386929	426	.387355	426	.387781	425	.388206	425	.388631	425	.389056	424	.389480	424	.389904	424	.390328	423
1.71	.390751	423	.391174	423	.391597	422	.392019	422	.392441	422	.392863	421	.393284	421	.393705	421	.394126	420	.394546	420
1.72	.394966	420	.395386	419	.395805	419	.396224	419	.396643	418	.397061	418	.397479	417	.397896	417	.398313	417	.398730	417
1.73	.399147	416	.399563	416	.399979	416	.400395	415	.400810	415	.401225	415	.401640	414	.402054	414	.402468	413	.402881	413
1.74	.403294	413	.403707	413	.404120	412	.404532	412	.404944	412	.405356	411	.405767	411	.406178	410	.406588	410	.406998	410
1.75	.407408	410	.407818	409	.408227	409	.408636	409	.409045	408	.409453	408	.409861	407	.410268	407	.410675	407	.411082	406
1.76	.411488	406	.411894	406	.412300	406	.412706	405	.413111	405	.413516	404	.413920	404	.414324	404	.414728	404	.415132	403
1.77	.415535	403	.415938	403	.416341	402	.416743	402	.417145	402	.417547	401	.417948	401	.418349	401	.418750	400	.419150	400
1.78	.419550	400	.419950	399	.420349	399	.420748	399	.421147	398	.421545	398	.421943	398	.422341	397	.422738	397	.423135	396
1.79	.423531	396	.423927	396	.424323	396	.424719	395	.425114	395	.425509	395	.425904	395	.426299	394	.426693	394	.427087	394
1.80	.427481	393	.427874	393	.428267	392	.428659	392	.429051	392	.429443	392	.429835	391	.430226	391	.430617	391	.431008	390
1.81	.431398	390	.431788	390	.432178	389	.432567	389	.432956	389	.433345	388	.433733	388	.434121	388	.434509	387	.434896	387
1.82	.435283	387	.435670	386	.436056	386	.436442	386	.436828	386	.437214	385	.437599	385	.437984	385	.438369	384	.438753	384
1.83	.439137	383	.439520	383	.439903	383	.440286	383	.440669	382	.441051	382	.441433	382	.441815	382	.442197	381	.442578	381
1.84	.442959	380	.443339	380	.443719	380	.444099	380	.444479	379	.444858	379	.445237	379	.445616	378	.445994	378	.446372	378
1.85	.446750	377	.447127	377	.447504	377	.447881	376	.448257	376	.448633	376	.449009	376	.449385	375	.449760	375	.450135	374
1.86	.450509	374	.450883	374	.451257	373	.451630	373	.452003	373	.452376	373	.452749	373	.451122	372	.453494	372	.453866	372
1.87	.454238	371	.454609	371	.454980	371	.455351	370	.455721	370	.456091	370	.456461	369	.456830	369	.457199	368	.457567	368

VALUES OF $\frac{N^2-1}{N^2+2}$ CORRESPONDING TO SCALE READINGS OF DIFFERENT REFRACTOMETERS

Scale Reading	IMMERSION REFRACTOMETER					BUTYRO REFRACTOMETER					MILK FAT REFRACTOMETER				
	^{n}D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.	^{n}D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.	^{n}D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.
–5	1.32539	.20142		.30410											
–4	1.32578	.20164	22	.30457	47										
–3	1.32618	.20186	22	.30505	48										
–2	1.32657	.20208	22	.30553	48										
–1	1.32696	.20230	22	.30600	47										
0	1.32736	.20253	23	.30648	48	1.4220	.25412	42	.40504		1.3332	.20581		.31347	
1	1.32775	.20274	21	.30695	47	1.4228	.25454	42	.40576	72	1.3343	.20642	61	.31475	128
2	1.32814	.20296	22	.30742	47	1.4236	.25496	42	.40649	73	1.3353	.20698	56	.31593	118
3	1.32854	.20319	23	.30790	48	1.4244	.25539	43	.40720	73	1.3364	.20760	62	.31723	130
4	1.32893	.20341	22	.30837	47	1.4252	.25580	41	.40790	70	1.3375	.20821	61	.31850	127
5	1.32932	.20364	23	.30885	48	1.4260	.25622	42	.40861	71	1.3385	.20877	59	.31967	117
6	1.32971	.20385	21	.30931	46	1.4268	.25665	43	.40934	73	1.3395	.20934	57	.32085	118
7	1.33010	.20407	22	.30978	47	1.4276	.25706	41	.41003	69	1.3406	.20995	61	.32203	118
8	1.33049	.20428	21	.31022	44	1.4284	.25748	42	.41074	71	1.3416	.21050	55	.32325	118
9	1.33087	.20450	22	.31069	47	1.4292	.25790	42	.41145	71	1.3426	.21106	56	.32441	116
10	1.33126	.20472	22	.31116	47	1.4300	.25832	42	.41216	71	1.3436	.21162	56	.32556	115
11	1.33165	.20494	22	.31162	46	1.4308	.25874	42	.41286	70	1.3446	.21218	56	.32670	114
12	1.33204	.20515	21	.31209	47	1.4316	.25916	42	.41357	71	1.3456	.21273	55	.32783	113
13	1.33242	.20537	22	.31254	45	1.4324	.25958	42	.41427	70	1.3467	.21333	60	.32905	118
14	1.33281	.20559	22	.31300	46	1.4331	.25999	41	.41496	69	1.3477	.21390	57	.33021	116
15	1.33320	.20581	22	.31346	46	1.4339	.26040	41	.41564	68	1.3487	.21445	55	.33133	112
16	1.33358	.20602	21	.31391	45	1.4347	.26079	39	.41629	65	1.3497	.21500	55	.33244	111
17	1.33397	.20624	22	.31437	46	1.4354	.26115	36	.41689	60	1.3507	.21556	56	.33357	113
18	1.33435	.20645	21	.31482	45	1.4362	.26157	42	.41759	70	1.3517	.21611	55	.33467	110
19	1.33474	.20667	22	.31528	46	1.4370	.26196	39	.41823	64	1.3527	.21666	55	.33578	111
20	1.33513	.20689	22	.31574	46	1.4377	.26235	39	.41888	65	1.3537	.21722	56	.33690	112

VALUES OF $\frac{N^2-1}{N^2+2}$ CORRESPONDING TO SCALE READINGS OF DIFFERENT REFRACTOMETERS

Scale Reading	IMMERSION REFRACTOMETER					BUTYRO REFRACTOMETER					MILK FAT REFRACTOMETER				
	n_D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.	n_D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.	n_D	$\frac{N^2-1}{N^2+2}$	Diff.	Log.	Log Diff.
21	1.33551	.20710	21	.31619	45	1.4385	.26277	42	.41958	70	1.3547	.21777	55	.33800	110
22	1.33590	.20732	22	.31664	45	1.4392	.26314	37	.42019	61	1.3557	.21832	55	.33909	109
23	1.33628	.20753	21	.31708	44	1.4400	.26355	41	.42086	67	1.3567	.21888	56	.34021	112
24	1.33667	.20775	22	.31754	46	1.4408	.26396	41	.42154	68	1.3577	.21943	55	.34130	109
25	1.33705	.20796	21	.31798	44	1.4415	.26433	37	.42215	61	1.3587	.21998	55	.34238	108
26	1.33743	.20818	22	.31843	45	1.4423	.26475	42	.42284	69	1.3597	.22053	55	.34347	109
27	1.33781	.20839	21	.31887	44	1.4430	.26511	36	.42343	59	1.3607	.22108	55	.34455	108
28	1.33820	.20861	22	.31933	46	1.4438	.26553	42	.42411	68	1.3616	.22158	50	.34553	98
29	1.33861	.20882	21	.31977	44	1.4445	.26589	36	.42470	59	1.3626	.22213	55	.34661	108
30	1.33896	.20903	21	.32021	44	1.4452	.26625	33	.42529	59	1.3636	.22268	55	.34768	101
31	1.33934	.20924	21	.32065	44	1.4460	.26667	42	.42597	68	1.3645	.22317	49	.34864	96
32	1.33972	.20945	21	.32108	43	1.4467	.26703	36	.42656	59	1.3655	.22372	55	.34970	106
33	1.34010	.20965	20	.32148	40	1.4474	.26739	36	.42714	58	1.3664	.22420	48	.35064	94
34	1.34048	.20987	22	.32197	49	1.4481	.26776	37	.42775	61	1.3674	.22476	56	.35172	108
35	1.34086	.21008	21	.32238	41	1.4488	.26812	36	.42833	58	1.3683	.22526	50	.35268	96
36	1.34124	.21030	22	.32284	46	1.4495	.26848	36	.42891	58	1.3692	.22575	49	.35363	95
37	1.34162	.21052	22	.32329	45	1.4502	.26884	36	.42949	58	1.3702	.22630	55	.35468	105
38	1.34199	.21072	20	.32371	42	1.4510	.26926	42	.43018	69	1.3711	.22679	49	.35562	94
39	1.34237	.21093	21	.32414	43	1.4517	.26962	36	.43075	57	1.3721	.22733	54	.35666	104
40	1.34275	.21114	21	.32458	44	1.4524	.26998	36	.43133	58	1.3730	.22782	49	.35759	93
41	1.34313	.21135	21	.32501	43	1.4531	.27034	36	.43191	58	1.3739	.22832	50	.35854	95
42	1.34350	.21156	21	.32544	43	1.4538	.27070	36	.43249	58	1.3748	.22880	48	.35946	92
43	1.34388	.21177	21	.32587	43	1.4545	.27106	36	.43307	58	1.3758	.22935	55	.36050	104
44	1.34426	.21198	21	.32630	43	1.4552	.27142	36	.43364	57	1.3767	.22984	49	.36143	93
45	1.34463	.21219	21	.32672	42	1.4559	.27178	36	.43422	58	1.3776	.23033	49	.36235	92
46	1.34500	.21240	21	.32715	43	1.4566	.27214	36	.43479	57	1.3785	.23082	49	.36327	92

VALUES OF $\frac{N^2-1}{N^2+2}$ CORRESPONDING TO SCALE READINGS OF DIFFERENT REFRACTOMETERS

Scale Reading	IMMERSION REFRACTOMETER					BUTYRO REFRACTOMETER					MILK FAT REFRACTOMETER				
	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff	Log	Log Diff.
47	1.34537	.21260	20	.32757	42	1.4573	.27250	36	.43537	58	1.3794	.23131	49	.36419	92
48	1.34575	.21281	21	.32799	42	1.4580	.27286	36	.43594	57	1.3803	.23180	49	.36511	92
49	1.34612	.21302	21	.32842	43	1.4587	.27322	36	.43651	57	1.3812	.23228	48	.36601	90
50	1.34650	.21322	20	.32885	43	1.4593	.27353	31	.43700	49	1.3821	.23277	49	.36693	92
51	1.34687	.21343	21	.32927	42	1.4600	.27389	36	.43758	58	1.3830	.23326	49	.36784	91
52	1.34724	.21364	21	.32969	42	1.4607	.27425	36	.43815	57	1.3839	.23375	49	.36875	91
53	1.34761	.21384	20	.33009	40	1.4613	.27455	30	.43862	47	1.3848	.23424	49	.36966	91
54	1.34798	.21405	21	.33052	43	1.4620	.27491	36	.43919	57	1.3857	.23473	49	.37057	91
55	1.34836	.21425	20	.33092	40	1.4626	.27522	31	.43968	49	1.3866	.23521	48	.37146	89
56	1.34873	.21446	21	.33136	43	1.4633	.27557	35	.44023	55	1.3875	.23570	49	.37236	90
57	1.34910	.21466	20	.33175	40	1.4640	.27594	37	.44481	58	1.3884	.23619	49	.37326	90
58	1.34947	.21487	21	.33218	43	1.4646	.27624	30	.44129	48	1.3892	.23662	43	.37405	79
59	1.34984	.21507	20	.33258	40	1.4653	.27660	36	.44185	56	1.3901	.23710	48	.37493	88
60	1.35021	.21528	20	.33300	42	1.4659	.27691	31	.44234	49	1.3909	.23753	43	.37572	79
61	1.35058	.21549	21	.33343	43	1.4666	.27727	36	.44290	56	1.3918	.23802	49	.37661	89
62	1.35095	.21569	20	.33383	40	1.4672	.27757	30	.44337	47	1.3926	.23844	42	.37738	77
63	1.35132	.21509	21	.33425	42	1.4679	.27793	36	.44393	56	1.3935	.23893	49	.37827	89
64	1.35169	.21610	20	.33465	40	1.4685	.27824	31	.44442	49	1.3943	.23936	43	.37905	78
65	1.35205	.21631	21	.33508	43	1.4691	.27854	30	.44489	47	1.3951	.23979	43	.37983	78
66	1.35242	.21651	20	.33548	40	1.4698	.27890	36	.44545	56	1.3960	.24028	49	.38072	89
67	1.35279	.21672	21	.33590	42	1.4704	.27920	30	.44592	47	1.3968	.24071	43	.38149	77
68	1.35316	.21692	20	.33630	40	1.4710	.27951	31	.44640	48	1.3977	.24119	48	.38236	87
69	1.35352	.21712	20	.33670	40	1.4717	.27987	36	.44696	56	1.3985	.24162	43	.38313	77
70	1.35388	.21732	20	.33710	40	1.4723	.28017	30	.44742	46	1.3993	.24205	43	.38391	78
71	1.35425	.21752	20	.33750	40	1.4729	.28048	31	.44790	48	1.4001	.24248	43	.38468	77

VALUES OF $\frac{N^2-1}{N^2+2}$ CORRESPONDING TO SCALE READINGS OF DIFFERENT REFRACTOMETERS

Scale Reading	IMMERSION REFRACTOMETER					BUTYRO REFRACTOMETER					MILK FAT REFRACTOMETER				
	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.
72	1.35461	.21772	20	.33790	40	1.4736	.28083	35	.44844	54	1.4009	.24290	42	.38543	75
73	1.35497	.21792	20	.33830	40	1.4742	.28114	31	.44892	48	1.4017	.24333	43	.38620	77
74	1.35533	.21812	20	.33870	40	1.4748	.28144	30	.44939	47	1.4025	.24376	43	.38696	76
75	1.35569	.21832	20	.33909	39	1.4754	.28175	31	.44986	47	1.4033	.24419	43	.38773	77
76	1.35606	.21852	20	.33949	40	1.4760	.28204	29	.45031	45	1.4041	.24461	42	.38847	74
77	1.35642	.21872	20	.33989	40	1.4766	.28235	31	.45179	48	1.4049	.24504	43	.38924	77
78	1.35678	.21893	20	.34029	40	1.4772	.28266	31	.45126	47	1.4057	.24547	43	.39000	66
79	1.35714	.21912	20	.34068	39	1.4778	.28296	30	.45172	46	1.4064	.24584	37	.39065	75
80	1.35750	.21932	20	.34108	40	1.4783	.28322	26	.45212	40	1.4072	.24627	43	.39141	76
81	1.35786	.21952	20	.34147	39	1.4789	.28351	29	.45257	45	1.4080	.24670	43	.39217	76
82	1.35822	.21972	20	.34187	40	1.4895	.28381	30	.45303	46	1.4088	.24711	41	.39289	72
83	1.35858	.21992	20	.34226	39	1.4801	.28413	32	.45352	49	1.4096	.24755	44	.39366	67
84	1.35894	.22011	19	.34264	38	1.4807	.28443	30	.45398	46	1.4103	.24792	37	.39431	75
85	1.35930	.22031	20	.34303	39	1.4812	.28468	25	.45436	38	1.4111	.24835	43	.39506	75
86	1.35966	.22051	20	.34343	40	1.4818	.28499	31	.45483	47	1.4119	.24877	42	.39580	74
87	1.36002	.22071	20	.34382	39	1.4824	.28529	30	.45529	46	1.4126	.24914	37	.39644	64
88	1.36038	.22091	20	.34422	40	1.4829	.28554	25	.45567	38	1.4134	.24957	43	.39719	75
89	1.36074	.22110	20	.34459	37	1.4835	.28585	31	.45614	47	1.4141	.24994	37	.39784	65
90	1.36109	.22130	20	.34498	39	1.4840	.28610	25	.45652	38	1.4148	.25031	37	.39848	64
91	1.36145	.22150	20	.34537	39	1.4846	.28640	30	.45697	45	1.4156	.25074	43	.39922	74
92	1.36181	.22169	19	.34575	38	1.4851	.28665	25	.45735	38	1.4163	.25111	37	.39986	64
93	1.36217	.22189	20	.34614	39	1.4857	.28695	30	.45781	46	1.4171	.25153	42	.40059	73
94	1.36252	.22209	20	.34653	39	1.4862	.28721	26	.45820	39	1.4178	.25190	37	.40123	64
95	1.36287	.22228	19	.34690	37	1.4868	.28751	30	.45865	45	1.4185	.25227	37	.40187	64
96	1.36323	.22248	20	.34729	39	1.4874	.28781	30	.45911	46	1.4192	.25264	37	.40250	63

VALUES OF $\frac{N^2-1}{N^2+2}$ CORRESPONDING TO SCALE READINGS OF DIFFERENT REFRACTOMETERS

Scale Reading	IMMERSION REFRACTOMETER					BUTYRO REFRACTOMETER					MILK FAT REFRACTOMETER				
	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.	^nD	$\frac{N_2-1}{N_2+2}$	Diff.	Log	Log Diff.
97	1.36359	.22267	19	.34766	37	1.4879	.28811	30	.45956	45	1.4199	.25301	37	.40314	64
98	1.36394	.22287	20	.34805	39	1.4884	.28832	21	.45987	31	1.4206	.25338	37	.40377	63
99	1.36429	.22306	19	.34842	37	1.4890	.28862	30	.46033	46	1.4213	.25375	37	.40441	64
100	1.36464	.22325	19	.34879	37	1.4895	.28887	25	.46071	38	1.4220	.25412	37	.40504	63
101	1.36500	.22344	19	.34916	37										
102	1.36535	.22364	20	.34955	39										
103	1.36570	.22383	19	.34992	37										
104	1.36605	.22412	19	.35048	36										
105	1.36640	.22431	19	.35085	37										

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DOSAGE DU CARBONE TOTAL DES ACIERS ET DES FERRO-ALLIAGES PAR COMBUSTION SOUS PRESSION D'OXYGENE

PAR P. MAHLER ET E. GOUTAL

1. — *Principe de la Methode*

Le dosage du carbone total des aciers, par combustion dans l'oxygène, a d'abord été réalisé à l'aide de l'appareil à analyse élémentaire, c'est-à-dire dans un courant d'oxygène. L'introduction dans les laboratoires de fours à chauffage électrique a, ensuite, beaucoup amélioré le procédé.[1]

Le chauffage électrique d'un tube de porcelaine permet d'obtenir la température élevée indispensable pour brûler, non seulement, les aciers mais aussi les alliages réfractaires. Cette méthode n'admet que des prises d'essai de faible poids. C'est ainsi qu'on ne peut guère traiter plus de un demi gramme de ferro-chrôme: premier inconvénient. Il est, en outre, très difficile de brûler le métal, au four électrique, sans observer dans le courant gazeux des quantités parfois importantes d'oxyde de carbone, indices d'une combustion incomplète. C'est un second inconvénient qui a conduit à compliquer l'appareil par l'emploi d'un four complémentaire. Mais malgré cette précaution, nous verrons que l'oxydation complète des carbures métalliques reste toujours aléatoire.

Un procédé plus nouveau[2] consiste à allumer le métal électriquement, dans une enceinte fermée, remplie d'oxygène, sous une pression un peu supérieure à la pression atmosphérique. Ce second procédé est beaucoup plus rapide que le premier. Son principal inconvénient est de n'admettre que des prises d'essai d'un très faible poids, surtout quand il faut brûler des ferro-alliages. A quelle incertitude ne s'exposet-on pas, avec une prise d'essai de moins de un demi gramme, par exemple, d'un ferro-silicium

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[1] Traité d'analyse des substances minérales par Ad. Carnot, T. III, p. 783.

[2] Procédé de détermination rapide du carbone total dans les fers, les aciers et les ferro-alliages par H. de Nolly, Revue de Métallurgie 1911, p. 391 et p. 717.

dont la teneur en carbone ne dépasse guère 0,10 gr. pour cent grammes?

Nous avons présenté, le 11 Septembre 1911, à l'Académie des Sciences, une méthode qui paraît offrir des avantages sérieux par rapport à celles dont il vient d'être question. Depuis cette époque, nous l'avons améliorée, nous en avons examiné tous les détails et nous l'avons étendue aux ferro-alliages les moins faciles à brûler.

L'idée de notre méthode est aussi vieille que l'obus calorimétrique.[1] C'est tout récemment que les circonstances nous ont permis de l'étudier.

Le procédé consiste à brûler la prise d'essai au sein de l'obus, sous une pression d'oxygène, assez élevée pour assurer l'oxydation du métal et du carbone qu'il contient. La combustion est donc accompagnée d'une élévation de température instantanée considérable. Il suffit ensuite d'extraire les gaz et d'y doser l'anhydride carbonique pour en déduire la quantité de carbone cherchée. Le lavage des gaz de la combustion dans un volume connu d'une solution alcaline titrée, fournit un moyen facile de pratiquer le dosage de l'anhydride carbonique puisqu'il suffit de titrer la solution après le lavage.

L'appareil dont nous nous servons à l'Ecole des Mines permet d'arriver aisément au dosage du carbone des aciers et des ferro-alliages. Il admet des prises d'essai d'un poids important, pouvant au besoin dépasser 10 grammes. Il se prête à toutes les vérifications désirables, notamment au contrôle de la combustion complète du carbone, sous forme d'anhydride carbonique.

Nous avons mis ce point eu évidence, dans des expériences spéciales, en recherchant l'oxyde de carbone dans les gaz résultant de quelques combustions; nous n'en avons jamais trouvé.

Enfin, notre appareil réduit au minimum l'intervention de l'habileté professionnelle de l'opérateur. C'est ainsi que mis entre les mains d'élèves de l'Ecole des Mines, dès le mois de Décembre dernier, il a fourni, tout de suite, des résultats exacts; alors que les jeunes chimistes n'eussent obtenu des chiffres accep-

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[1] P. Mahler: Compte Rendus 30 Novembre, 1891; Contribution à l'étude des combustibles (Bulletin de la Société d'encouragement à l'Industrie Nationale 1892); Etudes sur les combustibles, 1903.

tables, soit au four électrique, soit suivant la méthode de Wiborgh, qu'au prix d'un apprentissage assez long.

Le tableau suivant permet de comparer nos résultats (colonne A) à quelques-uns de ceux trouvés par les Elèves:

		A	B	MM.
Acier extra-doux Trignac	C. pour cent	0.060	0.060	Lemoine
Acier nickel du Creusot	C. pour cent	0.370	0.370	Cellier
Acier silicium d'Imphy	C. pour cent	0.485	0.485	Puiseux
Acier tungstène Creusot	C. pour cent	0.521	0.520	Calliès
Acier chrôme Creusot	C. pour cent	0.560	0.570	d'Anglejan
Acier extra dur Creusot	C. pour cent	1.365	1.320	Lehmann
Fonte Thomas Creusot	C. pour cent	2.950	2.950	Boulzaguet

II. — Description de l'Appareil

Notre instrument est une chambre de combustion en acier doux, forgée à Imphy expressément en vue de nos recherches. Son volume est bien supérieur à celui de l'obuscalorimétrique. Elle est cylindrique avec 200 millimètres de hauteur et 85 millimètres de diamètre, correspondant à un peu plus de 1100 centimètres cubes de capacité.

La prise d'essai est placée dans une petite capsule en terre réfractaire, exempte de carbonate de calcium. Nous avons fait usage de trois modéles de capsules, l'un petit, de 40 millimètres de diamètre pour les prises d'essai de 3 ou 4 grammes de métal, l'autre moyen, de 50 millimètres de diamètre pour les prises d'essai de 5 grammes environ de métal; enfin, la plus grande de nos capsules a 60 millimètres de diamètre, elle convient aux prises d'essai atteignant et même dépassant 10 grammes. Les capsules résistent parfaitement à l'opération.

L'allumage se fait à l'aide d'un fil très léger de fer, d'un poids connu, qu'un courant électrique enflamme, au moment voulu.

La plupart des détails de l'appareil sont la reproduction de ce qui existe dans l'obus calorimétrique. Cependant, les tiges de suspension de la capsule et les électrodes dans le nouvel appareil, ne sont pas en platine, mais en cuivre rouge. Ces tiges sont encore en excellent état, après plus de deux cents combustions.

La nouvelle chambre de combustion n'est pas émaillée.[1]

Le couvercle porte deux robinets pointeaux identiques: l'un d'eux est en relation avec un tube de cuivre qui descend jusqu'au fond de la chambre de combustion, disposition adoptée dès l'origine, dans quelques obus construits envue de la combustion calorimétrique non seulement des substances solides mais aussi du gaz d'éclairage; elle permet de balayer à volonté les gaz existant à l'intérieur de l'instrument.

La fermeture est assurée par un couvercle qui, serré par des boulons, vient comprimer une bague de plomb.

Le dessin que nous donnons ci-contre figure d'une façon très claire les départs de l'appareil et de ses accessoires.

Au milieu, la chambre de combustion. La charge est prête dans la capsule pour l'allumage. On remarque le fil de fer qui sert d'amorce et qui, en serpentant, prend le plus de contact possible avec la prise d'essai.

Après la combustion, on ouvre le pointeau de droite et les gaz sont évacués et lavés dans des éprouvettes garnies d'une solution alcaline. Ces éprouvettes sont munies de tubes, modification et agrandissement du dispositif adopté par Maquenne, assurant un lavage rapide et efficace. La figure indique trois grands absorbeurs. Le quatrième, plus petit, reçoit de l'eau de baryte. C'est un tube témoin.

Le flacon, à l'extrémité droite, où vient aboutir le courant gazeux, débarrassé de son anhydride carbonique sert pour les opérations ultérieures de titrage.

Quand la plus grande partie des gaz a été évacuée, le courant s'arrête sous la pression du liquide des tubes laveurs. Il faut alors balayer à l'aide d'un courant d'air pur ce qui reste à l'intérieur de l'appareil et entraîner les moindres traces d'anhydride carbonique dues à la combustion. On admet donc par le robinet de gauche de l'air ou de l'oxygène sous pression, décarbonaté par des solutions de potasse et de baryte. Des barboteurs originaux, à disques de nickel perforés, réalisent ce lavage dans les meilleures conditions.

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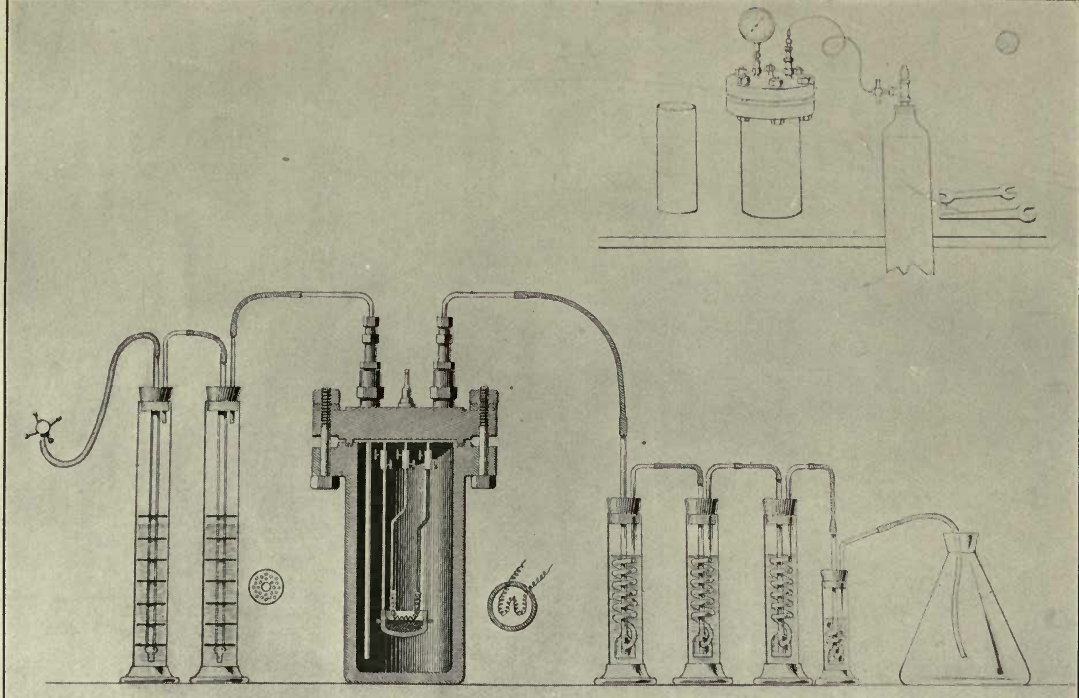
[1] Quand on se propose de recueillir et d'étudier certains produits de la combustion, comme l'acide sulfurique provenant du soufre du métal brûlé, l'appareil reçoit un vase cylindrique en porcelaine ou en tôle émaillée qui constitue un émail amovible.

La vignette à la partie supérieure de notre dessin, présente un de ces vases.



Appareil pour le dosage du Carbone total des Aciers & Ferro-Alliages

Des clefs, un manomètre, des tubes de raccord complètent l'appareil. Une vignette montre ces accessoires: on y voit l'obus au moment où, la charge étant préparée, on introduit l'oxygène dans la chambre de combustion par le pointeau qui est en relation avec le tube intérieur. L'oxygène en entrant, ainsi, ne soulève aucune partie de la matière contenue dans la capsule. Le manomètre est fixé à l'autre pointeau.

L'appareil de l'Ecole des Mines, créé en vue de diverses recherches est bien plus résistant qu'il ne convient pour le dosage du carbone. Il a été éprouvé à 400 atmosphères. Or, nous n'avons opéré aucune combustion à une pression supérieure à 12 atmosphères; et, encore, faut-il noter que dès l'inflammation de la prise d'essai, la pression intérieure s'abaisse, par suite de l'oxydation du fer.

A cet égard, un appareil réservé au dosage du carbone, serait bien moins résistant et plus léger que le nôtre, et son mode de fermeture pourait être simplifié.

Nous ne doutons pas que l'on puisse obtenir des dosages satisfaisants de carbone à l'aide de l'obus calorimétrique ordinaire, en prenant des précautions particulières.

Enfin, la méthode que nous décrivons s'applique au dosage du carbone dans n'importe quelle matière organique. Berthelot avait indiqué cet emploi de la bombe.

III. — Examen de la Methode

Les lignes suivantes font connaître comment nous employons, pour doser le carbone des aciers et des ferro-alliages, l'appareil qui vient d'être décrit. Elles insistent sur la critique des causes d'erreur.

1°. — Preparation de la Prise d'Essai

A.— Cas des Aciers.— L'état de la prise d'essai importe peu. Nous avons brûlé des aciers à l'état soit de fines perçures, soit de copeaux, soit de sable grossier.

Le poids de la prise d'essai peut être assez élevé jusqu'à 10 grammes d'acier et même davantage. Le poids de la charge est limité cependant par les dimensions de la capsule. Nous pensons que le résidu fondu trouvé après l'opération ne doit pas avoir plus de cinq millimètres d'épaisseur. D'autre part, si l'on assigne un volume (100 centimètres cubes, par exemple) de solution alcaline pour absorber l'anhydride carbonique, on doit, par précaution, admettre que ce volume sera d'un tiers au moins plus que suffisant pour obtenir un protocarbonate avec l'anhydride carbonique correspondant à la teneur en carbone présumée du métal.

En fait, dans la plupart de nos essais, les prises d'essai ont varié de 3 à 5 grammes.

Quand la prise d'essai est convenablement placée au fond de la capsule, on obtient fréquemment la combustion complète de la charge. Mais, il arrive aussi que le bain d'oxyde de fer fondu dans une capsule trop petite s'étant figé très rapidement, sur une trop grande épaisseur, on trouve au fond de la capsule, sous forme d'un globule fondu, quelques centigrammes du métal qui ont échappé à l'oxydation. La composition de ce résidu métallique est incertaine. Il y a donc là une cause d'erreur que l'on évite, en grande partie, par l'emploi d'une capsule plus grande.

En plus, nous avons observé que les aciers silicieux brûlés sans addition, et en apparence oxydés complètement, ne donnaient par combustion qu'une partie de leur carbone sous forme d'anhydride carbonique.

C'est ainsi que la combustion d'un acier à 1,28 de silicium d'Imphy, ne nous a révélé que 0,20 de carbone contre 0,48, teneur vraie; que la combustion d'un acier à 1,98 de silicium d'Imphy, ne nous a révélé que 0,16 de carbone contre 0,49, teneur vraie.[1]

Dans ces conditions, nous estimons nécessaire une addition au métal d'un fondant oxydant, capable de retarder la solidification du résidu oxydé et de compléter l'oxydation du métal.

Nous avons étudié l'emploi du protoxyde de plomb, du bioxyde de plomb et de l'oxyde de cuivre pur et calciné.

Tous ces corps permettent d'arriver au résultat.

L'oxyde de plomb doit être exempt de poussières organiques et d'acide carbonique. Nous le préparons en calcinant le bioxyde du commerce, exempt de matières organiques.

Nous ne l'employons que nouvellement préparé, pour écarter la cause d'erreur provenant de la carbonatation par l'air.

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[1] Ces expériences mettent en évidence la présence dans les aciers silicieux d'une quantité importante de carbone, sous une forme difficile à brûler.

Le bioxyde de plomb doit être pur, exempt de poussières et d'acide azotique. Nous avons eu quelques difficultés à nous en procurer, dans ces conditions.

Nous avons reconnu que, pour obtenir l'oxydation complète du métal, il suffisait d'ajouter, dans la capsule, à la prise d'essai, sous forme de PbO, la moitié au plus du poids du métal à brûler. C'est principalement du protoxyde de plomb que nous avons fait usage.

Nous préparons la charge comme il suit:

La capsule est d'abord portée au rouge et débarrassée ainsi de toutes traces de poussières organiques. Elle reçoit ensuite, encore rouge, l'oxyde de plomb qui fond aussitôt; enfin refroidie, elle reçoit, au-dessus de la masse d'oxyde de plomb, la prise d'essai elle-même.

L'oxyde de plomb peut apporter une cause d'erreur éventuelle par suite de sa carbonatation à l'air. D'autre part, la combustion vive a pour effet de tapisser la paroi de la chambre de combustion d'une certaine quantité d'oxyde pulvérulent, qui peut retenir un peu d'anhydride carbonique. C'est une cause d'erreur, par défaut.

Or, nous avons brûlé 5 grammes d'acier doux de Trignac, sans addition, dans l'appareil, résultat: 0.068% de carbone; 3 grammes sans addition, résultat: 0.071 de carbone; 6 grammes avec 3 grammes d'oxyde de cuivre, résultat: 0.070 de carbone; enfin, 5 grammes avec 3 grammes d'oxyde de plomb, résultat: 0.071% de carbone.

Nous concluons de la concordance de ces essais que l'emploi de l'oxyde de plomb est sans influence sensible sur la précision du dosage.

B.— Cas des fontes et des ferro-alliages.— La combustion des fontes et des ferro-alliages ordinaires, tels que le silico-spiegel et le ferro-manganèse, n'offre pas de difficultés. Ce que nous venons de dire s'applique à ces métaux. En outre, nous jugeons commode de placer dans la capsule un gramme, par exemple, de fer métallique facile à brûler et de teneur en carbone connue, entre la prise d'essai et le fil de fer qui sert d'amorce. On assure ainsi la parfaite inflammation du métal. Nous reviendrons bientôt sur cet emploi du fer, comme combustible auxiliaire.

La combustion des ferro-alliages, tels que le ferro-vanadium et le ferro-molybdène, est aisée.

Nous avons, par ailleurs, traité ces alliages comme les alliages très réfractaires dont il va être question.

La combustion complète des ferro-alliages réfractaires, tels que le ferro-silicium, le ferro-chrôme, le ferro-tungsténe, le ferro-titane, exige, en plus d'un fondant comme l'oxyde de plomb un combustible auxiliaire. On ne manque jamais de recourir à un semblable artifice, quand une combustion dans la bombe offre quelques difficultés.

Nous avons étudié l'emploi du fer métallique[1] qui a l'avantage de diminuer la teneur moyenne en élément réfractaire de la charge de la capsule.

Nous avons étudié aussi l'emploi du manganèse aluminothermique, concurremment avec le fer et avec l'oxyde de cuivre. Nous avons ainsi obtenu de bons résultats. Mais, le manganèse ne peut être ajouté qu'en très faible quantité: le moindre excès ayant pour effet de percer la capsule pendant la combustion.

L'emploi du fer en quantité suffisante est préférable. Il est légitime, puisque notre méthode permet de titrer, avec une grande précision, même sur une prise d'essai de 10 grammes, la teneur en carbone de l'échantillon adopté comme combustible auxiliaire.

Pour l'essai des ferro-alliages réfractaires, nous avons séparé deux cas:

1°.—Cas des ferro-alliages à faible teneur en carbone.—

C'est peut-être le plus intéressant. Parmi ces ferro-alliages, on trouve le plus difficile à brûler des ferro-alliages courants, le ferro-silicium et il importe d'opérer sur une prise d'essai un peu considérable, au moins deux grammes.

D'une façon générale, nous avons reconnu que la quantité de fer suffisante, à mélanger à la prise d'essai était d'environ 3 fois le poids de cette prise d'essai; la quantité d'oxyde de plomb à ajouter restant représentée par la moitié de la charge métallique de la capsule. Règle qui n'a rien d'absolu. A deux grammes de ferro-alliages, par exemple, correspondent 6 grammes de fer et 4 grammes d'oxyde de plomb.

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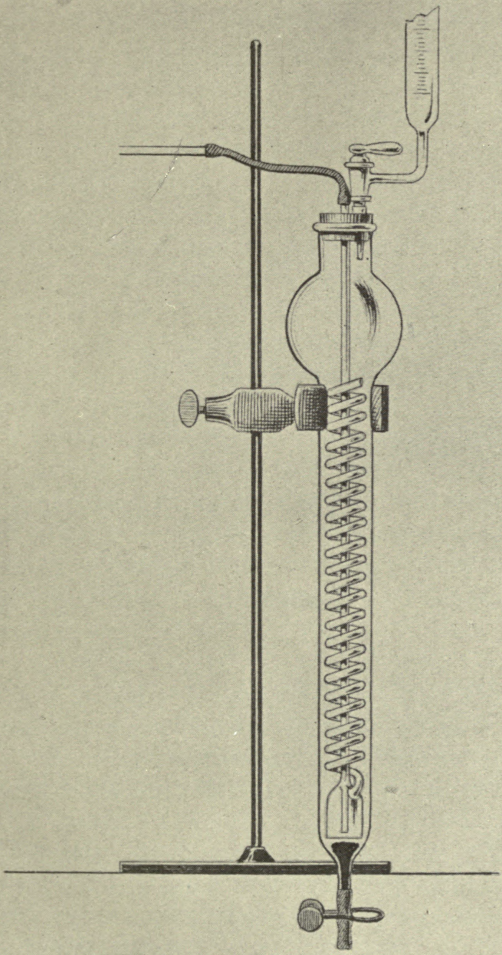
[1] M. de Nolly a fait connaître en Septembre dernier l'emploi du fer métallique pour assurer la combustion des ferro-alliages dans son ingénieux appareil (loc. cit.)



Tube laveur grand modèle
pour absorption & titrage

Pratiquement, nous fondons d'abord 3 grammes d'oxyde de plomb dans le fond de la capsule et nous versons, audessus de cet oxyde, la charge composée du mélange de 2 grammes de ferro-alliages, de 6 grammes de fer en fines perçures et de 1 gramme de bioxyde de plomb en poudre.

2°.—Cas des ferro-alliages riches en carbone.—

Certains de ces alliages, comme le ferro-chrôme peuvent retenir plus de 10% de carbone. Limités par le volume de liqueur titrée que nous nous sommes assigné, 100 centimètres cubes, nous préférons ne brûler qu'un poids assez faible de métal, par exemple 0,400 gr. de ferro-chrôme riche. Comme la combustion d'une masse métallique un peu importante est indispensable pour assurer l'oxydation de la prise d'essai, même en faible poids, nous ajoutons du fer de façon à ne pas abaisser au-dessous de trois grammes la quantité à brûler.

Dans les conditions que nous venons de dire, nous n'avons pas rencontré d'insuccès.

Nous ajoutons qu'au cours de nos expériences, nous n'avons admis comme satisfaisantes que les combustions laissant dans la capsule un résidu parfaitement fondu et oxydé. La faculté d'examiner le résidu de la combustion et de l'étudier est un des avantages de notre méthode.

2°.— *Pression de l'Oxygène*

La charge étant préparée dans l'appareil, on admet l'oxygène. On commence par chasser l'air de la chambre de combustion; on fixe alors le manomètre et on laisse monter la pression jusqu'au point voulu. Les robinets étant fermés, on s'assure alors de l'étanchéité du système, au besoin en le plongeant dans l'eau. Enfin, on enflamme électriquement l'amorce comme cela a lieu pour l'obus calorimètrique. La combustion ne demande que quelques instants.

Nous avons été conduits à établir la pression convenant à chaque expérience, comme il suit:

Aciers.—Pour le premier gramme à brûler, 3 atmosphères; pour chacun des grammes en plus, une demi atmosphère. Ainsi, 5 atmosphères correspondent à une prise d'essai de 5 grammes.

Ferro-alliages.— Pour le premier gramme, 5 atmosphères; pour chacun des grammes en plus de la charge métallique, une demi atmosphère. Ainsi, 8 atmosphères conviendront pour brûler un mélange de 2 grammes ferro-silicium et de 6 grammes de fer.

L'oxygène du commerce est le plus souvent assez pur. Des trois réservoirs que nous avons employés, pour nos recherches, deux ne contenaient pas d'anhydride carbonique en quantité sensible, le dernier en retenait une proportion correspondant à 0,1 mg. en carbone par atmosphère. Nous en avons tenu compte.

Nous avons aussi opéré la combustion des prises d'essai différentes d'un même échantillon, sous des pressions variées et trouvé des dosages concordants. Nous concluons que l'emploi de l'oxygène dans les conditions ci-dessus, ne saurait introduire d'erreurs dans nos dosages. D'autre part, la pression élevée de l'oxygène assure la combustion complète du carbone à l'état d'anhydride carbonique.

3°.—*Dosage Volumetrique du Carbone*

Le procédé que nous avons adopté consiste, on le sait, à laver les gaz de la combustion et à absorber l'anhydride carbonique dans une solution alcaline titrée, de volume déterminé. L'anhydride modifie le titre de la solution; la mesure de cette modification fixe la quantité de carbone cherché.

La solution alcaline dont le titre est connu est titrée à nouveau après le lavage des gaz, à l'aide d'une solution acide fixée par cette condition que 1 centimètre cube, par exemple, y corresponde à un milligramme de carbone. La différence des deux titrages donne donc immédiatement le carbone de la prise d'essai. Nous avons également employé des solutions cinq fois plus étendues.

Aussitôt après l'inflammation, l'instrument est mis en relation avec les flacons laveurs. Le lavage peut être conduit assez rapidement. Nous donnons cinq quarts d'heure à cette opération, quand l'appareil a été chargé à 5 atmosphères, y compris une demi-heure que nous avons reconnue utile pour balayer, à l'aide de l'air pur. les dernières traces d'anhydride carbonique. La vitesse du courant gazeux correspond à l'écoulement d'un litre en dix minutes.

Il importe qu'aucun élément étranger ne joigne son action à celle de l'anhydride carbonique. Nous avons donc contrôlé, dans les gaz, l'absence de composés de l'azote pouvant donner naissance éventuellement à un peu d'acide azotique.

Nous remarquerons aussi que les acides résultant de la combustion vive de certains alliages, comme l'acide vanadique et l'acide molybdique, restent, après la combustion, soit dans la capsule, soit sur les parois de l'instrument, condensés à l'état pulvérulent. Le courant gazeux ne saurait entrainer aucune trace de ces acides.

Nous ajouterons que la combustion du fil de fer servant d'amorce ne saurait apporter une surcharge appréciable. Cette amorce ne pèse ordinairement que quelques centigrammes: par gramme, elle ne renferme pas plus de 0,001 gr. de carbone.

Nous avons étudié, pour absorber l'anhydride carbonique, l'emploi de l'eau de baryte et l'emploi d'une solution de soude.

A.—Emploi de l'eau de baryte titrée par l'acide oxalique avec la phtalêine du phênol comme indicateur.

C'est la formule que nous avons appliquée à la détermination des diverses teneurs en carbone que nous avons publiées, au mois de Septembre dernier.

On obtient une solution de baryte de concentration suffisante en étendant un volume de solution saturée avec son volume d'eau distillée. La solution d'acide oxalique correspondant à un milligramme de carbone par centimètre cube, contient théoriquement par litre 10,5 gr. d'acide. L'acide du commerce n'est pas toujours rigoureusement pur. En vue de recherches précises, il convient donc de comparer l'acidité d'une solution d'acide sulfurique, titrée pondéralement. Cette comparaison fixe le poids exact d'acide oxalique à dissoudre. La solution dont nous avons fait usage contenait, dans ces conditions, 10 gr. 6 par litre.

Pour une expérience, on commence par fixer le titre de la solution de baryte employé. On répartit ensuite entre les barboteurs la quantité voulue de solution. Si l'on emploie 60 centimètres cubes par exemple, le premier barboteur reçoit 30 centimètres cubes, le second 20 centimètres cubes et le troisième 10. On complète le volume des barboteurs avec de l'eau distillée. Enfin, le lavage des gaz étant terminé, on ver se le contenu des barboteurs dans une fiole, on y ajoute l'eau du rinçage des barboteurs et on procède au titrage.

Les liqueurs sont faciles à préparer. L'emploi de la baryte met sous les yeux de l'opérateur l'absorption de l'anhydride sous forme de carbonate neutre de baryum. Le virage est très apparent.

Le mode de procédé que nous venons d'exposer doit être critiqué.

Nous avons vérifié que durant l'opération de titrage, la carbonatation par l'air des liquides était tout à fait négligeable, dans notre laboratoire.

Nous avons constaté une cause d'erreur, par excès plus grave. Cette cause d'erreur, suivant nos mesures, peut ajouter à la teneur en carbone environ 3% de cette teneur. La surcharge est peu importante avec des aciers à faible teneur en carbone elle ne doit pas être négligée avec les métaux plus carbonés.

Voici en quoi consiste cette cause d'erreur; la détermination du titre en présence de la phtaléine du phénol, donne lieu à un virage net et définitif quand la liqueur est limpide. C'est le cas où l'on se trouve quand on fixe le titre initial de la solution. Mais, quand la liqueur titrée contient en suspension du carbonate de baryum, précipité, c'est le cas à la fin de l'opération, les choses se passent autrement. On observe généralement, quelque temps après le virage présumé définitif, la réapparition de la couleur rosée. Il faut alors ajouter une goutte d'acide. Souvent, bientôt, nouvelle apparition de la couleur rosée demandant encore une goutte d'acide et le phénomène peut se prolonger assez longtemps, mettant en évidence que le tirage n'était pas définitif et qu'il restait encore des traces d'alcali à saturer. Cela provient de ce qu'un peu de baryte, adhérant au carbonate, se remet peu à peu en dissolution.

On peut, par ailleurs, obtenir un virage définitif, tout de suite. Il suffit de porter à l'ébullition la liqueur à titrer, de la refroidir pour éviter la formation d'oxalate acide de baryum et de procéder au titrage dans la liqueur froide.

Dans ces conditions, les chiffres obtenus sont exacts. Nous avons comparé quelques unes des teneurs déterminées, comme il vient d'être dit, aux résultats obtenus à l'aide du titrage à la soude décrit plus loin.

C'est ainsi que nous avons trouvé avec l'eau de baryte, pour un acier silicieux d'Imphy, 0,483 pour 100 de carbone.

La charge de la capsule avait compris 3 grammes d'acier, 6 grammes d'oxyde de plomb et 1 gramme de fer métallique interposé entre l'acier et l'amorce en fil de fer.

Titre de 50 c/mc de liqueur initiale en milligrammes de carbone 41,70

Titre de la liqueur après absorption 26,50

Différence 15,20

à déduire le carbone de 19 de fer métallique 0,7

Teneur en carbone de 3 grammes d'acier 14,50

Carbone de l'acier p. 100 0,483

Pour un essai, la capsule avait reçu 1 gramme du même acier, 3 grammes d'oxyde de plomb sans addition de fer métallique, le tirage, à l'aide d'une solution de soude a donné p. 100 0,485

La concordance ne laisse rien à désirer.

B.—Emploi d'une solution de soude titrée par l'acide sulfurique avec la phtaléine du phenol comme indicateur.

Le chauffage à l'ébullition et le refroidissement de la liqueur de baryte avant le dosage final, augmentent la durée de l'opération. Si le précipité formé est abondant, il reste fortement attaché aux parois de la fiole d'absorption et échappe ainsi en grande partie à l' épuisement par l'action de la chaleur. L'emploi d'une solution de soude évite ces inconvénients et permet d'arriver à des résultats très précis. Nous avons fait usage de cette dernière formule pour l'étude d'un grand nombre d'échantillons, notamment des ferro-alliages.

La concentration du liquide absorbant est dans certaines limites arbitraire, puisqu'elle dépend du degré d'approximation que l'on veut obtenir. De même, pour la solution acide.

La solution alcaline dont nous faisons usage contient 4 grammes de soude par litre. La solution sulfurique contient 4 gr. 083 d'acide, mesurée pondéralement avec les précautions habituelles et correspondant à 1 milligramme de carbone par centimètre cube. Ces solutions ne diffèrent pas de celles indiquèes par M. de Nolly, en vue de l'application de son procédé.

La conduite d'une expérience avec la solution de soude est ce que nous avons dit à propos de la solution de baryte.

La quantité de liqueur absorbante à employer, suivant la teneur présumée en carbone à doser, ressort des réactions mises en oeuvre, d'abord pour l'absorption de l'anhydride carbonique, ensuite pendant le titrage à l'acide sulfurique.

$$4\,(NaOH)+2CO_2=2\,(Na_2CO_3)=2H_2O$$
$$2\,(Na_2CO_3)+SO_4H_2=2\,(NaHCO_3)+Na_2SO_4$$

Un assez grand excès de liqueur alcaline est indispensable. Le virage est plus délicat à saisir que dans le cas de l'eau de baryte, et il est bon de revenir en arrière, avec un peu de solution de soude, jusqu'à réapparition de la couleur rosée.

Le lavage des tubes absorbeurs, avant le titrage se fait bien plus facilement dans le cas de la liqueur sodique que dans le cas de la liqueur de baryte plus ou moins chargée de carbonate précipité. Mais il faut se méfier de l'eau distillée, employée pour le lavage. Cette eau distillée peut retenir une petite quantité d'anhydride carbonique en dissolution et introduire une surcharge appréciable, si le volume d'eau de lavage employée est un peu considérable.

On annule aisément cette cause d'erreur assez faible, en procédant comme nous l'avons fait dans l'étude des ferro-alliages.

On fixait le carbone total d'une charge composée de la prise d'essai, d'un certain poids de fer et d'un peu d'oxyde de plomb. En opérant identiquement dans les mêmes conditions (même volume d'eau de lavage, même volume de solution alcaline etc.), on déterminait ensuite le carbone d'une charge composée seulement du même poids de fer et de l'oxyde de plomb. Il est clair que la différence des chiffres fournis par les deux expériences, correspondait au carbone de la prise d'essai du ferro-alliage, abstraction faite des incertitudes connues ou inconnues.

Enfin, nous avons tout récemment amélioré notre appareil. Aux deux ou trois tubes absorbeurs, nous avons substitué un tube absorbeur unique. Le tube est assez grand pour servir non seulement à l'absorption de l'anhydride carbonique, mais aussi au titrage. Il peut recevoir 100 centimètres cubes de solution alcaline correspondant à 0,2 mg. de carbone par c_3. Pendant le titrage, effectué avec une solution acide équivalente, la liqueur est agitée avec le courant d'air décarbonaté. L'emploi de ce tube dont nous donnons un dessin, évite tout lavage et tout transvasement, au bénéfice de la précision de la méthode. Une burette dont le robinet est également représenté sert à l'introduction de l'acide; elle porte à sa partie supérieure un renflement de 50 c_3 représentant la quantité de liqueur acide devant saturer l'excès de soude employé pour l'absorption.

IV.—Resultats d'Experiences

Nous avons appliqué la combustion sous pression au dosage du carbone d'un nombre important d'échantillons déjà analysés dans des laboratoires d'usines. La complaisance des Etablissements Métallurgiques nous avait fourni une collection si étendue et si variée d'acier et de ferro-alliages qu'il n'est pas possible de douter de la généralité de notre méthode.

Les chiffres que nous publions ci-après, sont les résultats de plus de deux cents combustions.

En plus de ces expériences, nous avons déterminé le carbone de quelques uns de nos échantillons d'aciers, en attaquant des prises d'essai de 10 grammes par le chlorure de cuivre et de potassium en dosant le carbone du gaz mis en liberté pendant l'attaque et en brulant sur la grille à analyse élémentaire le résidu carboné. Nous avons fait usage du chlorure de cuivre dans les conditions que l'un de nous a précisées au cours d'un travail récent.[1] Ce procédé est ainsi à l'abri de toute critique, et les chiffres qu'il nous a donnés peuvent être regardés, pour les métaux attaquables dans ces conditions comme un contrôle des teneurs obtenues suivant la nouvelle méthode.

Nous avons aussi recherché le carbone de quelques ferro-alliages par combustion directe, dans un courant d'oxygène, en nous servant de deux fours électriques, l'un pour brûler le métal, l'autre pour oxyder, par l'oxyde de cuivre, l'oxyde de carbone résultant de la combustion incomplète. Nous considérons ce procédé comme moins certain que le nôtre car il ne donne souvent qu'une oxydation incomplète et nous n'en avons retenu les indications qu'à titre de comparaison.

Deux tableaux réunissent les résultats de notre travail.

[1] Emploi des sels cuivriques pour l'analyse des fontes et des aciers par A Carnot et E. Goutal (Annales des Mines 1898).

E. Goutal compte-rendus 13 Avril 1909 et Etude des Gaz dégagés par l'action des sels cuivriques sur les aciers. (Revue de Métallurgie 1910, page 6.)

Le premier tableau indique l'analyse des divers échantillons étudiés, telle qu'elle nous a été communiquée par les usines; le deuxième tableau compare les teneurs en carbone déterminées à l'aide de la nouvelle méthode (colonne A) soit à l'aide du chlorure de cuivre (colonne D) ou du four électrique (colonne E) aux teneurs obtenues dans les laboratoires des usines (colonne B).

Notons que pour l'analyse des aciers les laboratoires industriels se servent en général de l'appareil Wiborgh et que pour l'analyse des ferro-alliages ils n'ont, jusqu'en ces derniers temps, eu à leur disposition que la combustion dans un courant d'oxygène. Les chiffres ainsi fixés figurent dans notre tableau.

A ces méthodes, il faut ajouter celle de M. de Nolly.

M. de Nolly, chef du service chimique de la Société des Forges et Aciéries de la Marine, nous a confié très obligeamment un assortiment complet de ferro-alliages déjà analysés suivant son procédé. Il a bien voulu aussi rechercher, avec son appareil le carbone de plusieurs échantillons que nous possédions déjà. Une colonne du deuxième tableau (colonne C) réunit les teneurs ainsi observées, complètant les éléments de comparaison que nous mettons sous les yeux du lecteur.

1er. TABLEAU

		C	Si	S	Ph	Mn	Elem. spéc.
Acier extra-doux	(Imphy)	0,060	0,350	0,022	0,025	0,19	
Acier extra-doux	(Trignac)	0,070	Traces	0,053	0,008	0,23	
Acier extra-doux	(Creusot)	0,110	0,012	0,018	0,016	0,40	
Acier de moulage	(Imphy)	0,190	0,310	0,033	0,024	0,30	
Acier demi-dur	(Creusot)	0,290	0,340	0,030	0,060	0,75	
Acier Nickel-Chrome	(Imphy)	0,290	0,380	0,043	0,046	0,80	Cr 1,03 Ni 31,36
Acier Silicieux spécial	(Imphy)	0,410	1,280	0,041	0,062	0,54	
Acier Silicieux spécial	(Imphy)	0,420	1,970	0,044	0,078	0,57	
Acier Nickel-Chrome	(Creusot)	0,350	0,093	0,040	0,008	0,22	Cr 2,00 Ni 31,90
Acier Dur	(St. Chamond)	0.950	0,260	0,014	0,073	0,60	
Acier Nickel-Chrome	(Imphy)	0.420	0,260	0,034	0,041	00,64	Cr 2,05 Ni 21,60
Acier Mangano-silicieux	(St. Chamond)	0,590	1,650	0,034	0,041	0,47	
Acier Chrome	(Creusot)	0,365	0,175	0,014	0,031	Trac.	Cr 5,10
Acier Tungstène	(Creusot)	0,510	0,116	0,030	0,013	0,12	Tu 9,99
Acier Trempant	(Imphy)	0,690	0,220	0,016	0,011	0,43	
Acier rapide	(Imphy)	0,630	0,260	0,006	0,011	0,04	Cr 5,07 Tu 19,65
Acier suédois	(Imphy)	0,960	0,020	0,022	0,034	0,14	
Acier extra-dur	(Creusot)	1,360	0,175	0,040	0,018	0,15	
Fonte Thomas	(Creusot)	2,746	0,280	0,082	1,870	2,12	
Fonte Martin acide	(Creusot)	3,650	2,074	0,043	0,068	3,50	
Fonte Martin basique	(Creusot)	3,550	1,280	0,056	0,068	1,46	
Silico-spiegel	(Creusot)	2,420	8,710	0,023	0,110	17,98	
Ferro-manganèse	(Creusot)	5,830	0,930	0,027	0,270	81,94	
Ferro-silicium	(St. Chamond)	0,120	74,80				
Ferro-silicium	(Creusot)	0,140	26,200	0,018	0,130	0,25	
Chrome aluminothermique	(St. Cham'd.)	0,180					Cr 96,75
Ferro-Chrome	(Giffre)	0,750					Cr 67,00
Ferro-Chrome	(Giffre)	1,440					Cr 70,19

TABLEAU—*Continué.*

		C	Si	S	Ph	Mn	Elem. spéc.
Ferro-Chrome	(Giffre)	3,400					Cr 73,30
Ferro-Chrome	(Giffre)	5,800					Cr 73,37
Ferro-Chrome	(Creusot)	6,530	0,600	0,021	0,036	Trac.	Cr 67,10
Ferro-Chrome	(St. Chamond)	10,640					Cr 68,80
Ferro-Tungstène	(Creusot)	0,870	0,093	0,015	0,003	0,12	Tu 85,28
Ferro-Vanadium	(St. Chamond)	0,320					Va 41,00
Ferro-Vanadium	(St. Chamnod)	3,810					Va 43,80
Ferro-Molybdène	(St. Chamond)	4,090					Mo 74,22
Ferro-Titane	(St. Chamond)	0,100					Ti 20,40
Ferro-Aluminium	(St. Chamond)	0,180					Al 16,75

2e. TABLEAU

		A	B	C	D	E
Acier extra-doux	(St. Chamond)	0,044	0,045	0,044		
Acier extra-doux	(Trignac)	0,060	0,070			0,060
Acier extra-doux	(Imphy)	0,070	0,060			
Acier extra-doux	(Creusot)	0,115	0,110			
Acier de moulage	(Imphy)	0,194	0,190			
Acier demi-dur	(Creusot)	0,303	0,290		0,303	
Acier Nickel-Chrome	(Imphy)	0,336	0,290			
Acier Nickel-Chrome	(Creusot)	0,370	0,350			
Acier silicieux-spécial	(Imphy)	0,485	0,410		0,475	
Acier silicieux-spécial	(Imphy)	0,492	0,420	0,530		
Acier Nickel-Chrome	(Imphy)	0,510	0,420			0,500
Acier Tungstène	(Creusot)	0,521	0,510			
Acier Chrome	(Creusot)	0,570	0,365		0,570	
Acier mangano-silicieux	(St. Chamond)	0,600		0,590		
Acier rapide	(Imphy)	0,680	0,630	0,700		
Acier trempant	(Imphy)	0,714	0,690			
Acier dur	(St. Chamond)	0,990	0,950			0,980
Acier suédois	(Imphy)	1,010	0,960			
Acier extra-dur	(Creusot)	1,365	1,360		1,377	
Fonte Thomas	(Creusot)	2,950	2,746			
Fonte Martin basique	(Creusot)	3,910	3,550	3,990	3,918	
Fonte Martin acide	(Creusot)	3,930	3,650		3,900	
Silico spiegel	(Creusot)	2,580	2,420		2,575	
Ferro-Manganèse	(Creusot)	5,810	5,830			
Ferro-silicium	(St. Chamond)	0,198		0,120		0,11
Ferro-silicium	(Creusot)	0,183	0,140	0,130		0,13
Chrome aluminothermique	(St. Chamond)	0,180		0,180		
Ferro-Chrome	(Giffre)	0,810	0,750	0,745		
Ferro-Chrome	(Giffre)	1,530	1,440			
Ferro-Chrome	(Giffre)	3,530	3,400			
Ferro-Chrome	(Giffre)	6,200	5,800			
Ferro-Chrome	(Creusot)	6,700	6,530	6,665		
Ferro-Chrome	(St. Chamond)	10,560		10,640		9,73
Ferro-Tungstène	(Creusot)	0,890	0,870	0,890		
Ferro-Vanadium	(St. Chamond)	0,317		0,320		
Ferro-Vanadium	(St. Chamond)	3,650		3,810		3,650
Ferro-Molybdène	(St. Chamond)	3,670		4,090		3,700
Ferro-Titane	(St. Chamond)	0,060		0,100		
Ferro-Aluminium	(St. Chamond)	0,785		0,950		

Les teneurs en carbone que nous avons trouvées sont voisines de celles des usines, dans les aciers ordinaires. Mais, elles sont souvent plus élevées que celles-ci, dans les aciers spéciaux et particulièrement dans les aciers silicieux. D'autre part, la nouvelle méthode a donné des chiffres coïncident, autant que l'on pouvait le souhaiter, avec ceux des expériences de contrôle (emploi de chlorure de cuivre). Il résulte de là que l'on doit tenir pour suspect le procédé de Wiborgh, en usage dans les usines, puisque ce procédé ne fournit pas dans tous les cas des chiffres exacts. Il résulte, aussi, de notre travail que la combustion sous pression apporte dans la comparaison des teneurs en carbone des aciers, depuis les moins carbonés jusqu'aux aciers les plus durs, une précision incontestable. Nous avons constaté que l'on peut, sans difficulté, obtenir des chiffres ne s'écartant pas l'un de l'autre de plus de 0,01 pour cent, pour le même acier essayé dans des conditions différentes.

Pour les ferro-alliages, nos chiffres diffèrent souvent et sensiblement des chiffres indiqués par les usines, tantôt par défaut, tantôt par excès. Le résultat était, en quelque sorte, prévu.

Nous croyons que l'emploi de la combustion sous pression aura pour effet de substituer, dans la détermination du carbone des ferro-alliages, beaucoup de rigueur et de simplicité à l'incertitude et à la complication des autres méthodes.

THE ACTION OF BOILING SULPHURIC ACID ON PLATINUM

By Le Roy W. McCay
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In the course of my work on the analysis of tin-antimony alloys, which involves the use of hydrofluoric as well as nitro-hydrofluoric acid, I find it necessary to heat concentrated sulphuric acid in a platinum dish not only to moderate fuming, but even to boiling. The sulphuric acid is heated to moderate fuming to expel the hydrofluoric and nitric acids, and the acid is boiled in the presence of a piece of sulphur to reduce any antimonic oxide which may be in the solution to antimonious oxide.

Now although I have never found that the precipitates of antimonious and stannic sulphides contain platinum, it seemed advisable to make a careful study of the action of boiling sulphuric acid on the platinum dish used, particularly since I have been unable to find anything concerning the matter in the standard works on analytical chemistry[1]. As a matter of fact, boiling concentrated sulphuric acid does dissolve platinum[2]. This was first shown by Scheurer-Kestner and Hasenclever, who have made valuable observations on the rate at which the stills are attacked by the sulphuric acid, in the preparation of the ordinary oil of vitriol containing from 92–94 per cent H_2SO_4, as well as in the preparation of high grade acids containing from 97–98 per cent H_2SO_4. The loss in platinum suffered by the stills is from eight to ten times greater in the latter than in the former case. According to Scheurer-Kestner boiling concentrated sulphuric acid free from nitrous acid has no action on platinum. For the figures given I must refer the reader to the original articles[3].

[1] Such as those of Rose, Fresenius, Classen and Treadwell.

[2] Conroy, J. Soc. Chem. Ind. 1903, V. 22, 465. Delèphine, Compt. Rend. 1905, T. 141, p. 886 and 1013. Quennessen, Compt. Rend. 1906, T. 142, p. 1341. Delèphine, Compt. Rend. 1910, T. 150, p. 104.

[3] Scheurer-Kestner, Hofmann's Report to the Juries, 1862, p. 16. Compt. Rend. T. 81, p. 892; T. 86, p. 1082; T. 91, p. 59. Hasenclever, Hofmann's Bericht Für 1875, B. I. p. 188. See also G. Lunge, Sulphuric Acid and Alkali, Vol. I, pt. 2, 875–876.

The dish used by me holds comfortably 200 cc. It has been in use off and on for some twenty years, is of the best material and excellent workmanship. Before each experiment it was thoroughly cleaned and glowed. The sulphuric acid contained no nitrous acid, and was from 95–96 per cent pure. Heated to moderate fuming for from ten to fifteen minutes, it had no perceptible action on the platinum. When, however, the acid was heated to strong fuming, but not to boiling, for the same length of time, an appreciable amount of the metal dissolved.

10 cc. Conc. H_2SO_4 were heated in the uncovered dish to moderate fuming for ten minutes, the acid remaining was diluted to 300 cc., the solution heated to boiling and saturated with hydrogen sulphide. The flask containing the solution was then corked and allowed to stand for several days. Nothing separated out, barring a little white sulphur.

The experiment was repeated with 25 cc. acid. Here the dish was covered with a clock glass, and the acid heated to a point just below boiling for fifteen minutes. Since the precipitate obtained with hydrogen sulphide was dark in color, I filtered it off and ignited it strongly. There remained 0.0003 g. which on further examination proved to be platinum.

Since in my work on the tin-antimony alloys I never use more than 10 cc. of the concentrated acid, and since heating to moderate fuming for fifteen minutes is sufficient to expel the nitro-hydrofluoric acid, no further study of this phase of the matter appeared necessary.

When the acid was heated to boiling and kept boiling for some time it became yellow[1]. Two experiments were made to determine the exact amount of platinum dissolved in one hour. In each case the dish was covered with a clock glass, the acid heated to gentle ebullition over a free flame, and the boiling continued for

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[1] Fischer rectified some oil of vitriol by distilling it from a glass retort containing little pieces of platinum. The metal became crystalline in appearance, and the residue was brownish yellow from the formation of platinic sulphate. Kastner's Archive B. 14, p. 149.

According to Deléphine there are two sesquioxyplatinic sulphuric acids formed when boiling concentrated sulphuric acid acts on platinum—(1) Pt $(OH)_2$ (SOH_4) $+$Aq. (Acid of Blondel) which is yellow, and (2) Pt (OH) SO_4H_2 $+$Aq. which is reddish brown. Both are derivatives of trivalent platinum. Compt. Rend. T. 150, p. 104–106.

the time specified. What remained was strongly diluted with water, the solution heated to boiling and saturated with hydrogen sulphide. The platinic sulphide was allowed to settle completely before it was filtered off.

(1) 10 cc. conc. H_2SO_4 dissolved 0.0038 g Pt.
(2) 20 cc. conc. H_2SO_4 dissolved 0.0077 g Pt.

Practically, then, twice as much platinum was dissolved in the second as in the first case. The inner surface of the dish just above the tip of the flame was spotted in both cases, the spots being dull in appearance and about the size of pin heads. Indeed, I noticed that these spots always appeared, it mattered not what the conditions were under which the acid was boiled.

Tin-antimony alloys rich in lead — containing 60 per cent lead and upwards—are not completely decomposed by boiling concentrated sulphuric acid. The lead sulphate remaining is always gray, and contains several milligrams of antimony. An excellent solvent for such alloys is warm dilute nitric acid (1:4) to which ten to fifteen drops of 48 per cent hydrofluoric acid have been added (platinum dish). The nitric acid, however, converts some of the antimony from the lower to the higher stage of oxidation, which must be reduced to the former condition before the separation of the antimony from the tin in hydrofluoric acid solution with hydrogen sulphide can be effected. After adding concentrated sulphuric acid to the solution, evaporating on the water bath and heating to *moderate* fuming on the sand bath for fifteen minutes, to expel all nitro-hydrofluoric acid, the cover of the dish is removed, a piece of purest sulphur weighing about a gram is dropped in, the cover replaced, the acid heated to gentle ebullition, and kept in this state for half an hour. The reduction to the "-ous" condition is complete:

(a) $2H_2SO_4+S=3SO_2+2H_2O$
(b) $Sb_2O_5+2SO_2=Sb_2O_3+2SO_3$

The lead sulphate is then removed, and the antimony separated from the tin according to the direction given in my paper on the analysis of tin-antimony alloys[1].

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[1] Jour. Amer. Chem. Soc. V. 32, p. 1241, 1910.

When, now, we consider the fact that boiling concentrated sulphuric acid has such a marked solvent action on platinum, the question arises, why is it that the antimonious sulphide or, at all events, the stannic sulphide, contains no platinum? I have experimented largely in regard to this matter, and have convinced myself that it is the reducing action of the sulphur dioxide which counteracts the tendency on the part of the hot sulphuric acid to oxidize the platinum. Conroy[1] noticed this inhibitive action of sulphur dioxide, and he also attributes it to the reducing power of the gas. Concentrated sulphuric acid in the presence of excess of sulphur can be boiled for hours in a platinum dish, and yet no metal will be detected in *the acid* which remains. After two hours of boiling *the sulphur globules* contain platinum, but the quantity is exceedingly small. Since on cooling to room temperature they stick very fast to the dish, and a number of sharp blows are necessary to dislodge them, it occurred to me at first that the platinum they contain might be a tiny bit torn off mechanically from the dish. For reasons given below, however, it is certain that platinum is dissolved by the hot acid, but reduced later at the surfaces of the globules, where the concentration of the sulphur dioxide is a maximum. The reduced metal is then absorbed by the sulphur. The surfaces of the globules, even after long standing, are dark brown, but the dark coating is extremely thin, for a gentle scratch is sufficient to disclose the pure yellow color of the underlying sulphur. When a globule is heated in a porcelain crucible until all the sulphur has been expelled, the metal which remains is not in the form of little black particles, but in the form of either an exceedingly thin film or a spongy mass. The residues are insoluble in concentrated hydrochloric acid, but slowly and completely soluble in a little warm aqua regia. When the latter has been removed by evaporation on the water bath, and the yellow residue dissolved in the smallest possible amount of water, the addition of ammonium chloride and a few drops of alcohol to the solution occasion in time a very small but distinct precipitate of ammonium chlorplatinate. The platinum in these solutions, even when they

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[1] l. c. The inhibitive action of sulphur dioxide had been observed by me several months before I read Mr. Conroy's paper. Scheurer-Kestner had already observed that acid containing sulphur dioxide has less solvent action on the stills than acid free from this compound. Compt. Rend. T. 81, p. 892.

have been strongly diluted, can be more readily detected by adding some stannous chloride solution. The yellow or reddish yellow color produced is very characteristic[1]. In carrying out the experiments care was taken to have a considerable excess of sulphur always present, and if, on long boiling, the globule appeared to be markedly reduced in size, the cover of the dish was shoved to one side and another piece of sulphur dropped in. In the first two experiments I used 1 gram and in the last four 2 grams sulphur. The acid was boiled as gently as possible.

	H_2SO_4	Boiled	Pt in Globules	Pt in Acid
1	10 cc.	½ hour	unweighable	0
2	20 cc.	1 hour	unweighable	0
3	30 cc.	2 hours	0.0002 g.	0
4	50 cc.	2 hours	0.0002 g.	0
5	50 cc.	6 hours	0.0002 g.	0
6	50 cc.	6 hours	0.0002 g.	0

I repeated experiment 4, using about 1½ grams of sulphur and heating the acid to very brisk boiling. At the end of the two hours the globule was reduced to the size of a small pea. It contained only 0.0002 g. of platinum, but there was a dark deposit in the dish, which proved to be the metal and which weighed 0.0006 g. The spots on the bottom of the dish were larger and darker than those noticed in the other experiments. Some of them were perfectly black. They were composed of finely divided platinum which I found could be removed by rubbing the bottom of the dish with a small piece of damp filter paper. The residue left on burning the paper was dissolved and the solution tested for platinum with stannous chloride. I was also able to detect traces of platinum in the filtrate from this deposit. Under these circumstances, then, practically a milligram of platinum was dissolved by the acid, only part of which was absorbed by the sulphur. This experiment proves that, to protect the platinum, a high concentration of sulphur dioxide is necessary, a condition which can only be fulfilled by having plenty of sulphur present from the beginning.

I have found that results almost identical with those given in the above table are obtained when a current of sulphur dioxide

[1] Woehler. Zeit. Chem. Ind. Koll. 1910, B. 7, 243–249.

gas is kept bubbling rapidly through the boiling acid[1]. The sulphur dioxide was introduced through a tube of hard glass, passed through the opening between the lip of the dish and the glass cover, and shoved down until the end under the acid was a few millimeters above the bottom of the dish. The passage of the gas was continued during the period of boiling. After removing the flame, and permitting the acid to cool down until it was fuming moderately, the current of SO_2 was shut off, the cover removed and the whole system left until it had come to room temperature. In every case the acid remaining was limpid and colorless. The strongly diluted solutions were heated to boiling and the platinum precipitated with hydrogen sulphide as platinic sulphide. In all cases, however, the weights of the ignited precipitates were high. After digesting them with a little boiling concentrated hydrochloric acid for fifteen minutes, and then washing them carefully in the crucible by decantation, the following results were obtained:

H_2SO_4	Boiled	Pt in Acid
50 cc.	1 hour	unweighable
50 cc.	2 hours	.0004 g.
50 cc.	2 hours	.0003 g.
50 cc.	2 hours	.0003 g.

The washings were colorless and gave no reaction for platinum with stannous chloride. The purification of the platinum with hot concentrated hydrochloric acid was found to be necessary because the weight of the ash of the filter paper used was incorrectly given. A paper which should yield only 0.0001 g. ash, gives as much as 0.0003 g. The ash is almost completely soluble in concentrated hydrochloric acid, the residue being undoubtedly silica. The following experiment would indicate that the results are still a trifle high: 50 cc. of the acid, through which a current of sulphur dioxide was kept bubbling, were boiled gently for two hours in the covered dish. The gas current was then shut off, a piece of pure sulphur weighing two grams dropped into the dish and the boiling continued for half an hour. The cover was now removed, to facilitate the escape of the sulphur dioxide, and the

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[1] Compare the results of Conroy. 1. c.

whole allowed to cool to room temperature. I could detect no platinum in the acid, and the sulphur globule contained only 0.0002 g. The metal dissolved in the first part of the experiment seems to have been reduced in the second part at the surface of the sulphur, where the concentration of the SO_2 is a maximum, and then absorbed by the molten globule. Quennessen[1] found that concentrated sulphuric acid and platinum heated together in an evacuated tube to 400 degrees react to a considerably less extent than they do when heated freely exposed to the air. He concludes that it is the oxygen of the air which occasions this increase in the solvent action of the hot acid. The tube when opened contained sulphur dioxide, whose presence Delèphine accounts for thus:

$$2\ Pt + 7H_2SO_4 \leftrightarrows 2\ Pt\ (OH)\ (SO_4H_2) + 3SO_2 + 4H_2O$$

He regards the reaction as a reversible one, and calls in question the correctness of Quennessen's conclusion. My experiments in regard to this matter are in agreement with those of Delèphine. If air (oxygen) must be present in order that the boiling acid may attack the platinum, then any indifferent gas, such as nitrogen or carbon dioxide, should act in a protecting manner. To test this point I made two experiments, using a current of carbon dioxide in the place of one of sulphur dioxide. The solvent action of the boiling acid, however, was not in the least retarded, for in twenty minutes it was faintly yellow:

H_2SO_4	Boiled	Pt in Acid
50 cc.	1 hour	0.0129 g.
50 cc.	1 hour	0.0122 g.

The inactivity of the boiling acid must be due then to the reducing action of the sulphur dioxide which in some way counterbalances the oxidizing tendency of the hot acid. We may explain the matter in this way:

$$H_2SO_4 \leftrightarrows H_2O + SO_3$$

Assume that at the temperature at which the hot acid commences

[1] l. c.

to attack the platinum a very small but appreciable dissociation of the anhydride occurs:

$$2SO_3 \leftrightarrows 2SO_2 + O_2$$[1]

If we attribute the oxidation of the platinum to this oxygen, the inhibitive action of the sulphur dioxide would consist in its high active mass repressing the dissociation of the sulphuric anhydride. Conroy[2] found that carbon and arsenious oxide also serve as protectors. The action of the carbon is of course analogous to that of sulphur:

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O$$

Conroy noticed too that the inhibitive action of the arsenious oxide falls off gradually, and such has been my experience. Some experiments carried out with varying amounts of arsenious oxide and boiling sulphuric acid go to show that this is due to the arsenious being oxidized to arsenic oxide. For instance, 20 cc. of concentrated sulphuric acid containing 0.5 g. arsenious oxide were heated to boiling in the covered platinum dish for one hour. The cover was then removed, the flame lowered, and the heating continued until most of the acid had been expelled. A portion of the diluted residue gave no reaction for platinum with stannous chloride. The rest, rendered ammoniacal and treated with magnesia mixture, yielded a heavy precipitate of ammonium magnesium arseniate[3]. Here the oxygen from the dissociated sulphuric annhydride is taken up as fast as it is formed by the arsenious oxide, thus shielding the platinum:

$$As_2O_3 + O_2 \rightarrow As_2O_5$$

The behavior of antimonious oxide is similar. It does not, however, protect the platinum as effectively as sulphur dioxide and arsenious oxide:

$$Sb_2O_3 + O_2 \rightarrow Sb_2O_5$$

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[1] Knietsch has shown that, in the contact process, the maximum union of SO_2 and O_2 (excess) takes place at a temperature of about 425 degrees, but that a back action sets in when this temperature is overstepped. Ber. B. 34 (1901), 4069. When no oxygen is present, other things being equal, one would expect the reverse action to set in at an even lower temperature.

[2] l. c.

[3] When a solution of arsenious oxide in concentrated sulphuric acid is boiled for an hour in a covered *porcelain* dish, no perceptible amount of the oxide is converted into arsenic acid.

My experimental work then, along with that done by Conroy, explains why it is that in the previously mentioned process for reducing antimonic to antimonious oxide, in my hydrofluoric acid method for separating antimony and tin, no platinum is dissolved. And here I should like to state that the process referred to for reducing antimonic acid applies equally well to arsenic acid solutions. The protecting action of sulphur dioxide naturally suggests the possible use of this gas in the preparation of high grade acids in the platinum stills. Most of the sulphur dioxide escapes as the hot acid cools, and what remains could be expelled by heating. Perhaps too, any possible loss of platinum in the parting of silver-platinum alloys with boiling concentrated acid could be avoided by having a piece of sulphur present from the beginning.

SUMMARY

(1) Boiling concentrated sulphuric acid dissolves platinum in considerable amounts.

(2) Since the platinum dissolves fully as readily when the interaction takes place in a current of an indifferent gas, such as carbon dioxide, as it does when the experiment is made in air, the oxygen of the latter cannot be concerned in the change.

(3) The presence of excess of sulphur dioxide, generated by the interaction of the hot acid and sulphur or carbon, or introduced through a tube into the boiling acid, inhibits almost entirely its solvent action. Sufficient arsenious oxide dissolved in the acid likewise serves to protect the platinum, and even antimonious oxide manifests marked protective powers.

(4) If we assume that at the temperature of attack there is a slight but appreciable dissociation of sulphuric anhydride into sulphur dioxide and oxygen, and that it is this oxygen which is responsible for the solution of the platinum, the role played by the reducing agents would seem to consist (1) in a repression of the dissociation of the sulphuric anhydride on account of the high concentration of the sulphur dioxide, and (2) in the arsenious and antimonious oxides consuming the oxygen as fast as it is set free, arsenic and antimonic oxides being formed.

THE DETECTION AND ESTIMATION OF EXCEEDINGLY MINUTE QUANTITIES OF CARBON DIOXIDE

By Herbert N. McCoy and Shiro Tashiro
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The study of carbon dioxide has been so eminently connected with various forms of human activity that methods for its accurate quantitative determination have been highly developed in spite of the natural difficulties. Nevertheless, none of the various methods of analysis can be used for very minute quantities of carbon dioxide. The well known titration method of Pettenkoffer, later modified by Smith, Schulze, Blochmann, and Letts and Blake[1], can be used only when the amount of carbon dioxide is as great as that contained in a liter of natural air. A more delicate method consists in the determination of decrease in volume which takes place when the carbon dioxide contained in air absorbed in alkali. This method, originally invented by von Humboldt in 1797, has been modified and improved by Williamson and Russell[2], Pettersson, and Palmquist[3], Sondén[4], and finally so perfected by Haldane[5], that one can detect as small an amount of carbon dioxide as that contained in 15 to 18 cc. of natural air. This amount would be about 0.005 cc. of pure carbon dioxide or about 10^{-5} gram.

The development of the method here described was the result of the desire on the part of one of us (T) to find a means of detecting and estimating still smaller quantities of carbon dioxide than the minimum possible by known methods. The other of us had worked on several problems[6] involving the accurate de-

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[1] A very complete bibliography of the literature up to 1899 is given by Letts and Blake, Sci. Proc. Roy. Dublin Soc., 1899–1903.

[2] Jour. Chem. Soc. London *2*, 238 (1864).

[3] Ber. der. deut. Chem. Ges., *20*, 2129 (1887).

[4] Zeitschr. Anal. Chem., *26*, 593 (1887).

[5] Jour. of Hygiene, *1*, 109 (1901).

[6] McCoy, Amer. Chem. Jour., *29*, 437 (1903).
McCoy and Smith, Jour. Amer. Chem. Soc., *33*, 468 (1911).
McCoy and Test, *Ibid.*, *33*, 473 (1911).

termination of carbon dioxide and in the work with Mr. Smith had studied the solubility product of barium carbonate. Some considerations, based upon a knowledge of this constant, show that one ought to be able to detect very much smaller quantities of carbon dioxide than is possible by means of any of the methods described in the literature. The solubility product of barium carbonate was found to be 8.1×10^{-9}. This indicates that the amount of carbon dioxide required to saturate one cc. of decinormal barium hydroxide with carbonate would be only 3.5×10^{-9} gram or about the amount contained in 0.005 cc. of natural air. If a larger amount of carbon dioxide were added to 1 cc. of barium hydroxide solution it should separate as solid barium carbonate. This leads to the conclusion that the failure to detect minute quantities of carbon dioxide by means of barium hydroxide is not due to the appreciable solubility of the carbonate. Now, it is very easy by the aid of a simple lens, to see a white particle 0.01 mm. in diameter. If the particle were circular and 0.01 mm. thick, its volume would be 7×10^{-8} cc. and if the substance were barium carbonate, of density 4.3, its mass would be 3×10^{-7} gram. This would represent a little less than 1.0×10^{-7} gram of carbon dioxide; which is the amount contained in about 1/6 cc. of natural air. The method here described actually allows us not only to detect this very minute quantity of carbon dioxide, but also to estimate amounts of this order of magnitude with considerable accuracy.

The apparatus, which is made of glass, is shown in the accompanying figure. The bulb has a capacity of about 25 cc.; the tubes are thick-walled capillaries of about 1 mm. internal diameter excepting the upturned tube inside the bulb, which should be rather thin walled, especially at *F* where it is widened to an internal diameter of about 2 mm. It is important that the glass of which this latter tube is made should be of such quality that it is not readily attacked by barium hydroxide solution. One tube of the three-way stop-cock *B* is connected to a reservoir of carbon dioxide-free air[1], the other to the gas burette which

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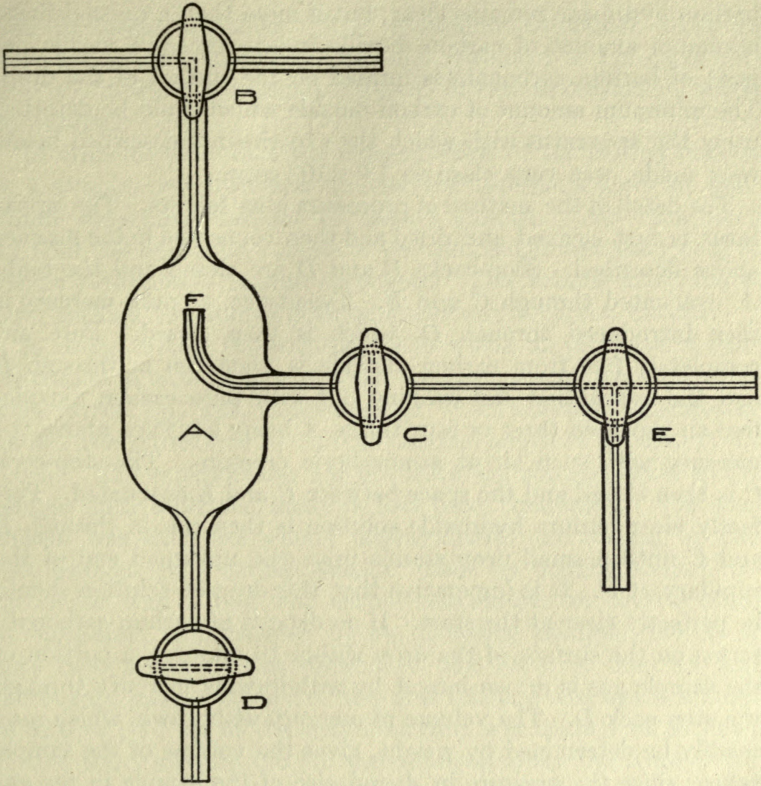
[1] Air cannot be freed completely from carbon dioxide by passing it through wash bottles. In our work, carbon dioxide-free air is prepared by shaking air with 20% sodium hydroxide in a tightly stoppered carboy, fitted with suitable tubes. When this air is to be used, it is displaced by running in a solution of sodium hydroxide.



contains the sample of gas to be tested or analysed. One tube of the three-way stop-cock *E* is connected with a bottle containing a perfectly clear solution of barium hydroxide of about decinormal concentration; the other tube is connected to a pump capable of giving a vacuum of 25 or 30 mm. of mercury.

In detection or estimation of carbon dioxide with this apparatus, about 20 cc. of pure mercury is brought into *A* and the remaining 5 cc. of space filled with carbon dioxide-free air. A drop of perfectly clear solution of barium hydroxide is formed above the end of the capillary at *F*. A known volume of the sample gas is then run into *A* by withdrawing mercury through *D*. If the sample gas run in is free from carbon dioxide, the drop of barium hydroxide remains clear; but if more than a quite definite minimum amount of carbon dioxide is introduced, a visible deposit of barium carbonate is formed on the surface of the drop. The minimum amount of carbon dioxide which could be detected using the apparatus with which the experiments described below were made, was very close to 1.0×10^{-7} gram.

The detail of the method of procedure is as follows. The apparatus is first cleaned and dried and then connected in the manner above described. Stop-cocks *B* and *D* are closed and the bulb, *A*, evacuated through *C* and *E*. Twenty cc. of pure mercury is then introduced through *D*, which is then closed. Pure air, completely free from carbon dioxide is then run in through *B* and the evacuation and washing out with pure carbon dioxide-free air repeated three or four times, *A* being left filled above the mercury with such air at atmospheric pressure. The stop-cock *C* is then closed and the space between *C* and *E* evacuated. Perfectly clear barium hydroxide solution is then run in through *E* and *C* until a small drop stands upon the upturned end of the capillary at *F*. It is imperative that this drop of solution should be perfectly clear at the start. If no deposit of barium carbonate forms on the surface of the drop within 10 minutes, a portion of the sample gas is drawn into *A* by withdrawing mercury through the stop-cock *D*. The volume of mercury withdrawn, which may readily be determined by weight, gives the volume of the sample taken; since the pressure in *A* and also of the sample in the gas burette is kept equal to atmospheric pressure during the transfer.

One now watches the surface of the drop at *F* with a lens to see whether any formation of barium carbonate occurs within ten minutes. In our experiments with the apparatus here described, we have repeatedly introduced accurately known quantities of carbon dioxide (always highly diluted) into *A* in the manner just described and as a result have found, with remarkable regularity, that 1.0×10^{-7} gram carbon dioxide is the minimum amount which will cause a formation of barium carbonate within a period of 10 minutes. Smaller amounts of carbon dioxide give no visible result[1]; while larger amounts give a deposit more rapidly

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[1] Since the minimum detectable amount of carbon dioxide, 1.0×10^{-7} gram, gives a quantity of barium carbonate which is easily seen with a lens; while

and in larger quantity. The minimum detectable amount, 1.0×10^{-7} gram is about the amount contained in 1/6 cc. of natural air, in which we assume 3.0 parts of carbon dioxide in 10000 by volume.[2]

In order to determine the concentration of the carbon dioxide in a sample, one must first find for the apparatus used the minimum detectable amount of carbon dioxide. One then finds by trial the minimum volume of the sample gas necessary to give visible formation of barium carbonate. This volume must, therefore, contain the known detectable amount of carbon dioxide.

In order to test the accuracy with which an estimate of concentration of carbon dioxide could be made many determinations were carried out with samples of air which contained accurately known concentrations of carbon dioxide prepared by Dr. F. C. Koch.[3] The experimenter did not learn the concentration of the sample until after the analysis had been completed. The conclusion was therefore wholly unprejudiced. In making up the test samples, pure carbon dioxide, made by heating sodium bicarbonate, was diluted with carbon dioxide-free air several times in succession, as illustrated by the following example: 5.5 cc. of pure carbon dioxide was diluted to 52.0 cc. over mercury and thoroughly mixed; 5.5 cc. of the first mixture was again diluted to 52.0 cc.; 7.1 cc. of the second mixture was diluted to 50.7 cc.; of this third mixture 5.6 cc. was received from Dr. Koch. We diluted this a fourth time to 255.6 cc. to form the mixture to be analyzed. The following observations were made: 0.5 cc. introduced into the apparatus produced no precipitate in 10 minutes; 0.5 cc. more of the same sample gave no precipitate in another interval of 10 minutes; 0.5 cc. more (a total of 1.5 cc.) was then run into the bulb. In 6 minutes the first evidence of a precipitate appeared on the surface of the drop at *F* and in 8 minutes the precipitate was well developed. Since the amount of carbon dioxide required to give a precipitate is 1.0×10^{-7} gram, this

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a smaller amount of carbon dioxide produces no visible result, it seems probable, in the latter case, that supersaturation must exist and that *no solid barium carbonate is formed.*

[2] Letts and Blake, *loc. Cit.*

[3] For his valuable assistance in this work, we wish here to express to Dr. Koch our best thanks.

amount is contained in 1.5 cc. of the sample or 1 cc. contained 6.7×10^{-8} gram, of carbon dioxide. The amount of carbon dioxide actually contained in the sample was $\frac{5.5 \times 5.5 \times 7.1 \times 5.6}{52 \times 52 \times 50.7 \times 255.6}$ cc. $= 6.2 \times 10^{-8}$ gram. In six such determinations, all made with samples the concentrations of which were unknown to the experimenter at the time of the analysis, the results given in the following table were obtained.

Volume of sample required to give a precipitate	Weight of Carbon dioxide in one cc.	
	Found	Taken
1.0 cc.	1.0×10^{-7} gram	0.92×10^{-7} gram
0.5	2.0	2.3
0.55	1.82	1.83
1.5	0.67	0.62
2.25	0.45	0.45

Since one cc. of natural air contains 5.4×10^{-7} gram of carbon dioxide, it will be seen that each sample in the above table contains considerably less carbon dioxide than natural air.

The application of this method for biological purposes has been made by one of us (T) and will be described in the Bio-Chemical section of this Congress.

A NEW METHOD OF TITRATION OF ARSENIC ACID

By Alan W. C. Menzies and Paul D. Potter
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It is well known that arsenic acid, when titrated with sodium hydroxide, appears to act as a dibasic or as a monobasic acid according as the indicator is phenolphthalein or methyl orange, the latter indicator being the more sensitive towards hydroxyl ion. In neither case, however, is the endpoint as sharp as could be desired; so that an accuracy of one part in 300 can be attained only by the help of good light, a comparison tint, patience and practice. In these circumstances, and as many titrations of arsenic acid were in prospect, it seemed desirable to cast about for possible improvements in the method.

Since both the too early appearance and the indistinctness of the secondary endpoint are due to the feebleness of the ionization $H_2AsO_4' \rightarrow H^+ + HAsO_4''$, it was evident that matters could be improved by replacing the acid $H^+ - HAsO_4''$ by a strong acid such as hydrogen chloride. Reference to the literature showed that $BaHAsO_4$ is very little soluble, so that such replacement promised to be fairly complete if sufficient barium chloride were added to the solution. Other circumstances favoring the use of this precipitant were the high degree of ionization of barium hydroxide and the obvious impossibility of a concentration of $HAsO_4''$ ion approaching that required to yield a H^+ion concentration that should prejudice the turning pink of phenolphthalein.

Preliminary experiments, in which solution of barium chloride was first added to the arsenic acid, having shown a marked sharpening of the endpoint with phenolphthalein, plans were made for a more careful study of the best conditions for titration. For this purpose two solutions were prepared: one containing 37.010 grams of arsenic acid (H_3AsO_4) per liter, and the other containing enough barium chloride to yield a solution saturated with respect to $BaCl_2, 2H_2O$ at a temperature a trifle below that of the room. Of the latter solution 10 cc. is a little more than is necessary to form $BaHAsO_4$ with the arsenic acid in 50 cc. of the former solution. The following data were obtained using a sodium hydroxide solution with a normality factor of 0.6513 as determined against Iceland spar weighed in air.

TABLE I

No.	C.C. H_3AsO_4. Solution	C.C. $BaCl_2$ Solution	Total Volume In C.C.	C.C. NaOH Solution
I	50	10	250	39.99
II	50	10	250	39.96
III	50	30	250	39.95
IV	50	30	250	39.97
V	50	30	250	39.94
VI	50	30	250	39.95
VII	50	30	250	44.14
VIIa	50	15	250	39.95
VIIb	50	15	250	39.99

The calculated number of cc. of the above alkali which should be required for 50 cc. of the solution of arsenic acid regarded as a dibasic acid is 39.95.

The endpoints of the titrations in experiments I and II were far inferior in sharpness to those in experiments III–VI and VII (a) and (b), in which latter groups, according to the principle of the solubility product, the precipitation process was more complete by reason of the very much higher concentration of Ba^{++} ion furnished by the excess of barium chloride beyond the required ten cc. Little difference in sharpness of endpoint could be distinguished between III–VI and VII (a) and (b).

The course of the titrations I–VI was somewhat as follows: The first drops of alkali added to the solution of arsenic acid, barium chloride, and phenolphthalein caused a local pink coloration and an amorphous curdy precipitate, both of which disappeared on stirring. After sufficient alkali had been added to neutralize the primary hydrogen, the redissolving of the curdy precipitate, which is probably tertiary barium arsenate, became slower. Since secondary barium arsenate, $BaHAsO_4$, is highly insoluble, the solution at this stage is obviously supersaturated with respect to this salt. This can be shown very clearly when, for example, half as much alkali has been added as would be necessary to neutralize the arsenic acid regarded as tribasic; for, at this stage, if the walls of the beaker be scratched below the surface of the clear solution, a copious crystalline white precipitate results that makes the liquor appear silky when stirred. This precipitate increases in quantity until the endpoint is reached at 39.9 cc.

When care was taken to stir the liquid only very gently and to avoid scratching the walls of the beaker, results like that shown in experiment VII could occasionally be obtained. In such cases the formation of insoluble $BaHAsO_4$ had apparently been delayed until more than 39.9 cc. of alkali had been run in. In order to test this point, a few titrations were carried out otherwise as before but with a total volume of 500 cc. instead of 250 cc. This dilution, by reducing the concentration of both Ba^{++} and $HAsO_4''$ to about one-half, should reduce the degree of supersaturation with respect to $BaHAsO_4$ to about one-fourth. Under these conditions it was easy to avoid the precipitation of any $BaHAsO_4$ as the following examples show:

TABLE II

No.	C. C. H_3AsO_4 Solution	C.C. $BaCl_2$ Solution	Volume in C.C.	C.C. NaOH Solution
VIII	50	30	500	59.99
IX	50	30	500	59.81
X	50	10	500	40.08

In experiment X, crystals of $BaHAsO_4$ were added as seed after about 30 cc. of alkali had been run in.

It is interesting to find the endpoints in experiments VIII and IX so close to that calculated for a tribasic acid (59.92 cc.). The presence of so large an excess of barium chloride is evidently effective in repressing hydrolysis. It is perfectly possible to obtain a good endpoint as for a tribasic acid even at the dilution of 250 cc., provided about 58 cc. of alkali is run in rapidly. In this way the stage at which the ion $HAsO_4''$ is at high concentration, namely when about 40 cc. of alkali have been added, is passed over very rapidly. If stirring is avoided, also, much of the arsenic, which, at this stage, would be present as $HAsO_4''$ if opportunity for equilibrium were allowed, is actually present as insoluble $Ba_3(AsO_4)_2$, locally precipitated. After 58 cc. of alkali have been added, stirring is unlikely to yield a precipitate of $BaHAsO_4$, for the $HAsO_4''$ ion is now again at low concentration; and the well-stirred white liquor may be turned pink at the endpoint by the addition of a single drop of alkali. For solutions of which the arsenic acid content is not known approximately beforehand, however, titration as for the tertiary endpoint is plainly too uncertain to be serviceable for scientific work.

It should, perhaps, be pointed out that once the crystalline $BaHAsO_4$ has formed, the solution remains permanently pink for any additions of alkali beyond 39.9 cc.; for, as long as this salt is present, the (fixed) concentration of its ion $HAsO_4''$ governs the concentration of the hydrogen ion possible, and this is sufficiently low to admit of a high enough concentration of hydroxyl ion to affect phenolphthalein.

The Best Procedure. — A sufficiently large sample of arsenic acid should be used to require, as a dibasic acid, between 30 and 40 cc. of normal alkali. Fifteen cc. of saturated barium chloride solution are added, the liquid diluted to 250 cc., boiled 15 minutes to remove carbon dioxide, cooled and titrated with phenolphthalein as indicator. The alkali, which may profitably contain barium hydroxide to insure absence of soluble carbonate, is added with stirring until the locally formed precipitate becomes slow in redissolving. The walls of the vessel are now, if necessary, scratched below the surface of the clear solution until the liquid, on stirring, appears lustrous with fine crystals, after which the titration is completed. The lustrous crystals and final pink color make the titration resemble that of the Zimmermann-Reinhardt method for iron.

The degree of concordance between duplicate determinations was well shown by the results of nineteen analyses, each made ne duplicate, the two members of which showed an aver age divergenic from each other by one part in 1500.

Instead of basing the calculation of results upon the acidimetric factor of the alkali employed, it may perhaps be more convenient to determine the titer of the alkali against solutions containing known weights of arsenic acid. These may be prepared in any one of three ways: (1) by oxidizing known weights of pure arsenic trioxide by nitric acid, and evaporating off the excess of the reagent below 200; (2) by synthesis from the 3-5 hydrate, the preparation of which will be given in a future publication; (3) by synthesis from arsenic pentoxide prepared as indicated elsewhere in these *Proceedings.*

In view of the satisfactory character of the endpoint of this titration, of the possibility of easy synthetical preparation of solutions of arsenic acid of accurately known concentration, and of the opportunity of simply relating this alkalimetric solution, through arsenious acid, to oxidimetric solutions, it appears likely that this titration could be profitably employed for the original standardization of alkalies. The subject will receive further investigation with this in view.

This work was carried out in the Kent Chemical Laboratory of the University of Chicago.

NOTE SUR LE DOSAGE DE L'ETAIN DANS SES MINERAIS

PRESENTEE PAR H. MILOU ET R. FOURET
Houlgate (Calvados), France

L'Etain est un métal d'un prix élevé. Il serait donc naturel d'exiger des méthodes de dosage de l'étain dans ses minerais une grande précision. Or, dans la pratique commerciale, il n'en est rien. Il est admis couramment qu'une différence de 0,8 à 1% entre les résultats de l'analyse du vendeur et celle de l'acheteur est négligeable. Et il n'est pas rare que sur le même échantillon différents chimistes trouvent des teneurs variant de 2 à 3 et même à 5 unités pour cent.

Il nous a donc paru intéressant d'étudier les différentes méthodes de dosage de l'étain employées dans les laboratoires et d'indiquer la méthode qui, d'après nous, donne les meilleurs résultats.

Les minerais d'étain sont constitués par de la cassitérite SnO_2 (avec parfois des traces de stannine $SnFeCu_2S_2$) mélangée à une gangue de composition variable. La teneur en étain des minerais traités en fonderie varie de 30 à 75%.

Nous distinguerons dans le dosage de l'étain dans ses minerais 2 parties:

I.– la désagrégation du minerai;

II.– le dosage de l'étain dans le produit de la désagrégation.

I.—Désagrégation du Minerai

Les méthodes de désagrégation des minerais d'étain peuvent être divisées en deux catégories:

1° celles basées sur la réduction de la cassitérite pour obtenir de l'étain métallique;

2° celles basées sur la salification de la cassitérite, en profitant de la fonction acide de l'oxyde stannique.

1° Méthodes basées sur la réduction de la cassitérite.

Les réducteurs employés sont: le charbon, l'hydrogène ou le gaz d'éclairage, le zinc et le cyanure de potassium.

(a) *Réduction par le charbon.* C'est la méthode des Cornouailles. Levol[1] et Moissenet[2] l'ont étudiée; elle est longuement décrite par M^r^ Beringer[3]:

80 grammes de minerai sont mélangés avec 15 gr. 5 d'anthracite en poudre et fondus dans un creuset Morgan. La température et la durée de la fusion doivent varier suivant la qualité du minerai et quand le minerai est fortement siliceux, il est nécessaire de rendre la scorie plus fluide en ajoutant du minerai de fer, du spath-fluor ou du borax. On joint au culot d'étain obtenu les grains de métal extraits par broyage et tamisage de la scorie et les particules d'étain obtenus par lévigation de la poussière provenant du tamisage.

Une variante de cette méthode consiste à fondre 10 gr. de minerai mélanges à 5 gr. de carbonate de soude dans un creuset (Cornish refining crucible—forme Julepp 49 round) brasqué avec un mélange de charbon et d'amidon.

(b) *Réduction par l'hydrogène ou le gaz d'eclairage.* Ce procédé dù à Hampe[4] est décrit dans tous ses détails par M^r^ L. Parry[5]: 5 gr. de minerai sont attaqués par l'eau régale, lavés, séchés et calcinés. On les met dans une nacelle placée dans un tube parcouru par un courant d'hydrogène ou de gaz d'éclairage; on porte la température au rouge sombre. L'opération dure deux heures. (Quand l'on se sert du gaz d'éclairage comme réducteur, il est nécessaire de faire barboter les gaz dégagés dans un peu d'eau car les composés sulfurés du gaz forment un peu de sulfure d'étain volatil). On obtient ainsi l'étain à l'état de particules métalliques disséminées dans la gangue.

Si la pratique de cette méthode est délicate, elle présente l'avantage de permettre à un seul opérateur de mener de front 7 ou 8 opérations.

Mr. J. H. Collins[6] a indiqué devant l' "Institution of Mining and Metallurgy" en mai 1904 une méthode de réduction par l'hydrogène naissant. Elle consiste à traiter dans un bécher un demi-gramme de minerai finement pulvérisé par 20 cc d'acide sulfurique au 1/5^e^ et 2 gr. de zinc pur, pendant douze heures.

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[1] Annales de chimie et de physique (3, t XLIX), page 87.
[2] Comptes rendus t LI, page 205.
[3] Text book of Analysis, page 278.
[4] Chemiker Zeitung — 1887, 11-19.
[5] The Assay of Tin and Antimony, page 34.
[6] Trans. Inst. Min. and Met., May, 1904.

(c) *Réduction par le zinc.* Cette méthode est préconisée par Mr. Beringer[1]. Elle repose sur la réaction suivante: $SnO_2 \div 2Zn = 2ZnO \div Sn$.

Il est nécessaire, pour faciliter les opérations subséquentes que la masse reste pulvérulente après la réduction. On obtient ce résultat en ajoutant une partie d'oxyde de zinc pour deux parties de zinc et une partie et demie de minerai porphyrisé. La température doit être maintenue pendant 10 minutes aussi élevée que le chalumeau gaz-air le permet. La réduction s'effectue généralement dans des creusets de Berlin de 15 cc de capacité.

(d) *Réduction par le cyanure de potassium.* Cette méthode est la plus généralement employée en France pour les analyses d'achat de minerais. Les essayeurs du commerce la pratiquent ainsi: 5 gr. de minerai passé au tamis 250 sont traités par 25 cc d'acide azotique et 50 cc d'acide chlorhydrique à l'ébullition. L'attaque dure environ une demi-heure.

Après filtration, l'insoluble est lavé, séché et calciné. On mélange le produit de la calcination avec 15 gr. de cyanure de potassium récemment broyé; on met le tout dans un creuset en terre de Paris No. 8 sous une couverture de 10 gr. de cyanure de potassium. On porte le creuset dans un four à coke. En dix minutes, on amène la température au rouge vif, on la maintient ainsi 5 minutes. On retire le creuset du four. On le laisse refroidir, puis on le brise. On a 1 bouton d'un poids p. On admet que $\frac{p \times 100}{5} =$ teneur en étain pour cent du minerai essayé.

(Certains chimistes ayant remarqué que la présence de tungstène, d'acide titanqiue ou d'une grande quantité de silice gênait la réduction de la cassitérite par le cyanure de potassium ont fait suivre l'attaque à l'eau régale de différentes opérations:

(α) *Elimination du tungstène.* Par l'attaque à l'eau régale, le wolfram et la scheelite ont été transformés en acide tungstique (WO_3) insoluble. Après filtration et lavage du résidu de l'attaque à l'eau régale, l'acide tungstique est extrait par une digestion avec de l'ammoniaque ou une liqueur de carbonate d'ammoniaque.

(β) *Elimination de l'acide titanique.* Dans le cas de présence de titane en quantité gênante, une fusion avec du bisulfate de potassium s'impose; ensuite, reprise par l'eau glacée.

[1] Text book of Analysis, page 285.

(γ) *Elimination de la silice.* Attaque à l'acide fluorhydrique suivie d'une évaporation.

—Le bouton d'étain obtenu contient toujours du fer en plus ou moins grande quantité, et du plomb, du cuivre, de l'antimoine, de l'arsenic, quand il n'a pas été possible de les éliminer en totalité lors de l'attaque à l'eau régale. Ces impuretés sont réputées compenser les pertes provenant de la dissolution dans l'eau régale de l'étain présent dans le minerai à l'état de stannine et celles provenant de la combinaison d'une certaine quantité d'oxyde d'étain avec l'alcali que contient toujours le cyanure de potassium.

Nous avons longtemps employé cette méthode qui a le mérite d'êrte rapide; nous avons dû l'abandonner parce que, si dans le cas d'un minerai relativement pur, elle donne des résultats à peu près exacts; quand il s'agit d'un minerai riche en impuretés, les résultats obtenus sont déplorables.

Nous avons remarqué que certaines variétés de minerais semblent renfermer l'antimoine, l'arsenic et le plomb en combinaison intime avec l'oxyde d'étain sous une forme résistant à l'action de l'eau régale.

Nous indiquons ci-dessous les résultats obtenus par cette méthode avec deux minerais:

I.– Pris 5 gr. de minerai. Ataaque préalable à l'eau régale. Fusion au cyanure de potassium.

Poids du bouton d'étain obtenu: 2 gr. 435;

d'où: teneur en étain du minerai: $\frac{2{,}435 \times 100}{5} = 48{,}7\,\%$.

L'analyse du bouton a donné les résultats suivants:

Impuretés contenues:	fer:	0^{gr} 0510
	plomb:	0, 0094
	cuivre:	0, 0024
	antimoine:	0, 0510
	total:	0, 1138

Ce qui correspond à $\frac{0{,}1138 \times 100}{5} = 2{,}276\%$.

La teneur corrigée devenait $48{,}7 - 2{,}276 = 46{,}424\%$.

II.– Pris 5 gr. de minerai. Attaque préalable à l'eau régale. Fusion au cyanure de potassium.

Poids du bouton d'étain obtenu: 2 gr. 747;

d'où: teneur en étain du minerai: $\frac{2{,}747 \times 100}{5} = 54{,}94\%$.

L'analyse du bouton a donné les résultats suivants:

Impuretés contenues:		
	fer:	0^{gr} 0412
	plomb:	0, 0280
	cuivre:	0, 0013
	antimoine:	0, 1455
	total:	0, 2160

Ce qui correspond à $\frac{0{,}216 \times 100}{5} = 4{,}32\%$.

La teneur corrigée devenait 54,94 − 4,32 = 50,62%.

—Si la méthode de dosage de l'étain dans ses minerais par fusion au cyanure de potassium donne des résultats erronés par suite de la plus ou moins grande impureté du bouton métallique obtenu, il est permis de se demander si, en ne considérant cette méthode que comme un procédé de désagrégation du minerai, et en titrant le bouton, les résultats obtenus ne seraient pas exacts. Nous pensons que non. Voici pourquoi: Nous avons fait des essais de fusion avec un même minerai, en prenant la même quantité (5 gr.), faisant subir à chaque essai le même traitement à l'eau régale, menant la fusion de chaque essai de la même façon et pendant le même temps; seule, la nature du cyanure de potassium variait.

Nous avons ainsi opéré avec les différentes qualités de "cyanure de potassium chimiquement pur" que nous avons pu nous procurer dans les maisons de produits chimiques françaises et allemandes. Nous avons obtenu des résultats absolument discordants. Sans doute, en se servant du même cyanure, cette méthode donne des résultats qui concordent souvent à moins de 0.1% près. Mais, en changeant la qualité de cyanure, les résultats que l'on obtient concordant toujours entre eux, sont très différentes des premiers.

A titre d'exemple, nous donnons ci-dessous les résultats obtenus sur un même minerai avec 2 qualités de "cyanure de potassium chimiquement pur," le cyanure de potassium "spécial" de la Maison Chanut, de Paris, et le cyanure de potassium 98 = 99% (Cod. franç. 1908) de la Maison Merck, de Darmstadt:

	Cyanure Chanut	Cyanure Merck
Etain %	51,30	51,76
	51,34	51,70

De ces résultats, nous tirons la conclusion que même comme méthode de désagrégation des minerais d'étain, la méthode de réduction au cyanure de potassium n'est pas recommandable.

Remarque. Les quatre méthodes de désagrégation des minerais d'étain décrites ci-dessus ont un défaut commun: La réduction du minerai laisse une gangue dont l'aspect seul ne permet pas de reconnaître si elle contient encore de la cassitérite. Il n'y a donc pas de contrôle immédiat possible.

2°– Méthodes basées sur la salification de la cassitérite.

Les réactifs employés la plus fréquemment sont: la soude caustique; le bioxyde de sodium; le mélange des carbonates de potassium et de sodium et le foie de soufre ou l'hyposulfite de sodium.

(a) *Salification par la soude.* M. M. Pearce et Low[1] recommandent cette méthode. La réaction peut-être représentée par: $SnO_2 \div 2\,NaOH = SnO_2, Na_2O \div H_2O$.

La fusion se fait au rouge sombre dans un creuset d'argent, de nickel, ou plus simplement de fer. L'eau d'hydratation que contient toujours la soude se dégage à l'état de vapeur au début de la fusion et occasionne parfois des projections. Il est assez difficile d'obtenir un mélange intime du minerai et du fondant. Toutefois, en opérant avec soin, les résultats obtenus par cette méthode sont très satisfaisants.

(b) *Salification par le bioxyde de sodium.* Cette méthode est, elle aussi, préconisée par Mr. Low.[2] La réaction est la suivante: $SnO_2 \div Na_2O_2 = SnO_2, Na_2O \div O$. On emploie le même matériel que pour la fusion avec la soude, mais l'attaque de la capsule est plus énergique. La pratique journalière de la méthode nous a prouvé que pour une fusion de 2 gr. de minerai avec 20 gr. de bioxyde de sodium—opération qui demande vingt minutes—il y a attaque de 1 gr. 4 de la capsule d'acier doux. La salification par le bioxyde de sodium présente sur la salification par la soude l'avantage que le réactif étant en poudre, il peut-être mélange intimement avec le

[1] Technical Methods of Ore analysis, 2^e Edition, page 185.
[2] Technical Methods of Ore analysis, 2^e Edition, page 188.

minerai. Quand l'on a soin de ne pas dépasser la température du rouge sombre, les pertes par projections sont impossibles.

(c) *Salification par le mélange des carbonates de potassium et de sodium.* La réaction est: $SnO_2 \div Co_3X_2 = SnO_2X_2O \div CO_2$, X étant K ou Na.

Le mélange de minerai et des carbonates alcalins est mis dans un creuset de platine, chauffé graduellement jusqu'au rouge vif que l'on maintient dix minutes. Quand le minerai n'est pas parfaitement porphyrisé, l'attaque est souvent incomplète.

(d) *Salification par le foie de soufre, ou par l'hyposulfite de sodium.* Le fondant est un mélange à poids égaux de carbonate de soude et de soufre ou bien de l'hyposulfite de soude préalablement desséché. On a: $SnO_2 \div 2\,CO_3Na_2 \div (5 \div n)S = SnS_2, Na_2S \div 2CO_2 \div 2SO_2 \div Na_2Sn$.

La fusion s'effectue dans un creuset de porcelaine. Elle doit être conduite de deux façons différentes, selon que l'on veut ou non attaquer la gangue siliceuse. Dans le 1^{er} cas, il faut chauffer progressivement jusqu'au rouge sombre; dans le 2^{e} cas, le plus fréquent, il faut chauffer seulement de façon à maintenir la masse fondue. Du reste, cette fusion est très délicate et souvent il s'est déjà formé du silicate de soude alors qu'il reste encore de la cassitérite non attaquée.

Nous avons remarqué que la présence d'acide titanique, même en petites quantités (1 à 2%) empêche la salification complète de la cassitérite par le foie de soufre. Dans le cas de présence de rutile dans le minerai d'étain, il est donc nécessaire, avant de fondre le minerai avec le foie de soufre, d'éliminer l'acide titanique par fusion avec le bisulfate de potassium et reprise par l'eau glacée.

Remarques—Les quatre méthodes de salification décrites ci-dessus exigent une porphyrisation aussi fine que possible du minerai. L'attaque préalable du minerai par l'eau régale n'est indispensable que pour la méthode de salification par le mélange des carbonates et pour la méthode de salification par le foie de soufre.

Le minerai ayant été désagrégé soit par réduction, soit par salification, il s'agit maintenant de doser l'étain dans le produit de cette désagrégation.

II.– *Dosage de l'étain dans le produit de la désagrégation du minerai.*

Avant d'étudier les différentes méthodes susceptibles d'être appliquées au dosage de l'étain, il nous paraît intéressant de rappeler certaines propriétés de l'étain et de quelques-uns de ses sels.

L'Etain est un métal blanc, gris clair, très malléable. Il est soluble dans l'acide chlorhydrique en donnant au chlorure stanneux $SnCl_2$. L'attaque par l'acide chlorhydrique est beaucoup plus rapide quand l'étain n'est pas pur mais contient 1% d'impuretés comme l'antimoine ou l'arsenic. La solution de chlorure stanneux est facilement oxydable; au simple contact de l'air, elle donne du chlorure stannique $SnCl_4$. Les oxydants: iode, perchlorure de fer, perchlorure de cuivre, permanganate de potassium et bichromate de potassium opèrent très aisément cette transformation.

Nous faisons remarquer que quand l'on porte à l'ébullition une solution chlorhydrique de chlorure stanneux ou de chlorure stannique, il y a entraînement de chlorure d'étain dans les vapeurs qui se dégagent; il est donc nécessaire de les condenser. L'entraînement de chlorure d'étain dans les vapeurs est d'autant plus fort que la proportion d'acide libre dans la solution est plus grande. Quand l'on évapore une solution de chlorure stanneux ou une solution de chlorure stannique, en ayant soin de maintenir la température aussi douce que possible, la perte de chlorure d'étain par entraînement est faible avec le chlorure stanneux et à peine appréciable avec le chlorure stannique. Elle est nulle si l'on prend la précaution d'ajouter à la solution chlorhydrique de chlorure stannique un peu d'acide sulfurique.

L'hydrogène sulfuré donne avec une solution de chlorure stanneux un précipité brun de sulfure stanneux SnS et avec une solution de chlorure stannique un précipité jaune de sulfure stannique SnS_2. En liqueur oxalique, la précipitation par l'hydrogène sulfuré n'a pas lieu avec le chlorure stannique mais se produit avec le chlorure stanneux (Clarke).

Le sulfure stannique SnS_2 est seul soluble dans les sulfures alcalins.

Les stannates et les sulfostannates sont solubles dans l'eau. L'addition d'acide chlorhydrique à une de leurs solutions produit, suivant le cas, un précipité d'hydrate ou de sulfure toujours soluble dans un excès d'acide. Aussi, peut-on vérifier rapidement si les attaques d'un minerai d'étain par salification sont complètes. La reprise par l'eau et l'acide chlorhydrique doit mettre tout en solution; il ne doit pas rester de résidu lourd. Parfois, il se forme des flocons de silice; mais la confusion n'est pas possible.

Le sulfure stanneux et le sulfure stannique, grillés, donnent de l'oxyde d'étain SnO_2; les différentes hydrates de l'oxyde stannique, calcinés, donnent le même composé SnO_2.

Le dosage de l'étain peut s'effectuer soit par des méthodes gravimétriques, soit par des méthodes volumétriques. Nous allons étudier les différentes méthodes préconisées pour ce dosage.

1°– *Méthodes gravimétriques.*

(a) Pesée de l'étain obtenu lors de la réduction du minerai par le charbon ou le cyanure de potassium. Méthode très rapide, mais peu précise comme nous l'avons montré lors de l'étude du procédé de réduction au cyanure de potassium. Son emploi n'est justifié que lorsqu'il s'agit de comparer les teneurs de minerais de même qualité.

(b) Dépôt par le zinc. On opère sur la solution chlorhydrique provenant de l'attaque du produit des différentes méthodes de désagrégation. On réunit à cette liqueur, quand il y a lieu, celle provenant de la purification préalable du minerai. On précipite l'arsenic, l'antimoine et le cuivre sur une lame de fer. De la liqueur débarrassée des impuretés on extrait l'étain au moyen d'une lame de zinc. L'éponge métallique obtenue est fondue avec du cyanure de potassium; le bouton est pesé. Cette méthode, assez rapide, ne donne pratiquement que de mauvais résultats.

(c) Dépôt par électrolyse. Le dosage électrolytique de l'étain a été étudié par Classen[1] parfois en collaboration avec Reis[2] ou avec Schelle[3] par Mr. Henz[4] et par MM. Hollard et Bertiaux[5]. Ce dosage se fait en solution chlorhydrique (10%) et oxalique (10%) avec une intensité de courant de 1 ampère. On obtient ainsi des résultats très précis; mais il faut éliminer au préalable l'arsenic, l'antimoine, le fer et les sels de sodium quand ils sont en grande quantité. On se débarrasse de l'arsenic et de l'antimoine par la méthode de Clarke (précipitation par H_2S en liqueur oxalique). Après avoir chassé H_2S par ébullition, on amène la liqueur à la concentration voulue.

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[1] Quantit. Anal. durch Electrolyse, 3e edit., page 104.
[2] D. Chem. G., *14*, 1628.
[3] D. Chem. G., *21*, 2897.
[4] Zeitschrift f. Anorg. Chemie, *37*, 39 (1902).
[5] Analyse des métaux par électrolyse, page 68.

Cette méthode présente deux inconvénients: elle est d'un emploi trop délicat et d'un rendement trop faible pour un laboratoire industriel.

(d) Pesée à l'état d'oxyde stannique. La précipitation de l'étain peut-être faite à l'état d'hydroxyde ou à l'état de sulfure. Le premier procédé a été étudié par Goldschmidt,[1] Loewenthal[2] et Rose;[3] le second par Barford,[4] Th. Scheerer,[5] Bunsen[6] et Mr. Henz.[7] Dans ces deux procédés, il faut séparer complètement l'étain de toutes les impuretés qui l'accompagnent, ce qui, pratiquement, est irréalisable.

2°—*Méthodes Volumétriques.* Sont basées sur la transformation du chlorure stanneux $SnCl_2$ en chlorure stannique $SnCl_4$ sous l'influence de certains agents d'oxydation.

L'étain peut-être amené à l'état de chlorure stanneux de deux façons:

(α) par réduction d'une liqueur par le fer en lame ou en limaille par le nickel (M. Beringer) ou par l'antimoine (MM. Brearley et Ibbotson). L'inconvénient de ce procédé est que rien ne permet de s'assurer que la réduction est totale.

(β) par dissolution de l'étain en atmosphère de gaz carbonique (CO_2). Ce procédé est très sûr, permet d'obtenir un volume de liqueur aussi faible que possible et un refroidissement rapide de cette liqueur.

—Les méthodes volumétriques de dosage de l'étain peuvent être divisées en 2 groupes, suivant que le dosage est fait à chaud ou à froid.

(a) Dosage volumétrique à chaud. Peut s'effectuer par le chlorure ferrique ($FeCl_3$) ou le chlorure cuivrique ($CuCl_2$). MM. Parry et Hocking ont étudié dans ses détails le dosage par $FeCl_3$; Strohmeyer[8] a étudié le dosage par $CuCl_2$.

Dans les deux cas, la manière d'opérer est à peu près la même: La liqueur de chlorure stanneux doit contenir 50% d'acide libre

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[1] Dinglers polytechn Journ., t CLXII, page 76.

[2] Journ. f. Prakt. Chemie, LVI, page 366.

[3] Poggend. Ann., CXII, page 164.

[4] Zeitschrift f. Analat. Ch., VII, page 260.

[5] Journ. F. Prakt. Chemie, N.F. III, page 472.

[6] Ann. der Chemie und Pharm., CVI, page 13.

[7] Zeits. f. Anorg. Chemie, XXXVII, page 39 (1903).

[8] Ann der Chemie und Pharm., CCXVII, page 261.

(en volume). Sa température doit être aussi voisine que possible de l'ébullition. On y verse à l'aide d'une burette la liqueur titrée ($FeCl_3$ ou $CuCl_2$) qui est fortement colorée. Quand l'oxydation est terminée, la première goutte de liqueur titrée ajoutée en excès produit immédiatement dans la liqueur une coloration jaune.

(b) Dosage volumétrique à froid. Peut s'effectuer par l'iode, le permanganate de potassium, ou par le bichromate de potassium.

Le procédé de dosage par l'iode présente les avantages suivants: grâce à l'usage d'empois d'amidon, le virage est d'une netteté incomparable; enfin, la teneur en acide de la liqueur peut varier dans de très larges limites sans gêner en rien le virage. Nous signalons que, contrairement à ce que l'on pourrait croire, la présence de plomb, même en grande quantité ne gêne pas le dosage à l'iode. Il se forme de l'iodure de plomb PbI_2 aux dépens de l'iodure de potassium que contient la liqueur d'iode. Nous devons signaler que Lenssen[1] a recommandé le dosage par l'iode en solution alcaline et que Crismer[2] a indiqué un dosage par le bichromate et l'iodure de potassium qui est en réalité un dosage par l'iode.

—Le procédé de dosage par le permanganate de potassium étudié par Jolles[3] est d'un emploi connode et donne un birage très net; mais il peut occasionner des erreurs lorsque les conditions d'acidité changent.

—Le procédé de dosage par le bichromate de potassium est peu employé, car le virage est difficile à saisir.

Après avoir étudié les différentes méthodes de désagrégation des minerais d'étain et les différentes procédés de dosage de l'étain dans le produit de cette désagrégation, nous donnons ci-dessous les détails de la méthode employée dans le laboratoire de l'usine de Dives pour le dosage de l'étain dans ses minerais.

Methode de dosage employé a Dives

Le minerai est porphyrisé au mortier d'agate. 2 gr. de minerai sont mélanges avec 20 gr. de bioxyde de sodium et mis dans une capsule de tôle d'acier doux. (Le diamètre de la capsule est de 60 m/m; son épaisseur de 2,5 m/m). La fusion, menée avec précau-

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[1] Journal f. Prakt Chemie LXXVIII and Ann. der Chemie und Pharm., CXIV, 113.

[2] D. Chem. G., *17*, 646 et Bulletin de la $S^{té}$ Chimique (2) *44*, 518.

[3] Chemik. Zeit., *12*, 597.

tion, est maintenue pendant 20 minutes. On laisse refroidir quelque temps. La capsule est mise dans un bécher de 500 cc. avec 150 cc. d'eau. On recouvre le bécher d'un verre de montre, car l'hydratation est vive. Lorsque la réaction devient plus lente, on ajoute peu à peu 70 cc. d'acide chlorhydrique à 23° B^{é}. Une fois l'attaque de la masse fondue terminée, on retire la capsule et la lave à fond à l'aide d'un agitateur muni d'un bout de caoutchouc et du jet d'une pissette. Si la désagrégation du minerai par Na_2O_2 a été totale, il ne doit pas se trouver au fond de al liqueur de parties insoluble dense.

Dans la liqueur portée à la température de 90°, l'on ajoute 4 gr. de limaille de fer pour précipiter l'arsenic, l'antimoine et le cuivre et pour réduire $SnCl_4$ en $SnCl_2$. L'opération dure environ une demi-heure. Ensuite; la liqueur est filtrée sur papier Berzélius et reçue dans un erlenmeyer de 500 cc.; le filtre est rincé plusieurs fois a l'eau chaude.

La liqueur est portée de nouveau à 95° environ. On y ajoute 10 gr. de forures de zinc pur (électro), pour précipiter l'étain. De temps en temps, on prélève une goutte de liqueur que l'on dépose sur une coupelle en porcelaine et que l'on traite par une goutte de solution d'acide sulfohydrique. D'abord, il se produit une coloration brune dûe à SnS puis, quand l'étain est précipité en totalité, il ne se produit plus qu'un trouble blanc dû à ZnS. Alors, on décante la liqueur sur un entonnoir garni d'un tempon de coton de verre. L'éponge d'étain reste dans la fiole avec le zinc en excès. On y joint le tampon de coton de verre qui a retenu les particules d'étain entraînées lors de la décantation.

La fiole est munie d'un bouchon de caoutchouc traversé par deux tubes: l'un sert à l'amenée d'un courant de gaz carbonique; l'autre à sa sortie. Après quelques minutes de passage de gaz carbonique, on soulève le bouchon et ajoute 30 cc. d'acide chlorhydrique à 23° B^{é}. Il se produit une réaction très vive. Le zinc en excès donne avec HCl un dégagement d'hydrogène qui achève de purger d'air l'atmosphère de l'erlenmeyer. On chauffe doucement jusqu'à dissolution complète de l'étain et du zinc. On ferme le tube abducteur et l'on refroidit la fiôle. CO_2 remplit le vide produit par la condensation. Après refroidissement, on sépare la fiole de l'appareil producteur de gaz carbonique. On rince les tubes avec de l'eau privée d'air (1 litre d'eau÷3 gr. CO_3-NaH÷HCl), on amène la liqueur à 250 cc. avec la même eau. On ajoute quelques gouttes d'empois d'amidon. On verse à l'aide d'une burette une liqueur titrée d'iode (1 cc. = 0 gr. 05 Sn) jusqu'à coloration bleue. Le virage est très net. Une goutte suffit pour le produire d'une façon indiscutable. Or, une goutte correspondant à 0^{cc} 05 équivaut à 0 gr. 0025 d'étain. La prise d'essai étant de 2 gr., l'approximation de cette méthode peut être définie ainsi: On sait que la teneur % du minerai est comprise entre deux valeurs différant entre elles de 0,125. Nous pensons que cette approximation est très suffisante pour les essais industriels.

La méthode ci-dessus décrite a été longuement pratiquée par nous. Elle nous a donné et nous donne encore d'excellents résultats. Nous lui trouvons les qualités suivantes:

1°– Elle permet de vérifier facilement si la totalité de la cassitérite a été désagrégée;

2°– Elle s'applique à tous les minerais, même très pauvres et même très impurs;

3°– Elle est rapide, car le résultat est obtenu en 4 heures;

4°– Elle permet le travail en série.

Dans ces conditions, nous pensons pouvoir en recommander l'emploi à nos collègues. Nous serons très heureux s'ils veulent bien nous faire part de leurs objections.

(*Extrait*)

ANALYSE DES COULEURS EN PATE ET EN PARTICULIER DES "LITHOPONES"

Par P. Nicolardot
Paris, France

Le principe de la méthode consiste á traiter par le toluène la pâte pour séparer l'huile de la matière minérale et à attaquer par de l'acide chlorhydrique dilué la matière minérale. L'acide n'est ajouté que par portions successives pour éviter la saponification de l'huile.

Les gaz qui peuvent se dégager pendant l'attaque de la partie minérale (H_2S provenant de la présence de lithopone) passent dans de l'acide nitrique fumant. Après attaque l'huile est séparée par décantation, puis par filtration, de la solution et du résidu insoluble. La solution et le résidu sont analysés par les procédés communs: la solution, pour plomb, zinc et acide sulfurique; le résidu, pour plomb, sulfate de baryte silice, etc. Dans l'acide nitrique, on dose l'acide sulfurique provenant de l'attaque du sulfure de zinc.

A NEW CALORIMETER BOMB WITH SPECIAL ADVANTAGES AS TO MATERIAL OF CONSTRUCTION AND METHOD OF OPERATION

By S. W. Parr
University of Illinois, Urbana, Illinois

In attempting to improve upon the oxygen bomb for calorimetric use the efforts have been directed along two distinct lines to meet what seemed to be the most pressing needs of the case: first, the discovery of some substitute for platinum which would resist the corrosive action of the acids formed and, second, the improvement of the methods for closing the receptacle so that a perfect seal could be secured with certainty and ease.

With reference to the first item, the development of a substitute for platinum, the problem is not without serious difficulties. It is to be borne in mind that in many instances as with coals and similarly constituted substances the nitric acid resulting from the combustion is produced under the best possible conditions for promoting a solvent action. The concentration of the acid in the bomb after a reaction is considerable. Moreover, the temperature, at least for a short period, is relatively high and the presence of corroding gases under high pressure may contribute to the activity. Again, in many substances a high percentage of sulphur exists and this burns to SO_3 or in the atmosphere of the interior, saturated as it is with water vapor, to H_2SO_4. For example a very large part of the coals of the Mississippi valley have a content of sulphur amounting to 3 or 4 per cent of the gross weight of the coal. Indeed, a content of sulphur is not infrequently met with of five and even six per cent. We have then in these cases of common occurrence conditions wherein both sulphuric and nitric acids are formed and these of a rather concentrated character. One of the common methods for counteracting the action of the acids is by use of some sort of resistant covering. As will be seen later the method devised for closing the bomb involves the machining of the parts to dimensions accurate within 1/50 of a millimeter. This feature, therefore, would make it impracticable to make use of an enamel as a protective covering. This expedient is also found, in practice, to be objectionable, owing to the frequent ruptures that are certain to occur in the enameled surface, thereby admitting the acid to the metal beneath. So far as a platinum lining is concerned in the device contemplated, and this was given an extended trial, the difficulties were as follows: First the cost of platinum, representing at the current prices approximately $400 per bomb, made the use of that metal prohibitive, especially where a considerable number of bombs were desired such as for use with large classes. Second, the method of closing the bomb called for an exact relationship as to dimensions, and, as in the case of enameling, this could not easily be secured or maintained with an inner shell or lining. Moreover, the device to be employed for the inlet valve was such as to make it a very difficult problem of construction to make use of a second metal in that part of the apparatus. Third, the inevitable corrosion which sooner or later begins under the platinum shell roughens the surfaces, especially those coming in contact with the gasket. In time the entire surface under the platinum is affected and the water equivalent as well as the strength of the bomb is modified. These reasons alone, even if there were no others, are quite sufficient for indicating that the bomb, if made at all in conformity with the design contemplated, should be made of a metal capable of being machined to exact dimensions and in conformity with a desired pattern.

For this purpose, therefore, a study of alloys was undertaken with a view to determining if one could be devised sufficiently resistant to acid to effectually replace platinum, and that at a cost in the massive form necessary to easily compete with that metal. It must be possible, moreover, to either cast or stamp the metal into proper form suitable for machining into the final and exact shapes desired. The alloy finally developed has proved to be eminently satisfactory as far as its acid-resisting properties and strength are concerned. It is complex in composition, having as the chief components, nickel, copper, tungsten and chromium with smaller and more or less adventitious amounts of manganese, aluminum, titanium, boron and silicon. The details of composition and properties of the alloy as finally adopted are presented under another title.[1] Concerning the securing of this material in forms suitable for machining to the desired patterns, only the method of melting and casting has so far been undertaken. The difficulty of securing perfect castings has seemed at times almost insurmountable. This is due to the fact that the melting point of the alloy is relatively high, approximately 1300° and at the point of solidification the shrinkage is so great that cracks or flaws are opened up which render the casting unfit for use. Again the occlusion of gases at the high melting temperature is great and pin holes are apt to be a source of much annoyance. The overcoming of these difficulties is however a mechanical rather than a chemical problem and need not be entered into here.

That the material may fairly be considered a substitute for platinum in the service here described is shown in the article above referred to wherein is given a table of solubility tests. Also in another article accompanying this discussion[2] data are given upon a bomb of this new material in practical operation, which indicate that the alloy is entirely suited for use in the manner described.

The second improvement sought for relates to the method of closing the receptacle. The difficulties attending the use of lead gaskets relate chiefly to the stress and strain required to secure a perfect seal. Other objections relate to the chemical action upon the lead, and to the pitting or corrosion of the needle vale or seat, making it necessary to frequently reseat or repoint the valve parts. The substitution of rubber for lead is found to be entirely practicable if the conditions under which it is used are such that flame or any of the processes of combustion are not allowed to come in contact with the rubber. This is easily accomplished by interposing between the rubber gasket and the inner chamber a shoulder of massive metal so constructed that the cross section of the space between the two metallic parts is so small, say 1/25 of a millimeter, and the longitudinal measure-

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[1] "A New Alloy with Acid Resisting Properties" by S. W. Parr, Inorganic Section (Sec. II) this Congress.

[2] "Some Tests on a New Calorimeter Bomb" by Richard H. Jesse, Jr., Section I this Congress.

ment of the space, that is the distance from the rubber to the inner chamber, is so great, say 1½ or 2 millimeters, that the combustion processes may not travel along so narrow a passage and therefore do not come in contact with the rubber gasket. This principle is carried out in closing the main opening of the bomb and also in closing the valve through which oxygen is admitted. This will be made clear by reference to a sketch.

In figure 1, *B. B.* are the walls of the bomb which enclose the space *O*. The cover *C* is made with an encircling rim *R* which retains the rubber gasket *G*. The cover is so made that a shoulder *S. S.* passes the wall of the bomb as it comes up to position against the gasket. The machining of the parts is such that the space between the shoulder and the wall is about 1/25 mm. Moreover the distance from the lower edge of the shoulder to the gasket is about 2 mm. This is increased slightly by the pressure of the cover upon the gasket when the screw cap is brought down upon it. Conditions are thus secured which prevent the traveling of flame or any of the processes of combustion

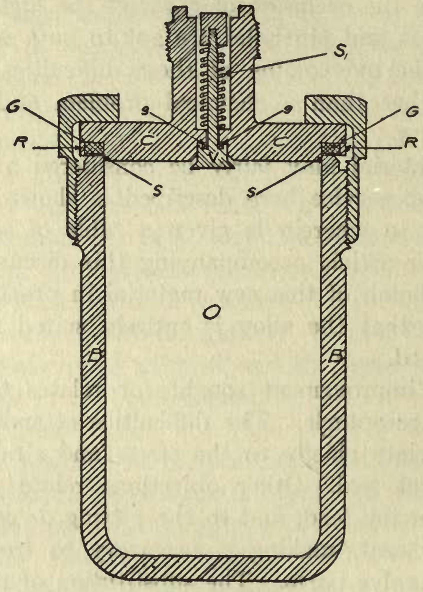


FIGURE 1

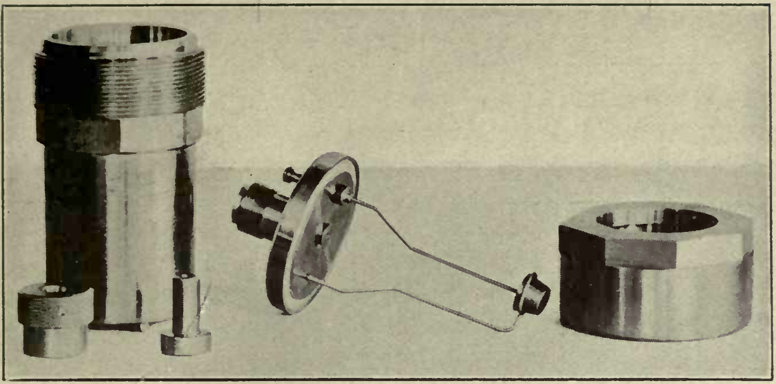


Figure 2. A New Calorimeter Bomb.

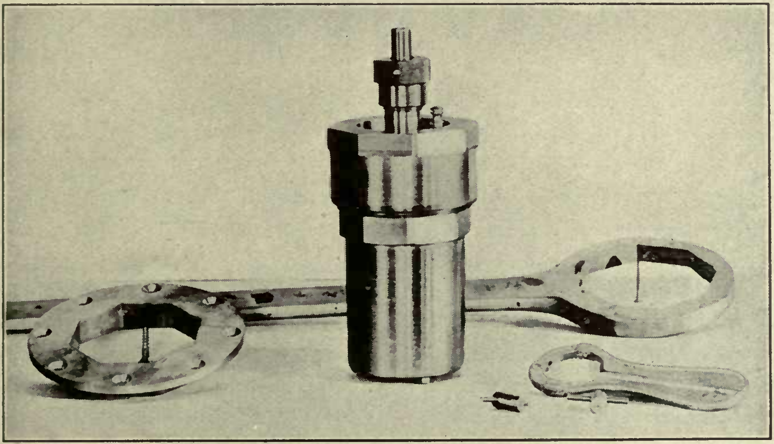
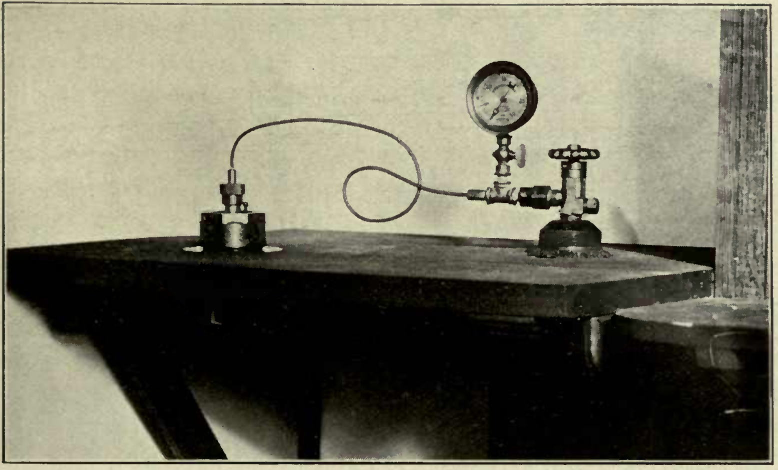


Figure 3. A New Calorimeter Bomb.



from the combustion chamber *O* to the rubber gasket *G*. The same principle is observed in the arrangements for the inlet valve *V*. The small gasket *g* is protected from the reactions or heat of the combustion chamber by narrow passages between metal walls. In this manner it is entirely possible to secure a perfect seal with a minimum amount of compression, by use of rubber gaskets and this without any burning whatever of the rubber.

A word further as to convenience of operation. The valve *V* works automatically thus —The valve is held lightly in place by the springs, but upon the admission of the oxygen above the valve it is forced downward admitting the gas to the chamber *O*. When the proper amount is admitted, say 25 atmospheres, the oxygen supply is shut off and immediately the valve is lifted into place by the spring. The strong pressure from within tends to seat the valve more firmly in place. After an extended experience with this type of valve, involving numerous modifications, the present form shown herewith has been found to be exceedingly effective and satisfactory. Thumb pressure on the top of the stem is found sufficient for releasing the gas at the close of an experiment. The most striking characteristic, however, in the manipulation of the bomb is the ease with which the cover may be fastened to withstand the necessary pressure without leakage. As may be seen in the accompanying illustrations a simple octagon plate is set into the table or shelf and an octagon wrench about 50 cm. long affords ample leverage for screwing down the cap and seating the cover. The expenditure of a great amount of force in this part of the procedure is quite eliminated. The ease and readiness with which a perfect seal can thus be obtained have done much to revolutionize the work of operating a calorimeter of the oxygen bomb type.

Figure 2 shows the cover and screw cap removed from the bomb. The small parts at the base of the bomb are couplings for oxygen connection at the top of the cover.

Figure 3 shows the bomb with the parts assembled with the octagon holder and wrench for setting the screw cap.

Figure 4 shows the shelf fittings and connection with the oxygen tank. The shelf is hinged at the left-hand edge. It may be unfastened at the right-hand edge and lifted for the removal of the tank when it is required to renew the supply of oxygen.

SUR L'ANALYSE DE L'"OLEUM"

PAR LE DR. J. PRATS

Professeur a l'Ecole Industriel et d'Ingenieurs Textiles à Tarrasa-Barcelona (Espagne)

Les procedés les plus suivis aujourd'hui pour l'analyse de l'"Oleum," ou acide sulfurique fumant, sont ceux de Lunge-Rey[1], de Treadwell[2] et de Vernon[3].

J'emploie aussi ces procedés fondés en la volumetrie du SO_3 avec la solution normal de NaOH, mais j' y fais quelques modifications à fin de pouvoir determiner rapidement, avec les données de l' analyse, le SO_4H_2 % et le SO_3% libre, qu'est ce dont on a besoin dans la pratique.

On pése dans une petite ampoule à verre une quantité *s* de l'oleum qu'on va analyser; ou le dissous dans l'eau jusqu'à former 1 litre et l'on fait deux volumetries.

1*ère*. On prend 250 cc. et on dose avec une solution normal (ou deci-ou quint-normal) de soude caustique, NaOH, en employant le methylorange pour indicateur:

$$\begin{aligned} 1 \text{ cc. NaOH normal} &= 0{,}040 \text{ g. de NaOH} \\ &= \tfrac{1}{2} \text{ mol. } SO_3 = 0{,}040 \text{ g. } SO_3 \\ &= 1 \text{ mol. } SO_2 = 0{,}064 \text{ g. } SO_2 \end{aligned}$$

de sorte que la NaOH depensée s'est employée à neutraliser le SO_3 et le SO_2 et pourtant faut il determiner celui-ci à nouveau pour en avoir le premier. Pour ça ou fait la volumetrie.

2*e*. On prend autres 250 cc. et on dose avec une solution deci-normal de iode:

$$1 \text{ cc. sol. } \frac{N}{10} \text{ de } I_2 = 0{,}0032 \text{ g. de } SO_2$$

$$0{,}0032 = \frac{1}{20} 0{,}064$$

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[1] Vademecum du fabricant de produits chimiques par Lunge — pag. 192.
[2] Analytische Chemie par Treadwell II, pag. 406.
[3] Chemiker Zeitung — a. 1910 — pag. 792.

Soient donc:

$$\begin{cases} a = \text{nombre de cc. de la première volumetrie} \\ b = \text{nombre de cc. de la deuxième volumetrie} \\ s = \text{le poids de l' oleum; } \frac{s}{4} \text{ pour chaque essaie.} \end{cases}$$

De la valeur d' *a* faut il vester la NaOH consommée pour neutraliser le SO_2 dont la valeur vient donnée par *b*.

$$\text{quantité } SO_2 = 0{,}0032.b = \frac{1}{20}\, 0{,}064.\ b.$$

mais comment 0,064 SO_2 equivalent à 0,040.SO_3, c'est à dire 1 cc. solution NaOH, nous aurons:

$$\text{quantité } SO_3 = 0{,}040.a - \frac{1}{20}\, 0{,}040b =$$
$$= 0{,}04 \left(a - \frac{b}{20}\right)$$

Ces quantités sont referées au poids $\frac{S}{4}$; pour le poids 100, elles seront:

$$\begin{cases} \frac{s}{4} : 0{,}04 \left(a - \frac{b}{20}\right) = 100 : r \\ \frac{s}{4} : 0{,}0032.b = 100 : t \end{cases}$$

c'est à dire:

$$\begin{cases} SO_3 \text{ total } \% = r = \dfrac{4\left(a - \frac{b}{20}\right)}{\frac{s}{4}} = \dfrac{4\,(20.a - b)}{5s} \\ SO_2 \text{ total } \% = t = \dfrac{0{,}32.b}{\frac{s}{4}} = \dfrac{1{,}28.b}{s} \\ H_2O \text{ total } \% = u = 100 - (r + t) = 100 - \dfrac{80.u + 2{,}4.b}{5s} \\ \qquad = 100 - \dfrac{16.a + 0{,}48.b}{s} \end{cases}$$

Mais pourvu que 80 de SO_3 se combinent avec 18 d' eau ou 1 d'eau avec $\frac{80}{18}=4{,}44$ de SO_3, en multipliant la quantité d'eau par 4,44 nous aurons le SO_3 que forme SO_4H_2, ou SO_3 combiné, et le SO_3 restant sera SO_3 libre.

$$\text{quantité de } SO_3 \text{ combiné} = 4{,}44.u$$

Pourtant la composition definitive de l'acide en SO_3 libre % et SO_4H_2 %, que c'est la forme la plus generalment usitée, sera:

$$\begin{cases} SO_4H_2\% = u + 4{,}44.u = 5{,}44.u = \dfrac{49}{9}\left(100 - \dfrac{16.a + 0{,}48.b}{s}\right) \\ SO_3\% \text{ libre} = 7 - 4{,}44.u = r - \dfrac{40}{9}u = \dfrac{4}{9}\left(\dfrac{196.a + 3b}{s} - 1000\right) \\ SO_2\% \text{ libre} = t \qquad = \dfrac{1{,}28.b}{s} \end{cases}$$

Ces formules sont d'application plus simple que celles de Vernon et au surplus on a compte du SO_2 %, ce qui donne une plus grande précision aux analyses.

Pour comprobation doit se verifier et, en effet, ou verifie:

$$SO_4H_2\% + SO_3\% \text{ libre} + SO_2\% = 100$$

$$100 = \frac{49}{9}\left(100 - \frac{80.a + 2{,}4.b}{5s}\right) + \frac{4}{9}\left(\frac{196.a + 3b}{s} - 1000\right) + \frac{1{,}28.b}{s}$$

Dans le cas, très frequent, d'être $b=0$, les anterieures formules se transforment en les suivantes:

$$\begin{cases} SO_4H_2\% = \dfrac{49}{9}\left(100 - \dfrac{16a}{s}\right) \\ SO_3\% \text{ libre} = \dfrac{4}{9}\left(\dfrac{196.a}{s} - 1000\right) \end{cases}$$

dont la somme est aussi égal à 100.

On peut modifier très simplement ces formules dans le cas où l'on emploie pour la première volumetrie une solution deci-normal ou quint-normal de NaOH.

Pour la solution $\frac{N}{10}$, on a:

$$\begin{cases} r = \dfrac{0{,}8\,(2a-b)}{s} \\ u = 100 - \dfrac{1{,}6.a + 0{,}48.b}{s} \end{cases}$$

et pour la solution $\frac{N}{5}$, on a:

$$\begin{cases} r = \dfrac{0{,}8\,(4a-b)}{s} \\ u = 100 - \dfrac{3{,}2.a + 0{,}48.b}{s} \end{cases}$$

CONTRIBUTION À L'ÉTUDE DES FORMULES POUR L'OBTENTION D'UN ACIDE SULFURIQUE FUMANT DE RICHESSE CONNUE EN SO_3

Par le Dr. J. Prats

Professeur à l'École Industriel et d'Ingenieurs Textiles à Tarrasa-Barcelona (Espagne)

J'ai donné dans le "Chemiker Zeitung"[1] des formules pour la preparation d'un acide sulfurique fumant de richesse connue en substitution de la formule de Guehm. Ces formules ont été reproduites en maintes Revues scientifiques et diverses ouvrages[2] et je veux insister sur elles en determinant l'erreur commis quand on emploie mes formules abregées et en donnant des graphiques pour le plus rapide calcul des quantités à determiner.

Mes formules exactes sont:

$$\begin{cases} x = a.\dfrac{9.h + 40\ (100 - s)}{9.k + 40\ (100 - s)} & (1) \\[2ex] y = a. - x = a.\dfrac{9\ (k - h)}{9k + 40\ (100 - s)} & (2) \end{cases}$$

où répresentent:

a = quantité d'acide fumant à preparer, avec h % de SO_3 libre
x = poids d'acide fumant à melanger, avec k % de SO_3 libre
y = poids d'acide sulfurique ordinaire, à melanger avec l' anterieur, avec s % de SO_4H_2.

Et mes formules abregées quand on emploie (cas courant) acide ordinaire de 66° Bé, sont:

$$\begin{cases} x = a.\dfrac{h + 20}{k + 20} & (3) \\[2ex] y = a.\dfrac{k - h}{k + 20} & (4) \end{cases}$$

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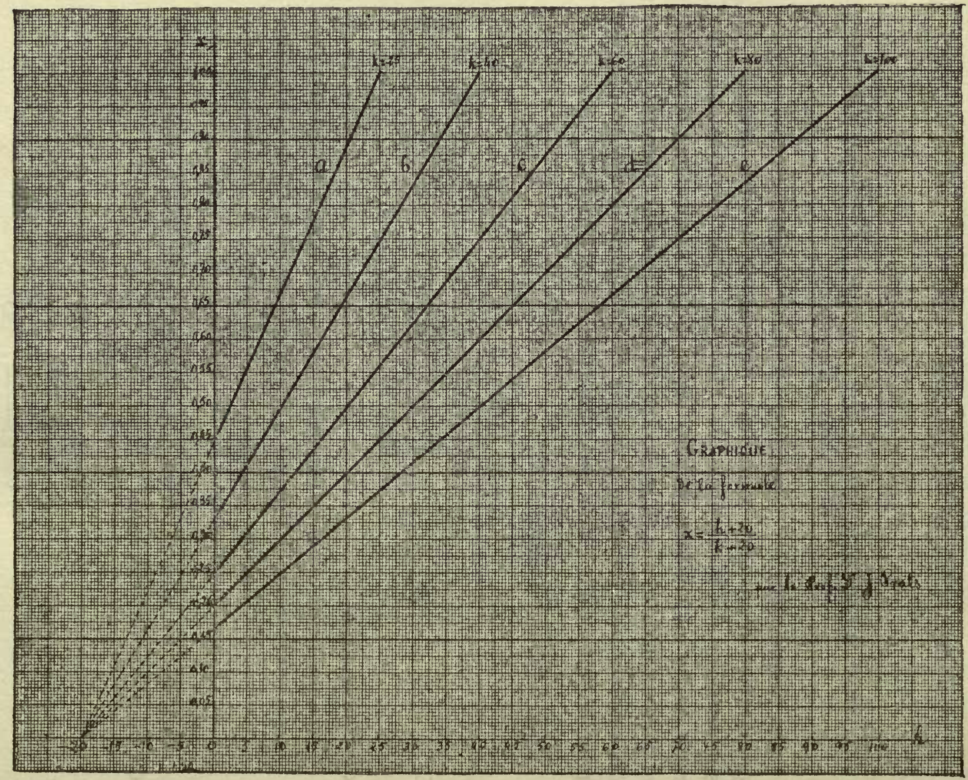
[1] a.—1910.—pag. 264.

[2] *H. Wichelhaus.* — Sulfurieren, alkalischmelze der sulfosäuren, sterifizieren. — pag. 59 a.1911; et d'autre.


x
1,00
0,95
0,90
0,85
0,80
0,75
0,70
0,65
0,60
0,55
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
-20
-15
-10
-5
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
k
k=25
k=40
k=60
k=80
k=100
a
b
c
d
e
Graphique
De la formule
$x = \frac{k+20}{k+20}$

dont la simplicité est evidente et au surplus elles n'ont besoin, comme celles de Guehm, des secours de tables.

Erreur.— L'erreur absolu qu'on commet en appliquant ces formules abregées est:

$$l=a\left(\frac{h+20}{k+20}-\frac{9h+40\times 4{,}4}{9k+40\times 4{,}4}\right)=a\left(\frac{h+20}{k+20}-\frac{9h+176}{9k+176}\right)=$$

$$=a.\frac{4(k-h)}{(k+20)(9k+176)}$$

Cette fonction ne presente pas maximum ni minimum puisque la derivée parciel $\frac{de}{dh}=\frac{-4}{(k+20)(9k+176)}$ ne peut pas être zero pour aucune valeur fini de k. La plus petite valeur (non le minimum) de *e* correspondra quand la difference (k–h) soit la plus petite possible avec *k* positif.

L' *erreur relatif* est:

$$E=a.\frac{4(k-h)}{(k+20)(9k+176)}:a.\frac{9h+176}{9k+176}=\frac{4(k-h)}{(k+20)(9h+176)}$$

Pour determiner la loi de variation de cet erreur nous commencerons par rechercher s'il y a une valeur maximum ou minimum. Des fonctions

$$\frac{dE}{dk}=0 \qquad \frac{dE}{dh}=0$$

on deduit:

$$h=-20; \qquad k=-19\tfrac{5}{9}$$

ce qu'indique, puisque *h* et *k* doivent être toujours positifs, que l'erreur n'a maximums ni minimums.

Graphique de la formule: $x=\frac{h+20}{k+20}$

Pour representer graphiquement cette formule on fait $a=1$ et on aura pour $k=25$ une ligne qu'aura par equation

$$x=\frac{1}{45}\,h+\frac{4}{9}$$

equation d'une droite (a) (voyez la figure ci-jointe) dont l'ordonnée à l'origine est:

$$x=\frac{4}{9}=0{,}444\ldots\ldots$$

Pour k=40, la droite aura par equation

$$x=\frac{1}{60}\,h+\frac{1}{3}\quad(b)$$

dont l'ordonnée à l'origine est

$$x=\frac{1}{3}=0{,}333\ldots\ldots$$

Pour k=60, la droite sera:

$$x=\frac{1}{80}\,h+\frac{1}{4}\qquad(c)$$

dont l'ordonnée à l'origine est

$$x=\frac{1}{5}=0{,}2$$

Pour k=100, la droite sera:

$$x=\frac{1}{120}\,h+\frac{1}{6}\qquad(e)$$

dont l'ordonnée à l'origine est

$$x=\frac{1}{6}=0{,}155\ldots\ldots$$

et ainsi de suite pour les autres valeurs de k.

Toutes cettes droites qu'ont comme equation general.

$$x=\frac{1}{k+20}\,h+\frac{20}{k+20}$$

concurrent au même point de l'axe des abscises, puisque pour $x=0$, on a

$$h=-20$$

Ce graphique est très utile dans les laboratoires, en substitution des formules, puisqu' il suffit chercher l'ordonnée correspondante au valeur de l'abscise qui donne la richesse en SO_3 de l'acide fumant qu' on cherche, pour avoir le numero dont le produit pour *a* donnera la quantité qu'il faut ajouter à l'acide sulfurique ordinaire pour obtenir la quantité d' acide fumant à richesse donnée qu' on désire.

THE CONTROL OF TEMPERATURE IN THE OPERATIONS OF ANALYTICAL CHEMISTRY

By Theodore W. Richards
Harvard University, Cambridge, Mass.

The control of temperature is a very important question in the work of the analytical chemist. The reason is at least threefold. In the first place, temperature affects greatly the speed of all chemical reactions, which are generally accelerated, to extents varying from perhaps seven to twelve per cent, by each degree's rise in temperature. In the second place, temperature affects the final equilibrium attained by many reacting systems, and therefore influences both the yield and the composition of the products dealt with by the analyst. In the third place, accurate physical measurements, to which the quantitative experimenter must frequently resort,—such as weighing the measurement of the volumes of gases and liquids, and the determinations of calorimetric or electrical magnitudes,—demand considerable control of temperature if any accuracy is sought.

Clearly the subject is too large for the brief ten minutes to be devoted to it; but a few words may be able to point out the more vital features.

Let us begin with the control of temperatures near that of the room. In the first place, it is clear that every chemical laboratory may advantageously have a thermostat attachment to its heating arrangements. For years I have used a commercial contrivance which when operating properly has kept my laboratory at 20° within half a degree, greatly to my satisfaction. In order to attain any such constancy, the air of the room must be efficiently agitated by means of an electric fan; just as any other form of thermostat should be adequately stirred. Of course when an operation affected by currents of air is undertaken, the fan must be temporarily stopped.

Entirely within this room, surrounded by glass walls and without any outside windows, is built a balance-room, which resembles a huge balance case; and this remains constant for long periods within one or two-tenths of a degree, because the somewhat larger fluctuations of the outer room do not quickly pass through the glass walls. The plan has worked so excellently that all balance-rooms in the new Wolcott Gibbs Memorial Laboratory at Harvard are to be built in this way entirely within other rooms.

A very suitable, sensitive, and easily constructed thermostat attachment for regulating the temperature of a room is the sealed hydrogen manometer, with electrical contact.[1] This consists of a large sealed bulb containing hydrogen, which gas is arranged to support a column of mercury having an electrical contact at its upper end,—the affair is a combination of a gas-thermometer and a barometer. The rapid heat conduction in hydrogen makes this gas especially suitable for the purpose. We have used the device for many years with great profit, and by its aid have been able to keep a cellar laboratory, which is protected by double windows, within 1/10 degree for weeks at a time. The electrical current, made and broken at the mercury surface in the top of the manometer by the fluctuations of the expanding or contracting hydrogen, may be made to operate a relay which in turn regulates the heating apparatus, whether this uses steam, hot air, gas or electricity. A form in which the current running through the mercury in the manometer itself is used for heating, has recently been described[2], but I should be afraid that this might not be able to maintain quite as accurate a constancy as an apparatus using a weaker current in its regulating manometer.

Often the yet more accurate regulation of the temperature of small objects is needed; of course the Ostwald toluene regulator in a bath of water or oil gives the most convenient thermostat for such purposes. Of late we have used, on account of its cleanliness and safety, only electricity as a means of supplying heat to this bath; the regulator is arranged so as to make and break a feeble electrical circuit which operates a relay through which in turn runs the stronger heating current. The chief, probably the only, disadvantage of electrical heating is the pos-

[1] Regand and Fouillard, Z. wiss. Mikroscop., *20*, 138 (1903); also Richards and Mark, Proc. Am. Acad., *41*, 119 (1905).

[2] Bonsfield, Chem. News, *105*, 13 (1912).

sible leakage of electricity. If it is used for electrochemical work, one must guard against stray electromotive forces by efficiently grounding the thermostat. The description of an arrangement of this kind making possible the maintenance of the temperature within 0.001° or 0.002° for days is perhaps not out of place. This has been used at Harvard for many years; it was briefly described several years ago and has been used independently by others.[1]

The thermostat consists of a large can which may be as large as 70 centimeters in diameter and 70 or more high. The can is covered on the outside with felt and may have its surface protected with oil if evaporation is to be prevented. Within this can is immersed a regulator similar in principle to the toluene thermostat regulator of Ostwald. The receptacle for the toluene is made with five large fingers having walls of moderately thin glass, and is arranged to have a capacity of over half a liter. The mercury column, raised and lowered by the expansion or contraction of this toluene, "makes" and "breaks" a feeble electrical circuit which governs through a relay the stronger current used for heating. The latter current passes through the relay and through a large insulated heating coil immersed deeply in the water of the thermostat.

The "making" and "breaking" happen advantageously in a somewhat narrow tube, perhaps two millimeters in diameter, and the mercury in this tube should be protected from the laboratory air by an atmosphere of pure hydrogen, supplied by a very small automatic hydrogen generator attached to the apparatus. This device is very important if great constancy is sought; it constitutes the only unusual feature of our apparatus.

The efficiency of this regulator, or indeed of any other, as a means of keeping the temperature constant depends greatly upon the agitation of the water in the thermostat. This should be violently stirred by means of a rather powerful motor in order to keep the temperature constant throughout and to effect a rapid exchange of heat between the bath and the toluene regulator. The degree of agitation usually employed is entirely inadequate. The temperature is obviously much more constant if the room containing the thermostat is allowed to vary but

[1] Richards, Carnegie Inst. Washington, Pub. 56, 22 (1906); 76, 9 (1907).

little in temperature; it is advantageously kept perhaps a degree below the temperature of the bath. By running a thin pipe containing cool water around the inner circumference of the top of the bath, compensation for a higher temperature may be easily obtained. If care is taken and the glass toluene receptacle is sufficiently large, and is well seasoned so that it has assumed a reasonably constant volume, the thermostat will keep constant within one or two thousandths of a degree for weeks.

This arrangement makes no pretense to novelty in principle, but in efficiency it probably exceeds most other forms because of the details heeded in its construction. A very similar apparatus has been more recently described by Hulett[1]; but he does not seem to have sought or attained quite the degree of precision which we have successfully employed.

Very satisfactory thermostats may be made from baths filled with pure salts in the act of transition from a state of greater to a state of less hydration. Such mixtures keep a striking degree of constancy for a long time. Sodium sulphate is the best substance for this purpose. For details a paper by K. L. Mark and the present author in Vol. 38 of the Proceedings of the American Academy of Arts and Sciences should be consulted.

The control of low temperatures and of high temperatures has received so much general notice recently that this expert audience needs no detailed exposition of these topics. The employment of pure ice for maintaining a definite degree of coolness is known to every one; but the almost equally serviceable use of ice mixed with solutions of definite concentrations for increasing coolness, is perhaps less generally recognized.[2]

For example, ice mixed with dilute hydrochloric acid containing 28.19 grams of hydrogen chloride per liter gives a perfectly constant temperature of $-3.00°$.[3] Of course, if heat is added, some of the ice melts, the solution becomes more dilute, and the temperature rises. This, however, may be easily prevented by enclosing the constant-temperature bath by another bath containing a mixture having the same freezing point. If an air

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[1] Physical Review, *32*, 277 (1911).
[2] This was suggested by Roloff, Z. phys. Chem., *18*, 572 (1895).
[3] Richards and Jackson, Proc. Am. Acad., *41*, 473 (1906).

space (or still better the evacuated space of a Dewar vessel) is placed between the two baths, the inner one will maintain an amazing degree of constancy for long periods of time, particularly if more dissolved substance from time to time is added to the outer vessel as its ice melts. The lower limits of the temperature attained in this way are of course the cryohydric temperatures of the more soluble substances.

Lower temperatures are customarily obtained by means of solid carbon dioxide with alcohol or ether, and still lower ones by liquid air and hydrogen. By boiling the liquefied gases under reduced pressure their temperature-range may be extended considerably. The details of working with these now familiar substances need hardly find a place in this brief review. Acquaintance with the necessary technique is becoming more and more an essential part of the complete chemist's outfit, although analytical operations rarely demand low temperatures.

Turning now to higher temperatures more frequently employed by analytical chemists, wide limits must receive consideration. Open steam baths are essential, and are too well known to need discussion. Thermostats of concentrated salt solutions or oil or paraffin, or of fused mixed sodium and potassium nitrate, may be used at fairly high temperatures, if proper regulating devices are employed. For most purposes, however, air baths regulated either by themostat-control or by approximately constant steam, gas, or electrical-heating are more commonly employed. If steam under constant pressure is available, it forms a very usual and convenient means of maintaining constant temperatures somewhat above 100° often needed in analytical laboratories. Gas, or more recently, electrical heating is more commonly used; the latter has the great advantage of cleanliness. Other vapors also, such as toluene (110°), the xylenes (140°±), and aniline (184°) are often used with advantage. Air-baths without thermostat attachments are usually arranged to maintain only a certain difference between the room temperature and the higher temperature sought. This is all very well if the room remains constant in temperature, but sometimes laboratories change as much as 10° or 15° during the day. and this change may have serious effects in some delicate operations when it reappears in the heated air-bath. For such operations a thermostat regulation of the temperature of the bath is almost essential.

The forms of air-bath which have been proposed are countless. Most of them lack the needful requisites of resistance to corrosion and therefore of cleanliness. The utensil containing the substance to be heated usually needs to be protected by some form of shelter or roof, such as a watch-glass, to keep out particles of impurity from the corroded walls of the oven. This is altogether unfortunate; the air-bath used by analysts should be free from such defects, therefore it should be made of glass or porcelain.[1] It is almost needless to point out that for many purposes the products of combustion also should be rigidly excluded from the inside of the oven if gas is to be used as a source of heat. Moreover, the air of the laboratory is often injurious to sensitive substances; such material should be heated in boats within tubes, even if only dried at 100°. The well known "bottling apparatus," so much used at Harvard makes this precaution easy.[2]

For higher temperatures burners of various shapes are available, and more and more use is being made of the yet greater possibilities of electrical heating.

Most of the gas-burners are either modifications of the Bunsen burner or the blast lamp, and some of the former, especially the Meker burner, have been made of such efficiency as to replace for many purposes the use of air under pressure. To obtain a constant temperature with these burners, it is necessary usually to attach to the gas-supply a contrivance for giving it constant pressure; otherwise the fluctuations are considerable. It is needless to point out that contrivances for preventing radiation, such as clay cylinders and other forms of furnaces, greatly promote the constancy of temperature attained.

Turning now to electric heating, we have not only the electric furnace so much used in technical work, but also, more suitable for analysts, a sort of electric muffle, a porcelain or other refractory tube wound with resistance wire, capable of producing and

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[1] A simple, clean, and inexpensive electric oven is described in Am. Chem. Jour., *22*, 45, (1899).

[2] See for example: The Faraday lecture of 1911; Jour. Chem. Soc. Trans. *99*, 1203 (London).

withstanding the high temperatures needed. For temperatures up to 1000° the alloy called "nichrome" works very well as the material of the resistance wire; for higher temperatures platinum is necessary, but even that is less refractory than one might wish. We have obtained excellent results with the type of furnace made in this fashion with tubes of pure silica as core. The maintenance of constant voltage and even conditions of radiation provides the operator with a very fairly constant temperature, which is most conveniently estimated by the platinum-rhodium thermopile.

In summing up, it may be said that attention has been called to the relative advantages and fields of usefulness of some of the more important methods of controlling temperatures between 3000° and −250°. A few of the most essential details of execution have been suggested and emphasis has been placed upon the frequent importance of constancy of temperature and of the exclusion of outside impurity.

THE MEASUREMENT OF TEMPERATURE IN THE OPERATIONS OF ANALYTICAL CHEMISTRY

By Theodore W. Richards
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The measurement of temperature is important in analytical work primarily in those problems which border upon physical chemistry. The approximate knowledge of temperature is necessary in many processes of precipitation and other treatment, but exact knowledge is demanded chiefly in the measurement of the volumes of either gases or liquids or the vapor tension in the latter; as, for example, in gas or liquid volumetric analysis of the determination of densities. Calometric analysis also demands very exact thermometry. Moreover, a new method of quantitative analysis has recently been suggested in which the accurate and precise estimation of differences of temperature is the crucial point. In these cases temperature is so important that it must receive careful and adequate treatment in exact analytical chemistry.

The present paper makes no attempt to present an exhaustive discussion of the measurement of temperature; its object is merely to make a few suggestions which may be useful to the analytical chemist unfamiliar with accurate work of this kind.

As every one knows, the measurement of temperature depends upon two entirely different considerations; first, upon a few satisfactory fixed standards of reference; and, secondly, upon some means of subdividing the intervals between these points.

The standards of reference usually employed, namely, the temperatures of freezing and boiling water, are well known, but they do not always receive quite adequate attention. With regard to the freezing point, which is taken under atmospheric pressure, the most important cause of uncertainty is the possible impurity in the water which must always surround the ice. Fortunately this difficulty is easily avoided. Water may be purified with great ease, and ice is usually purer than the water from which it separates. Moreover, even if the ice is not perfectly pure, very good results may often be got by washing and drenching it with pure distilled water, previously boiled in an insoluble vessel and cooled in a sealed flask to zero. Impurity within the body of the ice, of course, makes no difference, and traces of impurity on the surface may thus be greatly diluted. If only a small specimen of pure ice is at hand, it may be placed in a thin-walled beaker with pure water, and surrounded by a much larger vessel of common ice and water. Attention should be called in this connection to the danger of dissolving volatile impurities from the atmosphere. This danger is much reduced by filling the interstices between the pieces of the ice with pure water, a precaution which also eliminates irregularities due to currents of air. Because the equilibrium which establishes the constant temperature takes place only on the dividing surface between the solid and the liquid phases, this dividing surface must be made as extensive as possible by the subdivision of the solid.

The effects of usual changes of atmospheric pressure on the melting point of ice are so small as usually to be negligible, although larger changes of pressure cause appreciable changes in the freezing point. The usual barometric fluctuations plus the pressure due to the supernatant water may affect the freezing point by a range of almost 0.001°, a quantity which usually does not concern the analytical chemist, but may be of great importance to any one desiring very accurate temperature measurements.

The boiling point, on the other hand, as is very well-known, is highly sensitive to small changes of pressure, although the questions of purity of material and lack of homogeneity are not practical issues. A quarter of a millimeter's change in the barometer causes as much as 0.01° change in the boiling point — a matter which may become of serious moment; hence a very accurate barometer is needed. To this cause of uncertainty is added another, the danger of superheating, which must always be guarded against.

The boiling and melting points of many other substances besides water are used to establish a number of other fixed points above 100° and below 0°. Much the same considerations apply to these substances also, except that the greatest difficulty is usually here the presence of impurity. Since extreme temperatures need not usually be precisely known by the analytical chemist, the discussion of these substances may be omitted.

Much more important are the newly used transition temperatures of crystallized salts, which fix with very great precision various points between the freezing and boiling point of water, and therefore must be emphasized. These have been investigated chiefly by the present writer, who first suggested their use for this purpose in 1898. It has been shown by a series of investigations that these points are fully as certain as the two old long established ones. Indeed, it is probable that the temperature of the transition of sodium sulphate, for example, may be fixed in practice more accurately than either the temperature of ice or that of steam. Every chemist knows that at the first named point, 32.383°, the solubility curve of the common hydrated sodium sulphate crystallized with 10 molecules of water, cuts the solubility curve of anhydrous sodium sulphate; the two solutions are identical; and the two kinds of crystals, anhydrous and hydrated, are in equilibrium with one another. If heat is added to a mixture containing both solids and the solution, the result is simply the transition of some of the hydrated into the anhydrous salt and solution; and the temperature remains absolutely unchanged as long as any considerable amount of hydrated crystals is present. The situation is exactly parallel to the absorption of heat by the melting of ice, the difference being that in the case of ice only two phases are concerned, whereas in the case of the salt three phases, the solution, the hydrated crystals, and the anhydrous crystalline powder take part in the equilibrium. This temperature, about one-third of the way up the Centigrade interval, is a very convenient one for many purposes. As a rule, all thermometers intended for the exact determination of ordinary temperatures should cover the range between 0° and 32.383° so as to be verified by means of these two points.

Other important fixed points also have been more recently tested, namely, the transition of the deka-hydrate of sodium chromate into hex-hydrate and into tetra-hydrate. These two points, respectively 19.525° and 19.987°, are particularly convenient as being in the neighborhood of the usual room-temperature. For higher temperatures sodium bromide and manganese sulphate, respectively 50.674° and 58.09°, are valuable; and barium hydroxide gives an admirable transition temperature at 77.89°.[1] Pressure change within usual limits has very little effect on any of these points.

These transition temperatures may be determined in the ordinary Beckmann freezing-point apparatus with great precision if care is taken as usual always to surround the test-tube containing the mixture by a wider tube having a narrow air jacket, the outer tube being immersed in a bath kept about half a degree above the point desired. Of course great care must be taken in preparing the salts in a state of purity, and the trouble involved naturally varies in difficulty with different substances. Sodium sulphate is very easily prepared in the pure state, and is the most convenient of all. For the details the separate papers must be consulted.

Even if these transition temperatures were no more precise than the two old fixed points, they are practically superior to them in two important respects, for the purpose of verifying temperatures found by mercury thermometers between 12° and 85°. In the first place, at any point over this range some one of them is nearer to the temperature in question than the nearest of the two old fixed points. This nearness minimizes the effects of possible errors in the calibration. Again, the fact that with the aid of these new points the thermometer need not be much heated or cooled in the act of standardizing is by no means unimportant; for the internal structure of glass is much upset by sudden temperature changes, and the most elusive errors in mercury thermometers are due to the resulting eccentricities in the height of the enclosed mercury column.

Yet another cause of superiority over the boiling point lies in the fact that the transition temperatures of crystallized salts do

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[1] T. W. Richards, Am. J. Sci., (4) *6*, 201 (1898); Richards and Churchill, Proc. Am. Acad., 34, 277 (1899); Richards and Wells, *41*, 435 (1906); Ibid., *38*, 431 (1902); Richards and Wrede, Proc. Am. Acad., *43*, 343 (1907). These five papers are all to be found in full in the Zeitschr. für phys. Che., the references being respectively *26*, 690 (1898); *28*, 313 (1899); *43*, 465 (1903); 61, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin. The work on sodium chromate by Richards and Kelley will be found in Proc. Am. Acad., *43*, 171 (1911) and J. Am. Chem. Soc., *33*, 847 (1911).

not demand the use of a barometer — the sole requirement is unimpeachable purity in the substances concerned.

The second problem which confronts any one who wishes to measure temperature accurately is the subdivision of the intervals between these various fixed points. Everybody knows that this is accomplished by the precise measurement of some property of a substance or system of substances which possesses a high and easily measured temperature coefficient, the property varying continuously and if possible in a linear fashion over the temperature interval to be subdivided. The properties usually used are in the first place the volumes of mercury or of hydrogen or air, measured usually in glass tubes; secondly, the electrical conductivity of platinum; and thirdly, the electromotive force of a multiple thermopile. Each of these methods has its own advantages and disadvantages; and the intelligent choice between them depends largely upon the conditions which the especial problem in hand may present. The hydrogen gas-thermometer, the standard to which all others are referred, is not easily used with exactness. Many precautions are necessary for its precise employment. Therefore the determination of its indispensable data is now left as a rule to the national bureaus of the several countries, the standard values obtained by them being recorded on mercury thermometers and in that way transported from place to place.

Mercury thermometers in glass tubes, first proposed about the middle of the seventeenth century, still continue to be as a rule the most convenient means of subdividing the thermometer range in laboratory work. When properly made and intelligently used, they give very accurate indications; but if the necessary precautions are not observed, they may lead to highly erroneous and illusory results.

Every one knows nowadays that the first precaution to be observed in using a mercury thermometer is to keep the whole stem at the temperature to be measured, or else, less satisfactorily, to correct the reading by adding to it a calculated amount equal to the effect of the contraction of the mercury in the protruding stem. Nevertheless, a few years ago, this knowledge was not general, and many of the data concerning solubilities and melting points to be found in chemical literature are distinctly erroneous, because of the oversight of this precaution.

Another precaution, which also varies with the circumstances of the particular determination, is the observation of the effect of pressure, both of the mercury column inside and of the atmosphere and supernatant liquid above the bulb on the outside. Each source of pressure decidedly affects the size of the bulb and hence the reading.

The zero-point of a thermometer also changes from time to time, particularly if the thermometer itself is often subjected to widely varying temperatures. If neighboring fixed points cannot be employed to estimate such change, and ice must be employed, the only safe rule to heed with regard to this error is to take the zero-point immediately after the reading of the higher temperature —the lowest point recorded by the thermometer on being placed on ice (perhaps two minutes after the first immersion) being taken as the true value. This immersion in ice, if continued for more than a few minutes, so alters the glass that on being raised again to the higher temperature the instrument will indicate a slightly different temperature than before; and time is needed to cause this hysteresis-effect to disappear.

Because of the effect of large temperature-changes on the glass of thermometers, it is not a bad plan to have those intended to be used for precise work over a short range (as in calorimetry) made without the zero-point, so that one may be spared the temptation of plunging them into ice. They should be verified either with a suitable transition temperature or by means of standard thermometer.

Besides these irregularities, which depend upon the peculiar conditions to which the thermometer is subjected, there are of course certain constant corrections to be applied to every thermometer, which depend upon inequalities of bore and the coefficient of expansion of the particular glass used. These are best determined once for all at the Bureau des Poids et Mesures, the Bureau of Standards, or the Physikalisch-Technische Reichsamstadt where the needful corrections to the hydrogen scale will also be determined.

One of the great difficulties of mercury thermometers is the tendency of the thread to adhere to the tube, and therefore with a descending thread, to give incorrect readings. Even fairly energetic tapping is often insufficient to dislodge the column; therefore it proceeds in its downward course by jerks, obviously failing to give trustworthy indications of the temperature. For this reason thermometers should always be read when the thread is very slowly rising or in a stationary position approached from a low temperature. In this case, if the bore is clean, the pressure of the expanding mercury is enough to cause a perfectly even rise and a perfectly definite indication. Unfortunately the bore often is not perfectly clean, and even with a rising thread, some thermometers show inequalities. Several recent instruments for thermochemical work, which have been especially made for my use, seem to be entirely free from impurity in the mercury column; and a brief description of them is perhaps worth while. Each thermometer was sealed, with an intervening receptacle, to the mercury still. The mercury was first distilled in hydrogen into the receptacle, the apparatus exhausted, and the mercury absolutely free from air, was then run into the thermometer bulb and sealed off with due precautions. By wholly excluding oxygen in this way, the thermometer seems to give more satisfactory results. It is possible that an imperceptible film of an oxide of mercury forms on the surface of mercury in contact with the air, and that this is the cause of the fact that the mercury progresses irregularly. Whatever the cause, the usual method of calorimetry, in which the cooling correction is determined on a falling thermometer, is obviously quite inaccurate. On the other hand, attention should be called to the fact that the thermometer should not be read with a *rapidly* rising column, because then the temperature of the mercury in the bulb will lag behind that of the environment. For accurate work the temperature of the bath being determined should not rise faster than two or three thousandths of a degree per minute. In that case the average thermometer bulb is very nearly in equilibrium with its environment.

The preceding discussion alludes to the necessity of tapping the thermometer before reading it. This is essential in accurate work, but the tapping should be very gentle and should be applied at the side rather than vertically on the top of the thermometer. The latter form of impact sometimes causes the mercury column to jump, and it may then remain at an incorrect altitude.

Carefully executed experiments with the accurate thermometers just described, taking all the precautions indicated, show that a thermometer after being taken from a bath of perfectly constant temperature, cooled three or four degrees, and then returned to the bath, will give a result the second time within 0.0005° of the original indication, if allowance is made for the heat removed because of the heat capacity of the thermometer bulb. That is to say, when due care is taken with the thermometric readings, a very high degree of precision may be reached by means of mercury thermometers.

The comparison of two thermometers is a process often necessary in accurate thermometric work; it demands a bath of nearly constant temperature. This is best found in an adiabatic calorimeter[1] — a sort of submarine immersed in water in a large pail. Within the watertight sunken vessel is a can insulated by an air-jacket from its walls. Water in the inner can, if at about the temperature of the water in the outer pail, is surprisingly unchangeable in temperature. This somewhat complicated apparatus may be replaced in ordinary work by a much simpler one. Two large beakers of a nest, holding a litre or more, are arranged one inside of the other, with cotton wool between their upper edges. The inner is almost filled with water covered by a layer of non-volatile oil; and the Combination is then almost sunk in a large receptacle full of water, and properly supported. The temperature of the outer bath may be easily regulated by hand so that the inner one remains very constant, if the temperature is not very different from that of the room; and by starting with a temperature somewhat too high in the outer bath and subsequently cooling it, the thermometers may be made to assume their stationary positions with a rising thread, in the proper manner.

Pentane thermometers, for very low temperatures, and mercury thermometers (containing nitrogen or carbon dioxide under pressure) for temperatures up to 550°, are too well known to need description. Both are very convenient, and when properly standardized, with especial attention to the protruding steam, both will give fairly accurate results, adequate for many purposes. The

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[1] The best form is described in a paper by Richards and Jesse, Journ. Am. Chem. Soc., *31*, 273, (1910).

more recent thermometers of fused silica containing mercury and gas under great pressure, for very high temperatures, are less familiar and of course more expensive.

The electrical methods of determining temperature are of much less use to the chemist than the glass-mercury thermometric methods. When extraordinary pains is taken to exclude stray electromotive forces, there is no doubt that very great sensitiveness to changes of temperature may be obtained either in the measurement of the electrical resistance of a pure platinum wire or in the determination of the electromotive force of a multiple thermopile consisting for example of copper and constantan. In order, however, to get any sort of reliable results from this apparatus, the experimenter must have had great experience with precise electrical measurements, and the whole apparatus is so expensive and so sensitive to changes of temperature, to electrical and magnetic conditions, and to the injurious fumes only too often present in chemical laboratories, that for most purposes the analytical chemist will do well to forego any attempt to use the electrical methods with great precision. On the other hand approximate determinations of high temperatures by means of the platinum-rhodium thermopile are highly convenient and of very great use to the analyst, because he should have some idea of the temperatures at which ignitions and other high-temperature operations are to be executed. This instrument can be purchased in good condition and calibrated already with sufficient accuracy for approximate work, and it is easily verified to within a few degrees by the melting points of a few fixed substances such as sodium sulphate, etc.

It seems likely that in the future the thermometer will be used more and more for exact analytical purposes in methods which demand the precise estimation of comparatively small differences of temperature in the neighborhood of 20°. All calorimetric work, which may often with advantage be used for analytical purposes, comes under this head; for example, the determination of the value of coal by means of any form of combustion calorimeter. This is strictly a method of analysis, and it determines the most essential characteristic of coal; but the quantitative basis for the analysis is the thermometer. In the same way the method of analysis just advocated in a recent paper[1] from the Harvard

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[1] Richards and Shipley, Journ. Am. Chem. Soc., *34*, 600, May, 1912.

Laboratory depends essentially upon the precise measurement of small intervals of temperature. This method of analyzing solutions may be of very general application both in technical and in scientific work. The method depends upon noting the precise temperature at which the unknown solution attains exactly the same density as a given, previously calibrated solid float. This equality in density is marked by the familiar phenomenon which we may call "floating equilibrium," where the wholly immersed solid neither rises nor sinks in the liquid. When, as is usual, the solution is denser than the solvent, the more concentrated the solution, the higher is the temperature necessary to reach floating equilibrium; hence each concentration corresponds to a definite temperature, and after a few points on the almost linear curve connecting the two variables have been determined by means of known solutions, all the intervening ones are determinable by simply reading the thermometer at the points where floating equilibrium is attained. When the solution is less dense than the solvent, precisely the same method is used, except that the solution must be cooled instead of warmed to attain floating equilibrium, as the concentration increases. One should note that *differences* alone are the subject of study by this method; the exact density of none of the solutions need be known. The method is indeed more sensitive and accurate than any of the usual methods of determining the densities of liquids. The starting-point in each case should be the perfectly pure solvent, whose density, again, need not be known and the float is calibrated by solutions of known concentration.

This new method of analysis, as well as the older calorimetric method, may be conveniently carried out by means of a well calibrated Beckmann thermometer, or still better by means of a thermometer with a scale only covering a range through perhaps 15° to 21°, and without any zero-point. If such a thermometer has been kept for a long time at nearly constant temperature, its readings become extraordinarily trustworthy, and it serves with great advantage for the purpose under discussion.

In brief, this paper has attempted to give in a few words a statement of the most convenient methods for determining temperature suitable for work in analytical chemistry. The mercury thermometer, carefully constructed and calibrated, and used with proper precautions, has been advocated as the most convenient means at the disposal of the analyst; and a method of making very satisfactory mercury thermometers is briefly described. Further the wide application of the thermometer in several forms of analytical work has been emphasized.

NEPHELOMETRY

By Theodore W. Richards

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The nephelometer is a simple and generally applicable piece of apparatus for estimating traces of suspended precipitates in liquids. The determination is effected by measuring the brightness of the light reflected by the suspended particles; from the amount of this reflected light, the weight of suspended material may be inferred with considerable accuracy, provided that the proper precautions are taken concerning the standard of reference. The device is a great convenience for finding exceedingly small quantities of material too finely divided to be collected upon a filter and determined gravimetrically. The name nephelometer is derived from the Greek νεφέλμ, a cloud.

"The construction is very simple. Two test-tubes, near together and slightly inclined toward one another, are arranged so as to be partly shielded from a bright source of light by sliding screens. The tubes are observed from above through two thin prisms, which bring their images together and produce an appearance resembling that in the familiar half-shadow polarimeter. The unknown quantity of dissolved substance is precipitated as a faint opalescence in one tube by means of suitable reagents; and a known amount, treated in exactly the same way, is prepared in the other. Each precipitate reflects the light; the tubes appear faintly luminous. If the tubes show like tints to the eye when the screens are similarly placed, the precipitates may be presumed to be equal in amount. In case of inequality of appearance the changed positions of the screens necessary to produce equality of tint give a fairly accurate guide as to the relative quantities of precipitate in the two tubes. Traces of substance, which are too attenuated to be caught on any ordinary filter, may thus be estimated."[1]

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[1] Richards, "Faraday Lecture," J. Chem. Soc. Trans., *99*, 1206 (1912). The original publications are to be found as follows: Zeitsch. anorg. Chem., *8*, 269 (1895); Richards and Wells, Amer. Chem. J., *31*, 235 (1904); Richards, ibid, *35*, 510 (1906).

The two test-tubes are lighted by nearly horizontal rays from a powerful electric light at least one-half meter distant. The tubes should be protected from its heat by a suitable transparent screen.

The arrangement of the apparatus is described in full in papers published in the American Chemical Journal for 1904 and 1906, volume 31, p. 235 and volume 35, p. 510.

The apparatus has been thoroughly tested by comparing with its aid solutions containing known amounts of various precipitates, especially freshly precipitated argentic chloride in suspension. Its efficiency is most easily seen in series of results where portions of the same opalescent liquid are placed in the two tubes for comparison.

The following table gives actual successive readings obtained in this way, the first vertical row of figures giving the length of one column of liquid exposed to the light, and the second that of the other. The last vertical row records the ratios of the figures in the two preceding, which in this case should be exactly 1.00.

COMPARISON OF SIMILAR SOLUTIONS

Heights of Equal Intensity			$\text{Ratio}=\frac{a}{b}$
Tube a	Tube b		
53	56		0.95
53	51		1.04
53	54		0.98
77	77		1.00
34	34		1.00
67	64		1.05
	Average	=	1.003
	Theoretical	=	1.000
	Error	=	0.003

The close agreement of the average with the theoretical value shows the absence of any constant error greater than 0.5 per cent in the combination of the effects of the prisms, the tubes, the lighting, or the scale. Evidently, too, the length of tube exposed to the light makes no difference; but, nevertheless, in practice, settings were usually made at several different heights. The actual error (0.3 per cent) of the mean of the six settings corresponds to only 0.0001 milligram of argentic chloride and the maximum deviation (5 per cent) of a single observation from the true value corresponds to 0.0015 milligram. Thus the instrument is capable of a considerable degree of accuracy.

As an example of the details of experimentation, it is worth while to describe two typical experiments which had as their object the discovery of the concentration of certain very dilute solutions of silver nitrate by means of the nephelometer. In each case 10 milliliters (cubic centimeters) of the solution to be analyzed were placed in one of the nephelometer test-tubes, which was then almost filled with pure water, and a definite amount of hydrochloric acid added. For the purpose of comparison small known amounts of a standard solution of silver nitrate containing 5 milligrams of silver per liter were made up to the same volume and treated in the same way. In the first experiments too little of the standard solution was used; hence, to procure quality in the semicircular images viewed through the eyepiece, more of this tube had to be exposed to the light than of the tube containing the unknown solution. For the subsequent comparison 24 per cent (as indicated by the first trial) more of the standard solution was employed, and then the images after precipitation appeared almost exactly equal. This is shown in the column giving the ratio of the scale readings below. The table contains the experimental data and the results. Each value given for the ratio of the scale-readings is the average of many trials. In the second experiment these trials gave values ranging between 0.96 and 1.04, the average being 0.99+.

	Volume of Standard Solution Milliliters	Volume of Solution to be Analyzed Milliliters	Ratio of the Scale Readings $= \frac{\text{Standard}}{\text{Unknown}}$	Silver per liter found Milligrams
Exp. 1	10.00	10.00	1.24	6.2
Exp. 2	12.40	10.00	0.99	6.1
				6.1

This was within one per cent of the actual concentration.

These results illustrate sufficiently the degree of accuracy which may be easily obtained, as well as the best method of proceeding. The first comparison is made with solutions only approximately equal, and the succeeding observations are made upon tubes containing quantities of substance, computed from the first trial, which are much more nearly equal. In this way the greatest accuracy may be reached.

The utmost care must be taken to have the conditions in every way as parallel as possible in the two tubes to be compared. Time must be allowed for the opalescent precipitates to attain their full development; two hours or more should usually elapse between the precipitation and the observation. The mechanism of the precipitation seems to vary in different cases; thus the precipitate from a solution of silver chloride attains its full development at a different rate from that of the precipitate from sodium chloride, when both are treated with excess of silver nitrate. In such a case, equality of condition may be attained by dissolving each precipitate in ammonia and reprecipitating by nitric acid; and in other cases similar precautions must be taken.

In the manipulation the most scrupulous care must be taken to avoid the introduction of dust, which usually contains chloride enough to affect the test. Hydrochloric acid gas is also an insidious source of contamination.

This instrument is not intended for determining large amounts of substance which deposit easily from solution; ordinary quantitative methods serve much better in such cases. Its great usefulness appears when one is required to determine minute traces of precipitates which obstinately refuse to settle, or to be caught by an ordinary filter or Gooch crucible. It may be used not only with silver chloride, but also in many other cases in which a fine divided precipitate reflects light; and it provides an unusually sensitive means of detecting very faint cloudiness in a liquid. It has even been used for estimating bacteria in jelly. In every case, as already indicated, great care must be taken to have the standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use;

and for this reason any fixed standard of reference, such as a ground glass plate, is of very doubtful efficacy.

The contents of this paper may be summarized as follows: An instrument for the comparison of opalescent mixtures is described, which is able to detect and estimate very small amounts of suspended precipitate. The chief possibility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way.

CARACTERISATION DE TRACES INFINITESIMALES DE BORE A L'AIDE DE LA TEINTURE DE FLEURS DE MIMOSA

PAR M. LUCIEN ROBIN

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En 1904[1] j'ai fait savoir que la teinture de fleurs de Mimosa pouvait rendre quelques services en chimie analytique, pour deux raisons.

1. A cause de sa sensibilité aux agents acides et alcalins, ce qui permet de l'utiliser comme indicateur;
2. Parce qu'en se plaçant dans certaines conditions, on pourrait s'en servir pour caractériser l'acide borique.

Il m'a été possible pour cette seconde application, d'augmenter considérablement la sensibilité. Au lieu d'épuiser les fleurs par une solution hydroalcoolique, je me sers d'alcool pur et j'abandonne l'usage du papier imprégné de cette teinture.

Je prépare la teinture en plaçant dans un petit becherglass 5 grammes de fleurs de Mimosa soigneusement isolées, je verse dessus 50 cent. cubes d'alcool ethylique pur à 95° et je mets au bain-marie durant 10 minutes.

Après refroidissement complet je filtre; je verse à nouveau sur les fleurs 40 cent. cubes d'alcool que je décante sur le filtre pour joindre à la première portion, et j'exprime avec une spatule, le résidu.

Cette teinture est conservée dans un flacon bouché à l'émeri dont il est sage de recouvrir le bouchon et le col, d'une petite cloche pour éviter que les poussières ne la souillent, et de préférence on tiendra le flacon à l'obscurité.

Pour faire la recherche de traces de Bore, je me sers de petites capsules de porcelaine à fond plat, ayant 5 centimètres à peu près de diamètre; que je nettoie avec grand soin, à l'aide d'acide sul-

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[1] Comptes Rendus de l'Académie des Sciences, et Annales de Chimie Analytique.

furique, puis d'ammoniaque et que je lave enfin avec de l'eau distillée.

On doit effectuer toutes les manipulations avec une propreté méticulause, à cause de l'extrême sensibilité de la réaction.

En thèse générale, on opère comme si l'on se servait de papier au curcuma, c'est-à-dire en évaporant la liqueur rendue très légèrement chlorhydrique, et traitant le résidu par un alcali.

Il est prudent avant de faire une recherche de traces de bore, de faire un essai à blanc dans la capsule dont on voudra se servir.

Pour celà, il faut avoir à sa disposition une liqueur de soude pure à 1% environ, que l'on prépare suivant le procédé classique c'est-à-dire en projetant dans de l'eau distillée, de petits morceaux de sodium préalablement essuyés à l'aide de papier de soie parfaitement vierge.

On gardera cette solution de soude avec les précautions déjà citées pour la teinture.

Il est nécessaire aussi d'avoir une liqueur d'acide chlorhydrique à 5%.

On met dans la capsule 4 à 5 gouttes d'eau distillée, deux ou trois de liqueur sodique 2 gouttes de teinture de Mimosa, puis une goutte ou deux de solution chlorhydrique, pour acidifier légèrement ce qui est fait quand la liqueur perd sa couleur jaune. On met la capsule au bain-marie ou au dessicateur.

Aussitôt que le résidu est sec, on retire la capsule et après refroidissement le résidu est humecté assez largement avec de l'ammoniaque au quart; le résidu prendra une coloration jaune citron si l'acide borique est absent, dans le cas contraire on observera une teinte rose.

La capsule sera utilisée ensuite après un simple lavage àl'eau distillée, si la réaction a été négative; autrement il faudrait de nouveau la nettoyer à fond.

En outre de la coloration rose qui se développe sous l'action de l'ammoniaque, on remarque lorsqu'il y a de l'acide borique, que le résidu d'évaporation a une couleur d'un jaune brun particulier, tandis qu'elle est à peine jaune citron si le bore est absent.

La couleur rose se manifeste lorsqu'il n'y a que des tracs infimes de Bore, elle tend à être d'autant plus rouge, que le teneur en Bore est plus forte; elle est rouge sang pour quelques centièmes de milligrammes.

Cette teinture rose ou rouge ne persiste pas, elle passe aurouge brique puis au marron.

Sensibilité de la Méthode

En opérant avec une solution d'acide borique pur, on peut reconnaître 0 milligramme 0004 d'acide borique dilué dans un cent. cube, ce qui représente 0 milligramme 000071 de Bore.

Si au lieu d'évaporer au bain-marie, on place au dessicateur jusqu'à évaporation totale, la coloration est excessivement nette avec 0 milligramme 00027 d'acide borique soit 0 milligramme 000048 de Bore.

Recherche en présence des différents sels

J'ai fait ces essais en mettant en présence 1 goutte des solutions salines à 10% et 0 milligramme 00012 de Bore, laissant évaporer au dessicateur après addition de 2 gouttes de la solution de soude pure, autant de liqueur chlorhydrique, et 2 gouttes de teinture.

Avec le nitrate de potasse, la réaction a été intense. Avec les chlorure, bromure, iodure de potassium, ainsi qu'avec le chlore de baryum il en a été de même.

Le phosphate de soude a gêné et la teinte tout en étant rose, l'était moins qu'avec les autres sels.

Le sulfate de chaux n'apas gêné; une trace d'un fluoborate alcalin a donné manifestement la réaction.

Il m'a été possible de caractériser la présence de traces de Bore dans plusieurs échantillons de lait pur.

Pour cela, j'ai évaporé dans une capsule 12 à 15 gouttes de lait, et après avoir calciné, j'ai ajouté aux cendres blanches 3 ou 4 gouttes d'eau, deux de teinture et 2 d'acide chlorhydrique étendu, puis fait évaporer au bain-marie. Laissant l'évaporation se faire à froid, j'ai eu des réactions encore plus nettes.

Une seule goutte de vin suffit pour démontrer la présence normale du Bore avec l'évidence la plus manifeste.

Enfin, la présence d'acides organiques tels que les acides tartrique, citrique, oxalique, acétique, ne permet pas de retrouver des traces de Bore; mais il est facile de se débarrasser de ces acides par calcination.

Quant on a à chercher des traces d'acides borique dans des cendres dont le poids est assez important il convient de s'y prendre de la façon que voici:

Une portion de ces cendres grosse comme une petite lentille est mise dans un verre bien lavé tout d'abord, on délaye cette petite portion dans 3 à 4 centimètres cubes d'eau distillée, et on laisse reposer quelques instants. Trois ou quatre gouttes du liquide surnageant sont décantées dans une petite capsule et additionnées de deux gouttes de teinture de Mimosa qui doit colorer ces quelques gouttes en jaune, an raison de leur alcalinité après acidification ménagée avec l'acide chlorhydrique à 5%, on évapore. Si l'on opére sur une quantité relativement grosse de cendres, au lieu de 2 gouttes de teinture, on peut en mettre 3 ou 4, pour en saturer en quelque sorte, le résidu salin.

Je crois pouvoir dire en terminant que la sensibilité de la teinture de Mimosa dépasse de beaucoup encore celle du papier de curcuma.

THE EXTENSION OF POLARIMETRY IN CHEMICAL ANALYSIS

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There are enumerated some seven hundred organic substances whose solutions are optically active, that is optically active in the restricted sense that they actually can be tested on the polariscope. The polariscope is practically unknown to the general analyst except as a sugar testing instrument, although many of these optically active substances which are not sugars are by no means chemical curiosities, but commercially important. Among such can be mentioned tartaric acid, amyl alcohol, the camphors, the terpenes and their combinations in the essential oils, the majority of the alkaloids and the glucosides.

Furthermore, there are a number of excellent polarimetric methods already extant which have been proved reliable and useful in actual practice. It would seem certain that these would come more into general use and suggest a much wider field of activity for the polariscope in general analysis were the instrument better understood, as well as the great advantages in convenience, precision and rapidity possessed by polarimetric methods more generally known.

Most large commercial laboratories are equipped with a quartz-wedge saccharimeter usually of the half- or triple-shade type. It does not seem to be generally understood that such instruments are adaptable to practically all polarimetric work, enabling the analyst with little practice and experience to make readings to less than .02° of angular rotation, or to .05 of a scale division. Neither the principles of optics involved, the modifications of manipulation nor the calculations of results of polarimetric measurements on the saccharimeter are such as to deter any one from using it in general analysis, but these simple fundamental principles of the working of the saccharimeter must be understood.

The quartz-wedge saccharimeter does not directly measure the angle of rotation of the polarized light rays of one wave-length as does the polariscope, but the rotatory influence of the optically active solution on all the rays is balanced or "compensated" for by interposing what is in effect an oppositely rotating section of quartz but of exactly the same rotating value. The thickness of the quartz section required to produce this compensation or nullifying of the rotatory effect of the solution on all of the polarized rays is expressed on a scale in concentration of sugar, and gives directly the per cent of sugar in any sample when a solution of such is made and polarized under certain standard conditions. It is a simple matter, however, to convert the readings of the saccharimeter into angular degrees of rotation of polarized yellow light, which are the standard polarimetric units, by multiplying by a "light-factor" which has been obtained by direct comparison of the reading of a quartz plate on the saccharimeter with its rotation value obtained on a polariscope. This value for the standard commercial saccharimeter is .3465 expressed in angular degrees for spectically purified yellow light, — the mean of the two D-rays of the spectrum at 20° C. (.3458 when compared with the Laurent polarimeter). Therefore, $a = .3465$ R.

The saccharimeter when made with the highest refinements of optical and mechanical work, will give much more precise measurements than the ordinary commercial instrument is capable of. There is, moreover, a growing demand for instruments of higher precision owing to the fact that solutions of many optically active substances are so dark colored that it is impracticable to make readings except at low concentrations or with short tubes, owing to the strong light absorption. Such small readings, if read on the ordinary saccharimeter, are, of course, liable to large error. Dr. Frederick Bates has designed a quartz-wedge saccharimeter, made by the firm of J. and J. Fric, of Prag, which is capable of readings to within .01 division or about .0035° and, furthermore, has a very effective device for regulating the half-shade angle so that the field illumination can be suited exactly to the special requirements of the solution for most precise reading.

The wedges are enclosed in a dust-proof box which is equipped with a thermometer by which the observer can read their temperatures at a glance. The scales which are also enclosed are very accurately graduated on translucent glass, being illuminated by transmitted light much more effectively than are those of the ordinary type. The vernier divisions, owing to this excellent illumination and high magnification, can easily be read by interpolation to .01 division.

The sensitizing and illuminating regulator alluded to, which has been worked out to practical perfection by Dr. Bates, is an original and valuable feature. By a milled head, which has a graduated dial to show the angular position of the half-shade prism relative to the polarizer, the illumination can be regulated in an instant for maximum effective sensitiveness. A gearing connecting analyzer and polarizer automatically keeps the zero adjustment absolutely constant, even correcting for absorption error of the prism.

The polariscope has several other ingenious devices for convenient and effective working but the superiority of the Bates saccharimeter lies mainly in its greater precision and adaptability under all conditions of polarimetry, either for commercial work or scientific research. There is no doubt that scientific research in polarimetry has been impeded for want of instruments which can take maximum advantage of such conditions, and the Bates saccharimeter, although necessarily elaborate and expensive, will go far to fill such a want.

There is, however, a difficulty, due to rotary dispersion, which often arises in such observations with the quartz-wedge saccharimeter. Many of these organic solutions do not rotate the rays of different wave-lengths in the same ratio as does quartz. Consequently, no one thickness of left rotating quartz can be found, which will exactly balance the rotatory effect of the solution on all the rays of a compound light from an ordinary illuminant such as would be used with the saccharimeter. The effect of polarizing such a solution would be that there would appear at the endpoint a parti-colored field, irrespective of how carefully compensation was attempted, and this would prevent precise readings.

This difficulty is not insurmountable. In extreme cases, especially where great precision is necessary, sodium light can be used, but usually the disturbing rays can be eliminated sufficiently by means of colored solutions or screens; a cell containing a potassium bichromate solution is often used, but what are much more convenient are screens made by coloring gelatine films with a saturated alcoholic solution of aurantia, a common coal-tar dye. These screens are very conveniently made, as suggested by Prof. Louis Derr, by treating lantern-slide photographic plates in a "hypo" fixing bath in the dark, and then dyeing the colorless and well-washed plates with the color. The plates can then be finished with cover slip and binding like lantern slides. These screens cut out very effectively the rays of both ends of the spectrum (those of most unequal dispersion), allowing practically only the green and yellow to pass. Two or three such screens can be used together when necessary.

To illustrate the use of such screens, the following actual polarization of a solution of tartaric acid is briefly described: 20 grams of pure tartaric acid was made up to a water solution of 100 cubic centimeters. This, when polarized in a 2-decimeter tube, gave a strongly parti-colored field at the endpoint, one half being blue, the other red, showing that the rotary dispersion variation of tartaric acid and quartz was large. The average of the readings was 14.70 divisions. Two aurantia screens, made in the manner described, were then used as light-filters, which made the uneven coloring of the field almost imperceptible and the reading was 14.35. An unfiltered sodium-flame gave the same value, 14.35, which agrees well with the calculated one of 14.33. It is seen then that in the case of tartaric acid the dispersion error, which amounts to over 2% of the reading when polarizations are made with ordinary light, becomes negligible when aurantia screens are used.

For particular measurements on substances with a rotary dispersion on a curve different from quartz, Dr. Bates recommends "the yellow-green line of the mercury vapor lamp, which has a wave-length of .000546 mm. because of its great brightness and the ease with which it can be obtained pure. There are now on the market several types of the so-called monochromatic light-producing apparatus, essentially a spectroscope with a second slit in place of the observing eye-piece. When placed between a quartz mercury-vapor lamp and the saccharimeter, the latter is illuminated by sufficient light to permit the use of very small half-shadow angles with uniform color over the entire field."

It is advisable that the saccharimeter have a trough long enough to admit the mounting of a standard quartz-plate at the same time as a 2 dcm. tube, that is, instruments designed for 400 decimeter tubes are preferable, as it is often desirable to extend the scale, which can be done easily by insertion of quartz plates. These quartz plates are comparatively cheap and will be standardized by the Bureau of Standards for a small fee. They are necessary in polarizing laevo-rotatory substances, two dextro-rotatory plates being useful, one reading about 50 and another about 100. Some chemists regularly use a right-rotating plate in reading invert sugar solutions, preferring for various reasons to locate the readings on the plus side of the scale. The true reading of a left-rotating solution in such case is obviously given by the difference between the observed reading and the value of the standard plate. For instance, — an inverted sugar solution and a standard millimeter quartz-plate gave a combined reading of 49.09. As the rotation value of the plate is 62.67, the reading of the solution is -13.58.

Passing over the matter of temperature errors which can be dealt with by familiar methods according to their specific importance as determined in the analysis at hand, only two points may be mentioned: (1) the advantage of eliminating all question of temperature influence by making up solutions and polarizing as near 20° as possible; (2) that it is quite important that the saccharimeter itself be kept at the standard temperature as well as that the solutions be made up and kept at this standard temperature.

In this connection, glass polariscope-tubes with side tubulatures are recommended as especially convenient, not only for inserting a thermometer, but for ease in filling and emptying, as this can be done through the tubulus, which should have a bell mouth, thus making removal of the caps unnecessary. Such tubes are only surpassed for neat and rapid polarizing by the "diffusion tubes," which are needlessly complicated except for large-scale work where hundreds of polarizations are to be made.

Perhaps the most serious difficulty in developing polarimetric methods of testing for many substances has been the complicated and variable influence of many common solvents on their specific rotation. As is well known, the rotatory effect of many optically active solutions is affected by the amount of solvent quite independently of its concentration effect and of the fact that the solvent itself is optically inactive. This influence is negligible in the case of aqueous sucrose solutions, but is quite marked in substances like tartaric acid, camphor and many of the alkaloids. Hence, the apparent specific rotation of such substances is not a constant when calculated from solutions of different concentrations, and a simple relation between the reading and the substance in solution does not exist, such as is expressed by the equation

$$w = \frac{av}{\alpha l}\left(= \frac{.3465\ R\ v}{\alpha l}\ \text{for the quartz-wedge saccharimeter}\right)$$

applying to sucrose and other substances where the variation in rotation at standard temperature is due solely to change in concentration and tube-length.

This, again, is not an insurmountable difficulty, as this influence has been investigated and formulated for common solvents of many optically-active substances, so that it is possible to calculate equations which take this into consideration. For instance, the best solvent for camphor polarization is benzol. When the influence of this solvent is determined by plotting the apparent specific rotation of the benzol solution of camphor at different concentrations against the corresponding per cent of the solvent, this influence is expressed as a straight line of very steep slope and Landolt has derived from this the equation:

$$W = 2.4683\frac{a}{1} - .91747\frac{(a)^2}{1}$$

for the weight of substance in 100 cubic centimeters.

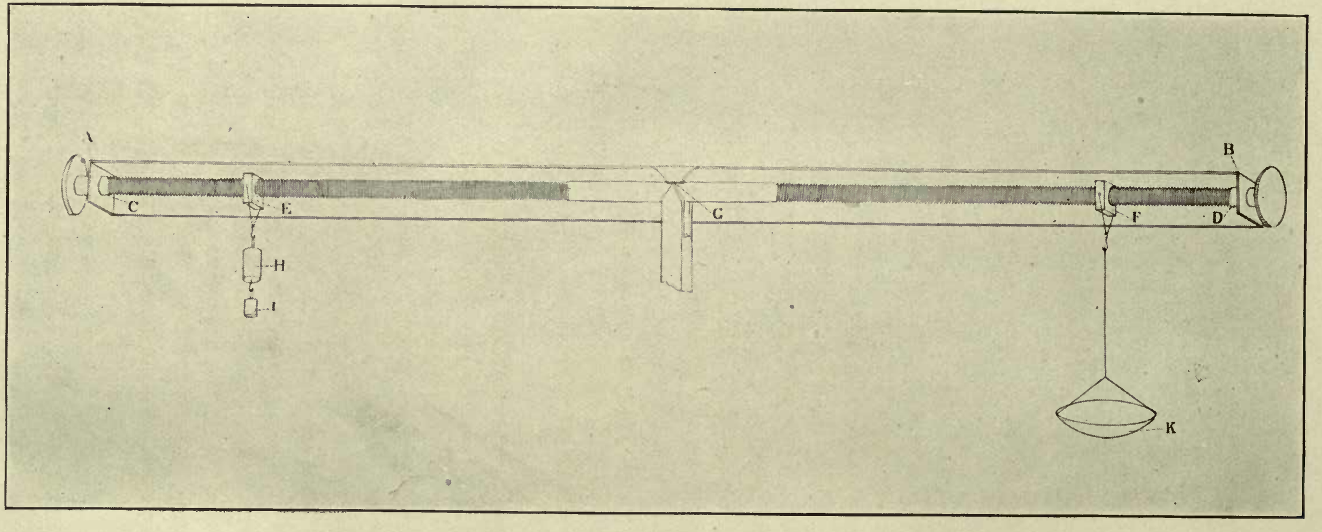
Such calculations are no more complicated than those of many common analytical methods and no more difficult of comprehension. A practical method of determining camphor in celluloid has been developed from these principles.

Complicated calculations can be eliminated in many cases by making the polarizations at concentrations which vary but little from some standard adopted as best for the method at hand. Then, the specific rotation can be taken as a constant and much computation saved, since simple equations analogous to those in saccharimetry can then be used. This is done in polarizations of hydrolyzed starch products which are made on solutions at a density of approximately 10%, and is an expedient common and vital to so many other analytical operations as to require but little comment here. It will be remembered, for instance, that all copper reduction methods require that solutions be made within very narrow limits of concentration variation.

In many cases, an inorganic compound in solution with an optically active substance, has a marked influence on the rotation of the latter, although the influencing substance is itself optically quite inactive. Sometimes the effect is to increase the rotation enormously, and such substances have been found very useful where the optically active substance to be polarized has a feeble rotatory power.

As an illustration, the determination of tartrates in baking powder and effervescent mixtures as worked out by the Kenricks (J. Am. Chem. Soc., *26*, 665) may be cited. Tartaric acid has a comparatively low rotation value, its specific rotation for a 2.5% solution being about 14.7, the value being very much influenced by the solvent. If, however, ammonium molybdate is added in proportion of one mol to three mols of tartaric acid, approximately, the rotation of the acid is increased nearly sixty times and is constant with considerable variation of solvent. By this means very small quantities of tartaric acid can be determined quantitatively. Two methods for the determination of malic acid in sirups and cider vinegars, this acid being important as a criterion of the genuineness of these products, have been worked out independently by Yoder (J. Indus. & Eng. Chem., *3*, 563) and Dunbar and Bacon (idem, *3*, 826). In these methods, uranyl acetate is used to increase the rotation of the malic acid.

These methods are mentioned as examples of some of the expedients which are at the command of the analyst in developing polarimetric methods. If these and other hints set forth in this paper prove suggestive to him for making a more extended use of his saccharimeter in his practice, it has not failed of its object. The writer in turn wishes to thank Dr. C. S. Hudson and Dr. Frederick Bates for helpful advice and encouragement in preparing this paper.



A Specific Gravity Balance for Solids.

A SPECIFIC GRAVITY BALANCE FOR SOLIDS

By A. H. Sabin, Brooklyn, N. Y.

The instrument consists of a beam *A B* of sufficiently rigid construction, which may be a channel beam or a truss of some kind, which forms the support of a rod *C D*, and is supported by a pair of knife-edges at *G*, one on either side of *C D*. One portion of *C D* is a screw with a right-hand thread, and a corresponding opposite portion is a screw with a left-hand thread of the same pitch; each of these portions carries a nut, *E* and *F*. By rotating the screw, as for example, by a milled head as shown, these nuts may be made to approach or recede from the centre at equal rates. From one of these, as *F*, is suspended a pan, *K*, and from the other, as *E*, a weight, *H*, which again carries a smaller detachable weight, *I*. The added weights of *H* and *I* equal the weight of *K*, and the weight of *I* alone equals the loss of weight of *K* when immersed in water.

It is obvious that in any position of the nuts *E* and *F*, $H+I$ will balance *K*, and also that at any point *H* alone will balance *K* when the latter is immersed in water.

If a weight, for example ten grams, is placed on the beam at *A*, so that it will not be moved by the rotation of *C D*, it will be counter-balanced by any weight greater than ten grams in the pan at some point between *D* and *G;* that is, by turning *C D* and causing the pan to move parallel to *A B*, a point may be found when it will balance the fixed ten-gram weight at *A*. In use, both *H* and *I* are attached to *E*, the object to be examined is put on the pan and brought to a point where it balances; then *I* is removed, *K* and the substance on it immersed in water, the buoyant effect of which is now perceived only on the substance under examination.

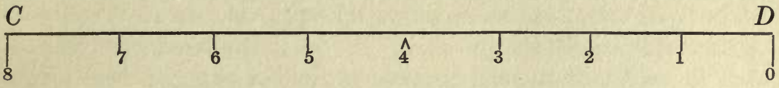
If, further, the beam *A B* carry a movable weight or rider, it is clear that when this rider is opposite *G*, it will have no effect; but as it is moved from *G* toward *B* it will tend to counteract the buoyant effect of the water on a solid substance, such as a piece of metal, and if the rider is of a suitable weight, it may be so placed as to do this exactly. Suppose this to be accomplished: if the piece of metal be removed from the pan, and another piece of the same metal but of larger size substituted, the supporting nuts *E* and *F* must be moved toward *G* to make the instrument balance; the total buoyant effect of the water on the larger piece will be greater, but will be exerted with less leverage as regards the rider, so that the latter will remain in the same place on the beam. If, however, a piece of another metal of the same weight but different density be substituted, the rider must be moved. Therefore, the point at which the rider rests on the beam will indicate a certain density of the body which is placed on *K*, and the beam may be graduated accordingly.

If the rider, in the conditions described, weigh ten grams, if it is placed on the beam at the right of *G*, a distance equal to *A G*, and in that position the immersed body is balanced, it is obvious that the latter has a density equal to that of water; but if balancing is effected when the rider is opposite *G*, the density would be infinite; that is, such a rider could be used for any substance with a density not less than that of water. This, however, would make the divisions on the beam inconveniently short; and it will be more convenient so to proportion the rider as to have longer scale-divisions, but a more restricted range.

How this may be done is best shown in a particular case. Suppose it is desired to be able to determine the densities of alloys of tin and lead. Tin has a density of 7.30 and lead 11.34; these will be the extremes of the scale. We may, therefore, after balancing the substance under examination, begin by attaching to the extremity *B* of the beam a small weight, nearly sufficient to counteract the buoyant effect of water on tin; let this counterweight be 1.11 grams, and let the rider be 270 milligrams; when this rider is also at *B*, it will correspond to a density of 7.25, but when it is at *A* it will correspond to a density of 11.9, thus giving a small range each side of the desired limits. It is obvious that, after balancing the substance under examination, instead of adding a weight of 1.11 gm. at *B*, the original ten-gram weight may be moved along the beam from *A* to a point .111 of the distance from *A* to *G;* having this point marked on the beam, this may be better than having an extra weight. It will further be obvious that in this case the rider traverses the whole beam, thus giving scale-divisions of sufficient extent.

The value of any point on the scale may be determined as follows: Suppose the point chosen be three-fourths of the distance from *A* toward *B;* the total weight, estimated as at *B*, counteracting the buoyant effect of water will be 1.11 gr.$+\frac{3}{4}$ of .27 gm.$=$ $1.11+.2025=1.3125$ gm. This operates against a weight equal to 10 gm. at *B;* and the density of the substance is $\frac{10}{1.3125}=7.62$

The density at any such point may be also found by this formula:



$a=$equivalent of weight at C after moving the weight (*e.g.* 8.89 gm.).

$b=$weight of original weight at *C*, the equivalent of which is supposed to be at *D* (*e.g.* 10 gm.)

$c=$ weight of rider (*e.g.* 0.27 gm.).

$y=$any equal length division point, counting from *D* toward *C*.

$x=$sp. g. when rider is at y, $= \dfrac{b}{b-\left[(a-c)+\dfrac{cy}{d}\right]}$

The following adjustments of the instrument must be provided: The surface at *G* which rests on the knife-edge must be adjustable vertically, so as to bring it into line with the knife-edges on *E* and *F;* and the bearings at the ends of the beam which carry the rod *C D* must be adjustable laterally, capable of a movement equal to the pitch of the screw, to make the nuts *E* and *F* equidistant from G. Any other adjustments are obvious. It is also obvious that the instrument may be so designed as to operate with more than one rider; and that other mechanical means than screws may be used to move supports corresponding to the nuts *E* and *F*, as, for example, a cord or chain operated by suitable mechanism; also that a scale-pan may be attached at *B*, and weights used instead of or in combination with a rider.

THE VOLUMETRIC DETERMINATION OF TITANIUM

By Porter W. Shimer and Edward B. Shimer
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The volumetric determination of titanium has been the subject of investigation by Pisani[1], Marignac[2], Wells and Mitchell[3] Newton[4], Knecht and Hibbert[5], Gallo[6], and Hinrichsen[7]. The main difficulties are that it is hard to get complete reduction of TiO_2 to Ti_2O_3 and that special precautions must be observed to prevent the reoxidation of the reduced solution. The above named investigators reduce by adding zinc in the form of rods or otherwise to the solution contained in a flask through which a current of carbon dioxide is passed. Reduction by this method seems to be slow and often imperfect; Gallo, for instance, requires from five to twelve hours.

Our contribution to the subject lies in the method of reduction, the elimination of the influence of vanadium, and certain details as applied to the various ores and products. In our work we pass the hot sulphuric solution of titanium and iron through a very long reductor filled with amalgamated zinc, the receiving flask being filled with carbon dioxide before and after the reduction; the time required for complete reduction need not be more than fifteen minutes.

When both iron and titanium are to be determined the iron may be reduced by hydrogen sulphide and titrated with potassium permanganate after boiling off the hydrogen sulphide and cooling in an atmosphere of carbon dioxide. For titanium, the reduction is made in the long reductor and both elements are titrated together with potassium permanganate. When titanium alone is to be determined it is better to use a standard-

[1] Compt. Rend., *59*, 298.
[2] Zeitschr. Anal. Chem., *7*, 112.
[3] Jour. Amer. Chem. Soc., *17*, 878.
[4] Amer. Jour. of Science, (4), *25*, 130.
[5] Ber., *36*, 166; *37*, 3475.
[6] Chem. Abstracts, *2*, 968.
[7] Chem. Ztg., *31*, 938, 1907.

ized solution of ferric ammonium sulphate, using a saturated solution of potassium thiocynate as an indicator.

The special apparatus required consists simply of the reductor and a carbon dioxide generator. The reductor is a piece of glass tubing three feet in length and three eighths of an inch in internal diameter, drawn out at the lower end, in which is placed a little glass wool. The upper end is connected by rubber tubing to a four-inch funnel. The reductor is suspended at such a height as to allow the gas bottle, when attached to it, to swing clear of the table. The reductor is filled with amalgamated zinc of a size that passes through a 10-mesh sieve and remains on one of 20 mesh; finer zinc is apt to clog the tube. A twenty-inch reductor of this simple form was described and figured by one of us in Vol. 21, p. 723, of the Jour. Amer. Chem. Soc. It may be stated, in passing, that the passage of a hot sulphuric molybdate solution through this twenty-inch reductor, previously heated, reduces MoO_3 completely to Mo_2O_3.

The lower end of the reductor passes through a two-hole stopper far enough to reach half way to the bottom of a 500 cc. gas bottle. The gas bottle is connected with suction provided with a valve or clamp to regulate the rate of passage through the reductor.

Before making a titanic reduction it is necessary to wash out the reductor with hot dilute sulphuric acid; this heats the zinc and makes the reduction more effective. The next step is to fill the gas bottle with carbon dioxide. Now connect the reductor and draw the hot sulphuric solution of titanium and iron through it, but not faster than by rapid dropping. Wash several times with hot water containing a little sulphuric acid, disconnect the gas bottle and quickly pass a rapid stream of carbon dioxide through it. When the air has been completely expelled add at least 5 cc. of a saturated solution of potassium thiocyanate and titrate with the ferric solution. The end reaction is rather slow and the solution must be added until the brownish color remains for at least a minute.

The ferric solution is made by dissolving 30 grams of pure ferric-ammonium sulphate in 1000 cc. of water acidified with sulphuric acid. Permanganate solution must be added drop by drop as long as the pink color disappears. This solution may be diluted to any point desired for the special work in hand; for most of the work of this investigation it was diluted with an equal bulk of water.

To illustrate the influence of the manner of reduction the following experiments will suffice:—50 cc. of a standard titanium solution, reduced in a 20-inch reductor, without use of carbon dioxide, required 16.00 cc. of ferric solution. Another 50 cc., put through the same reductor with use of carbon dioxide, took 17.30 cc. of ferric solution. A third 50 cc. put through the 36-inch reductor with use of carbon dioxide, required 18.65 cc. the correct amount, showing the necessity of using the long reductor, and carbon dioxide to prevent reoxidation.

Analysis of Rutile. A sample of purified rutile, weighing .1037 gr., was fused with potassium bisulphate. The fused mass was dissolved out of the deep crucible in a mixture of 15 cc. of sulphuric acid (1:1) and water by aid of carefully applied heat. The solution, after filtering off a slight insoluble residue, was transferred to a 500 cc. gas bottle and hydrogen sulphide was passed through for half an hour. The hydrogen sulphide was boiled off and, after cooling, the iron was titrated with potassium permanganate. After this titration the solution was heated to near boiling and passed slowly through the long reductor, previously heated by passing hot water acidified with sulphuric acid, through it. The gas bottle, as always, was filled with carbon dioxide both before and after the reduction. Five cc. of a saturated solution of potassium thiocyanate was added and the solution was titrated with the ferric solution, of which 41.38 cc. was taken. The calculation follows:—50 cc. ferric solution, when reduced, requires for its oxidation 13.90 cc. of permanganate solution whose strength against iron is .006095. One cubic centimeter of the ferric solution therefore contains .0016944 gram of iron. Dividing this figure by .697 we get .002431, the strength of the ferric solution against TiO_2. Therefore:—

$$\frac{41.38 \times .002431 \times 100}{.1037} = 97.01\% \ TiO_2.$$

The result of the analysis was:—

Titanic acid	97.01%
Oxide of iron	1.52%
Insoluble residue	1.40%
	99.93%

Titanic acid was determined in a sample of argillaceous limestone in which the Bureau of Standards found .230% and .210% of TiO_2. Three samples of one gram each were intimately mixed with .5 gr. of sodium carbonate and heated over the Meker burner. The sintered mass was dissolved in hydrochloric acid, precipitated with ammonia, filtered and washed with hot water, dissolved in dilute sulphuric acid and put through the reductor in the usual way. The results were .212%,. 223% and .200% TiO_2.

Titanium was next determined in a sample of Goldschmidt Ferro-Titanium, crushed to pass through a 40-mesh sieve. Three samples of .3000 gr. each were dissolved in dilute sulphuric acid and peroxidized, while boiling, with a strong solution of potassium permanganate. The excess of permanganate was reduced with a little ferrous sulphate and the hot solution was passed through the reductor. The results were 21.28%, 21.31% and 21.27% of titanium.

Three samples of high titanic iron ore were next treated in the following manner:—Fused 1 gr. of each ore with potassium bisulphate and a little sodium fluoride in a deep platinum crucible of 60 cc. capacity. Dissolved by aid of heat in the crucible in sulphuric acid and water, using about 20 cc. of (1:1) sulphuric acid diluted to 250 cc. and took out with a pipette two 100 cc. portions, each corresponding to .4 gram of the ore. Heated both portions to near boiling and reduced them in the long reductor. The first was titrated with permanganate and the result noted. The solution, after the titration, was saturated with hydrogen sulphide, the hydrogen sulphide was boiled off and the iron titrated, when cold, with permanganate. The other portion of the solution was reduced in the long reductor, with the precautions used in determining titanium, and titrated with ferric solution. The results in the three ores were as follows:—

	A	B	C
Iron, direct (H_2S)	50.59%	56.00%	34.02%
Iron indirect	50.65%	56.17%	34.00%
TiO_2 direct (ferric sol.)	21.75%	14.68%	44.91%
TiO_2 indirect	21.84%	14.93%	44.88%

The following work was done on the standard Magnetite on which the Bureau of Standards results are 1.01%, .98% and .99% TiO_2. by different methods. Our gravimetric results on the sample by the Gooch method were .99%, .99% TiO_2. For the volumetric determination we fused one gram with potassium bisulphate and a little sodium fluoride and put the hot sulphuric solution through the long reductor with the usual precautions. The result was 1.035% TiO_2. This high result is accounted for by the fact that this ore contains .08% V_2O_3. In order to eliminate the vanadium we fused an intimate mixture of the ore with four grams of sodium carbonate and four grams of sulphur in a porcelain crucible for 45 minutes over the Bunsen flame. The fused mass was dissolved out of the crucible with hot water and filtered. The filtrate contains the vanadium, which, by the way, may be determined by acidifying the cold solution with sulphuric acid, filtering off the precipitated sulphide of vanadium, incinerating in a porcelain crucible, dissolving the V_2O_5 in hydrochloric acid (1.20 sp. gr.) and evaporating twice with the same acid—the last time with the addition of sulphuric acid—and titrating with a very dilute potassium permanganate solution.

The above insoluble residue contains the iron and the titanium. It is treated on the filter with dilute sulphuric acid, which dissolves the iron suphide and probably a part of the titanium. The residue insoluble in sulphuric acid is incinerated in a platinum crucible, fused with potassium bisulphate and a little sodium fluoride, and dissolved in sulphuric acid and water. This solution is added to the solution of the iron and, after complete expulsion of the hydrogen sulphide, it is put through the reductor. The TiO_2 thus found was .996%.

A sample of titanium carbide, weighing .1000 gr, was dissolved in nitric acid: sulphuric acid was then added and the solution was evaporated to fumes of SO_3. The residue was dissolved in hot water, filtered and put through the reductor. The results of the analysis of the carbide were:—

Titanium Carbide (TiC)	88.28%
Graphitic Residue	7.64%
Silicious Residue	3.10%
Iron	.97%
	99.99%

Titanium was next determined in a sample of pig-iron containing vanadium. Five grams of the iron were dissolved in a mixture of 200 cc. of water and 20 cc. of hydrochloric acid (1.20 sp. gr.). Immediately before filtering about 1 cc. of hydrofluoric acid was added to the solution. The insoluble residue was filtered off, washed and transferred to a platinum crucible in which the graphite was burned off. The residue was carefully brushed out on a piece of glazed paper and the crucible, with the adhering residue, was set aside for use later. The residue on the glazed paper was well mixed with an excess of sodium carbonate and sulphur and fused for half an hour in a porcelain crucible. Before using the crucible it must be carbon-coated by melting a little sugar or tar in it, running it around the sides, and finally igniting with the lid on. This prevents the fluxing of any part of the residue with the crucible glaze. The fused sulphides are extracted with hot water and filtered. The residue contains the titanium and the filtrate contains the vanadium; they are determined in the same way as described in the analysis of the magnetite. The iron was found to contain .370% titanium and .042% vanadium. This method is based on the well founded assumption that all of the titanium in pig-iron is found in the residue insoluble in hydrochloric acid.

On the determination of titanium in steel the following tests were made:—One gram of plain .60% carbon steel was dissolved in sulphuric acid and peroxidized, while boiling, with potassium permanganate. The precipitated MnO_2 was reduced by ferrous sulphate solution. Added a measured amount of standard titanium solution. The solution was put *twice* through the long reductor with all the precautions. We found that, when there is a large excess of iron, as in the determination of titanium in steel, a single passage through the reductor does not suffice. The results of three tests using 5, 10 and 15 cc. of the titanium solution were as follows:—

No. 1—Titanium taken.....00032 gr Ti found.....00032 gr
No. 2—Titanium taken.....00064 gr Ti found.....00065 gr
No. 3—Titanium taken.....00096 gr Ti found.....00095 gr

We next dissolved 5 grs. of a plain .20% carbon steel in sulphuric acid and peroxidized with potassium permanganate and reduced the excess with ferrous sulphate. To this solution was added 25 cc. of the same titanium solution and it was passed *twice* through the long reductor.

Results:—Ti taken........0016 gr Ti found.......0016 gr

We next dissolved 3 gr. of a plain .60% carbon steel in 20 cc. (1:1) sulphuric acid and 100 cc. of water, oxidized with permanganate as before and added 100 cc. of titanium solution. Evaporated to 120 cc. reduced, heated the reduced solution to boiling in the gas bottle containing an atmosphere of carbon dioxide and reduced again, using carbon dioxide each time.

Result:—Ti taken..........0064 gr Ti found.......0062 gr

A SPECTROSCOPIC METHOD FOR THE DETERMINATION OF LITHIUM

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INTRODUCTION

In the examination of mineral waters for lithium there is need of a method by which small amounts of this substance may be determined with reasonable accuracy when only relatively small amounts (from one to five liters) of water are available for this determination in the general scheme of a complete mineral water analysis. Where the amount of lithium present is as small as 0.001 mg. per liter, the evaporation of a quantity of water large enough to give a weighable quantity of lithium salt consumes so much time and gives such large quantities of other salts that it seems better to use a small quantity of water and determine the lithium spectroscopically after it is separated from the other constituents.

In such cases the separation from the other substances in the water is carried out according to the provisional method of the Association of Official Agricultural Chemists[1] first proposed by Gooch[2]. The spectroscopic determination is made on a solution of the sulphates of lithium, sodium and potassium obtained by the Gooch method of separation with amyl alcohol[3]. A preliminary paper by one of the authors[4] gave a brief outline and review of the work, making use of the spectroscope in the quantitative determination of lithium and the effect of the masking of the red lithium line by various amounts of sodium and potassium. In this paper is given a review of methods which have been considered or tested and a method developed by the authors for the determi-

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[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 153.

[2] Amer. Chem. J., 1887, 9: 33–51.

[3] For a comprehensive review of the literature of the subject, together with certain experimental data, refer to Bureau of Chemistry, U. S. D. A., Bul. 153.

[4] Skinner. A spectroscopic method for the determination of lithium.

nation by the spectroscope of the small amount of lithium usually found in mineral waters and in some other substances.

HISTORICAL DATA

As early as 1826 Talbot[1] suggested that the various color lines in the spectrum were due to the different metals and were characteristic of them, and in 1836[2] suggested the measurement of the relative positions of the bright and dark lines. Although Swan[3] in 1856 had suggested the use of the collimator, the first comprehensive work on spectrum observations was issued by Kirchoff and Bunsen[4] in 1860. They made some accurate measurements of the sensitiveness of the tests with the spectroscope and were able to observe .00000006 mg. of sodium, .000002 mg. of lithium, .0003 mg. of potassium, .00003 mg. of strontium, .00002 of calcium and .0003 mg. of barium. They reported also the presence of lithium in a large number of substances; in the ash of various plants, in minerals, and in many waters. Cappel[5] in 1870, using a spark spectrum, was able to detect .000000025 mg. of lithium which was considerably less than the amount detected by Kirchoff and Bunsen. Others who worked on the same subject were Mitscherlich, Brassack, Church, Janssen, Champion, Pellet and Grenier, Lockyer and Roberts, and Truchot. The latter made some determinations of lithium in waters by comparing the intensity and duration of the lithium line obtained from the sample with that obtained from standards. This method has been used by us with the modification that the standards contained in addition to the lithium different amounts of sodium chlorid, either ten or 100 mg. per cubic centimeter, and the mixed chlorids obtained in the analyses which were to be tested for lithium were dissolved in such an amount of water that the solution contained either ten or 100 mg. per cubic centimeter. Using a straight wire, .01 mg. of lithium per cubic centimeter was about the lowest limit with a solution of lithium chlorid alone. When the solution of this strength contained 100 mg. of sodium chlorid, the

[1] Edin. J. Sci., 1826, 5: 77.
[2] Phil. Mag., 1836, (3) 9: 3.
[3] Phil. Mag., 1860, (4) 20: 173.
[4] Pogg. Ann., 1860, 110: 161–189.
[5] Pogg. Ann., 1870, 139: 628–639.

lithium was very much more difficult to see. The use of the small coil of wire suggested by Truchot by which a uniform drop of liquid is picked up each time is an improvement.

TABLE I

Determination of Lithium by Modified Method of Truchot
With no Sodium Chlorid

Lithium added to solution (mg. per cc.)	Lithium found by comparison with standard containing the same amount of sodium chlorid			Lithium added to solution (mg. per cc.)	Lithium found by comparison with standards containing the same amount of sodium chlorid		
	Analyst A		Analyst B		Analyst A		Analyst B
	1st day	2d day			1st day	2d day	
0.70	0.50	0.50	0.50	1.00	0.80	0.90	0.80
.20	.10	.10	.30	.05	.08	.05	.04
.80	.70	.80	1.00	.80	1.00	.80	1.00
.01	.02	.01	.01	.40	.60	.50	.20
.05	.03	.03	.05	.01	.01	.01	.01
With 10 mg. Sodium Chlorid per Cubic Centimeter							
0.01	0.03	0.02	0.01	0.05	0.06	0.10	0.10
.01	.02	.02	.01	.70	.80	.50	.50
.50	.50	.50	.30	.40	.80	.50	.40
.20	.20	.40	.30	.10	.10	.20	.08
1.00	.90	1.00	1.00	.30	.20	.25	.25
With 100 mg. Sodium Chlorid per Cubic Centimeter							
1.00	0.80	....	1.00	0.10	0.06	....	0.20
1.00	.90	....	1.00	.01	.04	....	.00
.80	.60	....	1.00	.02	.06	....	.05
.20	.10	....	.05	.03	.03	....	.02
.50	.50	....	.25	.04	.02	....	.01

In Table I[1] are given some results showing the relative accuracy of readings made under strictly uniform conditions, using a straight wire and Bunsen lamp. Results are given on standards

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[1] Skinner. "A spectroscopic method for the determination of lithium," a paper read at the meeting of American Association for the Advancement of Science, 1908.

of known amounts of lithium chlorid without the addition of sodium chlorid, with varying amounts of lithium chlorid plus ten mg. of sodium chlorid per cubic centimeter, and with varying amounts of lithium chlorid plus 100 mg. of sodium chlorid per cubic centimeter. The masking due to potassium was tested and found to be very much less than that due to sodium; therefore, in view of the small amounts of potassium usually found in mineral waters as compared with sodium, the effect of potassium was not studied further.

In order to avoid the personal equation as much as possible, the solutions were prepared by an assistant and read by two persons unacquainted with the value of the solutions, one analyst making two sets of observations but on different days. A preliminary test of the unknown solution at once showed whether the standards to be used for comparison should be the set containing ten mg. of sodium chlorid per cubic centimeter or that containing 100 mg. of sodium chlorid per cubic centimeter. The appropriate set of standards for comparison was then selected. These standards were prepared in sets containing amounts of lithium varying from 0.01 to 1.00 mg. per cubic centimeter, and the comparisons made in a manner suggested by the comparison of colorimetric standards.

Ballmann[1] diluted a solution containing a known amount of lithium until the lithium line could not be seen in the spectroscope, and then diluted the unknown solution to the point where the line could not be seen. By considering the concentration of lithium the same in both cases he was able to calculate the amount in the unknown solution. In his experiments the lithium line was seen easily with a volume of 1,320 cc., seen faintly twice and missed once when the volume was 1,340 cc., and with a volume of 1,360 cc. could not be seen at all. This would appear to make the error of the method about two per cent. The lithium line could not be seen when one mg. of lithium chlorid was made up to 3,345 cc. (0.0003 mg. in 1 cc.). Ballmann used a spiral loop 2.5 mm. in diameter and 3.5 mm. along the axis.

Jones[2] described some experimental work which led him to the conclusion that satisfactory quantitative determinations could not be made by the spectroscope.

[1] Zts. anal. Chem., 1875, 14: 297.
[2] Chem. News, 1876, 34: 122.

The method published by Bell[1] is the same as that of Ballmann.

Foehr[2], commenting on Bell's[3] paper, stated that he himself had made many experiments on quantitative analysis by the spectroscope, but did not obtain as good results as those reported by Bell. Instead of diluting until the spectrum failed to appear, he added a solution of the substance a little at a time to pure water, testing the mixture by means of the spectroscope after each addition. The endpoint was the concentration at which the spectrum first appeared and was found to be much sharper by this method.

Nasini and Anderlini[4] determined lithium in a thermal water by the method of Foehr. At another time[5] in the analysis of a brine they used this method on the original water, first obtaining a rough approximation as to the amount and then making up a solution with a known amount of lithium and about the same content of other substances as the water under examination. When this solution was added to distilled water and tested with the spectroscope the amount of lithium present when the lithium line first appeared was different from the amount required when no other salts were present. They noted the necessity of having the wires and drops of uniform size, of keeping the Bunsen burner flame of constant size, and of always placing the wire in the same part of the flame.

Ranzoli[6] compared the spectroscopic and gravimetric methods for lithium, determining the lithium by Foehr's method and found 0.52078, 0.51688 and 0.5151 gram of lithium chlorid instead of 0.54 gram, the average being 4.15 per cent. low. Then he used the method as modified by Nasini and Anderlini[7] and found 0.53612 and 0.53914 instead of 0.5400 gram. On some solutions of unknown lithium content he obtained 0.2708 gram when the solution contained 0.2700 and obtained 0.18953 gram from a solution containing 0.189 gram. The average error on the three solutions was 0.365 per cent. Ranzoli advocated the use of this method in preference to the gravimetric method for all waters,

[1] Amer. Chem. J., 1885, 7: 35.
[2] Chem. Ztg., 1885, 9: 1013.
[3] Amer. Chem. J., 1885, 7: 35.
[4] Gaz. chim. ital., 1894, 24 (I): 327.
[5] Gaz. chim. ital., 1890, 30 (I): 305.
[6] Gaz. chim. ital., 1901, 31 (I): 40–48.
[7] Gaz. chim. ital., 1890, 30 (I): 305.

as the determination is made on the original water added to distilled water and there is no chance for loss or gain of lithium in manipulation.

Ranzoli[1], Hermann[2] and Nutting[3] also worked along similar lines.

Abati[4] determined the lithium in a mineral water by the method of Nasini and Anderlini. The water to be examined was diluted until the lithium line was barely visible. This diluted solution was added, a little at a time, to 25 cc. of distilled water until the line appeared in the spectroscope. A standard solution was made up of approximately the same composition as the water sample, but with a known amount of lithium. When 147 cc. of this solution was added to 25 cc. of distilled water the lithium line could not be seen. With 148 cc. one trial gave the lithium line, while with 149 cc. the majority of the drops taken showed the line, and when 150 cc. were added every drop gave the line. One hundred and forty-seven cubic centimeters of the water mixed with 25 cc. of distilled water failed to show the lithium line; with 146 cc. added the line appeared in a majority of the trials and with 149 cc. added, it was shown by every drop. These readings would indicate an error of less than one per cent in the determination, which is a greater accuracy than we have regularly obtained when working with this method.

While Nasini and Anderlini, Ranzoli and Abati all recorded most excellent results by the method proposed by Nasini and Anderlini, such close results have not been obtained by us when using this method. When, therefore, lithium is present in weighable amounts and reasonable quantities of water are available for examination, the amyl alcohol separation is preferred. For the estimation of lithium in many waters on which work has been done, the method of Nasini and Anderlini could not be used because the waters contained so little lithium that the spectrum could not be obtained from the water without considerable concentration. As in most of our work complete analyses are required, the alkaline chlorids are obtained pure, so that it is very little trouble to separate the

[1] Gaz. chim. ital., 1901, 31 (I): 40–48.
[2] Uber das Vorkommen des Lithions im menschlichen Organismus, 1905.
[3] Astrophys J., 1905, 22: 131–137.
[4] Gaz. chim. ital., 1906, 36 (II): 855–860.

lithium by amyl alcohol, and when it is separated the lithium can be determined by the spectroscope. The extraction by amyl alcohol from the solution of the chlorids seems the only way likely to give all the lithium when the total amount is less than one mg. On account of the fact that the lithium always remains in solution, there is no serious trouble from either of the difficulties mentioned by Ranzoli as objections to the gravimetric methods.

PROPOSED METHOD WITH EXPERIMENTAL DATA

After the preparation of the sulphates of sodium, lithium and potassium for weighing, they are dissolved in a small amount of water, from one to ten cc. according to the amounts of lithium expected to be found. By trying the solutions in the flame before the spectroscope it was quickly determined whether to dilute to the vanishing point of the lithium line, as did Ballmann[1] and Bell[2], or whether to make to a volume of 25 to 100 cc. and add to distilled water as Foehr did. In consideration of the errors of observation, it has not seemed worth while to add sodium and potassium sulphates to the lithium solution used for comparison. The potassium and sodium sulphates are rarely present to the amount of more than 0.0005 gram each or at the most 0.0010 gram each. In most cases the potassium spectrum does not appear at all in the work and the sodium line is not much brighter than it is in the lithium solution of known strength which has been kept in a glass bottle for a short time. The spectroscope used in the investigations is an ordinary high-grade instrument made by Krüss. The scale is illuminated by a small electric light, and switches under the edge of the table enable the observer to illuminate the scale or the room without moving.

Most of the experimental work has been done with a Bunsen burner having a rather small tip, which makes the flame steadier. A porcelain burner was used to eliminate the copper lines which occasionally appeared, but as in most of the work the telescopes were set so as to have the sodium line just barely out of the field, no other spectra came into view to interfere with the observation of the lithium line. A hydrogen flame, which, from some preliminary trials, gave promise of overcoming several difficulties

[1] Zts. anal. Chem., 1875, 14: 297.
[2] Amer. Chem. J., 1885, 7: 35.

encountered with other sources of heat was also used. With the burner which was devised for use with hydrogen and the apparatus for supplying the gas the variations in the intensity of the flame over a period of several hours could not be controlled as well as could be done with a Bunsen burner and ordinary gas, and it as finally concluded that the advantages of the hydrogen flame were not sufficient to warrant an elaborate apparatus for controlling and supplying the gas at fairly constant pressure over extended periods of time.

To bring the solution into the flame, platinum wires are used which are formed into cylinders at the ends by winding four times about a No. 10 wire. The four turns lie close together making almost a solid cylinder, and drops picked up in these loops are very constant in weight, some of the first loops used containing 0.010 to 0.012 gram of water. The cold loop is carefully plunged into the solution and taken out with the axis of the cylinder parallel to the surface of the water. The drop of water is carefully evaporated by placing it at such a distance above a flame that it is vaporized without spattering. The loop is then brought into the flame, usually after being warmed a little. With the apparatus used regularly by the authors, different observers usually have about the same limit for the amount of lithium which will barely show the lithium line. This varies from 0.000015 to 0.000025 mg. per cc. when no large amounts of other alkalies are present.

There is a possible chance for some slight variation in the amount of solution taken up by the loop, but weighings of the amounts taken up in many successive trials indicated that this is a wholly negligible source of error. The bringing of the loop into the flame is probably the chief source of error. None of the authors using a platinum wire made any mention of the difficulty of accomplishing this in a uniform manner. If the loop is made of moderately fine platinum wire, the wire is not likely to be perfectly straight, so that if it is held in a stand great care is needed to have the loop always at the same height. It would be entirely feasible to arrange a mechanical holder which would insure the proper placing of the loop in the flame, but it has been found more convenient to have one person put the loop into the flame while another makes the observation. With care and experience the one handling the wire can place it in the flame with loop always at the same height, using some object or part of the spectroscope as a gauge. When nearly at the limit of visibility of the lithium line he can make the line appear or not by varying the vertical position of the loop in the flame less than a centimeter. The position of the loop in the horizontal section of the flame also affects the brilliancy of the lithium line, probably due in part to the distance from the slit. It requires some practice and skill, therefore, on the part of the assistant holding the wire if concordant results are to be obtained.

In fact, the success of the observations depends upon maintaining strictly comparable conditions throughout an observation on both standard and unknown solutions. One of the chief reasons for trying the hydrogen flame was to lessen the variations due to the uncertainty of the position of the loop before the slit. With the conveniences at hand for controlling the supply of hydrogen, however, there were greater irregularities introduced by the varying size of the flame than were due to the position of the loop in the flame. With the use of illuminating gas it has been found that the pressure varies during the day so as to cause some slight irregularity in the minimum amount of lithium necessary to produce a spectrum and it is desirable to check the standard frequently. The distance from the slit in the collimator to the flame is a factor which may be kept constant, as may the width of the slit. The following figures show something of the effect of the width of the slit on the sensitiveness of the test. These trials were made with the hydrogen flame.

EFFECT OF THE WIDTH OF SLIT OF COLLIMATOR ON THE SENSITIVENESS OF THE TEST

Width of slit of collimator	Observed limit of lithium per cc.	Width of slit of collimator	Observed limit of lithium per cc.	Width of slit of collimator	Observed limit of lithium per cc.	Width of slit of collimator	Observed limit of lithium per cc.
mm.	mg.	mm.	mg.	mm.	mg.	mm.	mg.
0.04	0.000058	0.05	0.00006	0.14	0.000014	0.24	0.000012
.06	.000022	.06	.00004	.16	.000013	.30	.000010
.08	.000017	.08	.000019	.18	.000013	.20	.000010
.12	.000010	.10	.000015	.18	.000010	.16	.000012
.04	.00007	.12	.000014	.20	.000011	.12	.000015

Up to the width of 0.2 mm. the lithium line is visible with smaller amounts of lithium as the slit is made wider. If used wider than 0.2 mm. there is no very noticeable increase in brilliancy in the lithium line, while if other salts are present the light from them is so bright as to interfere seriously with the observation of the lithium. As the whole method rests upon the fact of the observer seeing or not seeing the lithium line, there enters also a question of the personal equation. In all experiments it is possible to keep the mind of the observer free from bias. No effect of the observer's desire or expectation has been noted on the visibility of the lithium line and so no special effort has been made to keep him in ignorance. There has been an attempt to make the dilutions such that the relations could not be readily calculated, so that each determination of limiting concentration was independent of the others on the same solution.

While working at determinations with the spectroscope the element of fatigue enters as Jones[1] observed and the eye may become less sensitive. On the other hand, up to a certain time it is quite likely that the eye becomes more sensitive with practice. If a complete determination could be carried out with trials at only six or seven dilutions as given by Abati[2], it is not likely at any time that the condition of the observer would enter very largely into the results, but it usually requires a number of trials to come anywhere near the proper dilutions where the final trials may be made. The suggestions given in the following description of the method should therefore be carefully observed.

To show what results could be obtained by the method outlined, four samples were taken through the regular procedure for the determination of lithium when present in small quantities; that is, the silica, sulphates, iron, aluminum, calcium and magnesium were removed in the usual way and the mixed chlorids were extracted with amyl alcohol and the extracted residue converted into sulphates. No. 1 was 250 cc. of the laboratory distilled water. No. 2 was 250 cc. of a mineral water at hand in the laboratory containing chiefly calcium sulphate with small amounts of sodium and potassium and a very small amount of lithium.

[1] Chem. News, 1876, 34: 122.

[2] Gaz. chim. ital., 1906, 36: (II): 855–60.

No. 3 was 250 cc. of the same water as No. 2 to which was added 0.0028 mg. of lithium as sulphate. No. 4 was 250 cc. of the same water as No. 2 with 0.0056 mg. of lithium as sulphate added.

The usual procedure in making a complete analysis was carried out and the sulphates of lithium, sodium and potassium were dissolved in definite quantities of water. The ordinary chemicals in use in the laboratory were employed in the various separations. It was known that these chemicals are frequently contaminated with very small quantities of lithium; in fact, it has been necessary to reject samples of calcium oxid and barium hydroxid which were found to contain excessive amounts of lithium. Where the lithium is present, however, in only very minute traces, it is generally better to use definite amounts of chemicals in making the various separations, always running a blank along with the unknowns and subtracting the corrections obtained in the blank, rather than to attempt to obtain chemicals which are entirely free of such minute amounts of lithium as can be detected by the spectroscope.

A standard solution of lithium sulphate was made containing 0.000113 mg. per cubic centimeter of lithium. This standard solution was added a little at a time to small quantities of distilled water which was known to be free from lithium, and the resulting solution tested. With 15 cc. of water and 1 cc. and 2 cc. of the above standard lithium solution, the red lithium line failed to appear in two trials. With 15 cc. of water and 3 cc. of the standard solution, the line appeared strongly once, moderately twice, was doubtful once, and failed to appear twice. This was taken for the limit of concentration and was equivalent to 0.000019 mg. of lithium per cubic centimeter. This determination was checked by taking a larger quantity of water, namely 25 cc., to which were added small amounts of the standard lithium solution, a spectroscopic observation being made after each addition. When to the 25 cc. of water had been added 5.5 cc. of the standard solution, the red line was again just visible, which indicated that the limit was again reached. This corresponded to 0.000020 mg. per cubic centimeter. The limit was checked a third time, using 45 cc. of water with gradual additions of the standard lithium solution, when it was found that the line faintly appeared when 9 cc. had been added, making the limit equivalent to 0.000019 mg. per cubic centimeter. The average of the three determinations showed the limit to be for the particular conditions under which the experiments were conducted, 0.000019 mg. per cubic centimeter.

It is desirable always to make an observation of the limit at the beginning and at the end of each series of determinations. Samples 1 and 2 were made up to a volume of 10 cc. and 5 cc. of the solution diluted until the lithium line just disappeared. No. 1 showed the line with 5 cc. of the solution plus 15 cc. of water. When the water was increased to 20 cc. the line could no longer be detected. Five cubic centimeters of No. 2 showed the line when 35 cc. of water were added, but not when 40 cc. were added. In the case of No. 1, therefore, when the original 10 cc. had been increased in volume to 40 cc., the concentration of the lithium was the same as in the standard solution when the lithium line could barely be seen. The total amount of lithium present, therefore, was 40 times the amount in 1 cc. of the diluted standard solution, that is, 40 multiplied by 0.000019, equivalent to 0.0008 mg. of lithium. This is the blank and represents the amount of lithium obtained from the reagents used in making the separations. Using the same methods of dilution, No. 2 was found to contain 0.0016 mg. In the examination of these two samples, the dilution method was used rather than the addition of the unknown solution to a definite quantity of water until the appearance of the lithium line, which is the regular method.

The residues from Nos. 3 and 4 were dissolved in water and made up to 100 cc. each, and designated as solutions 3 and 4, respectively. The examination of these solutions was not made on the same day with Nos. 1 and 2, hence a new determination of the observable limit was made. Using the method as described before, the limit at this time was found to be 0.0000168 mg. of lithium instead of the 0.000019 found on the previous day. The determination was made by adding to 17 cc. of distilled water, portions of solution 3, 1 cc. or 0.5 cc. at a time, the mixtures being examined after each addition. When 9 cc. of solution 3 had been added, the lithium line was observed very faintly once in five trials, showing that the limit had very nearly been reached. When 9.5 cc. had been added, the line appeared three times in four trials, which was regarded as the limit. Therefore it will be seen that $17+9.5=26.5$ cubic centimeters, each of which contained the equivalent of the observed limit, that is, 0.0000168 mg. of lithium or 0.0004452 mg. in 9.5 cc. of solution 3. Hence, 1 cc. of solution 3 contained 0.000047 mg. of lithium or the 100 cc., the whole amount, contained 0.0047. When the blank which is equivalent to the amount found in No. 2, 0.0016 mg., is subtracted from the amount found in No. 3, there remains 0.0031 instead of 0.0028 mg. of lithium known to have been added to the original sample. In the case of solution 4, 10 cc. of distilled water was taken and 3 cc. of the solution added. Observation of this mixture gave the line faintly twice out of five trials. When 3.5 cc. was added, the line was seen in each of the three trials, from which it will be seen that 10 + 3.5 = 13.5 cubic centimeters each of which contained the observed limit of 0.0000168 mg. of lithium. The value of the 13.5 cc. was therefore 0.000227 mg., which is equivalent to the amount in 3.5 cc. of solution 4. One cubic centimeter of solution 4 is therefore equivalent to 0.000065 mg. and the total 100 cc. contained 0.0065 mg. When the blank determination in No. 2 which is equivalent to 0.0016 is subtracted from the above figure, there remains 0.0049 mg. instead of the 0.0056 mg. known to have been added. These results are shown in the following tables:

Determination of Lithium Added to Mineral Water (Combined Amyl Alcohol and Spectroscopic Method)

Number of solution	Volume of solution of sulphates	Used when lithium line was barely visible			Lithium per cc. to barely show lithium line	Lithium used in test
		Sulphate solution	Water	Total		
	A	B	C	C	D	C x D = E
	cc.	cc.	cc.	cc.	mg.	mg.
1	10	5	15	20	0.000019	0.0004
2	10	5	35	40	.000019	.0008
3	100	9.5	17	26.5	.0000168	.000445
4	100	3.5	10	13.5	.0000168	.000227

Lithium per cc. of sulphate solution	Total lithium in sulphate solution	Lithium found in mineral water samples; blank subtracted	Added lithium found	Amount of lithium added
$\frac{E}{B}=F$	A x F			
mg.	mg.	mg.	mg.	mg.
0.00008	0.0008	......	......	......
.00016	.0016	0.0008	......	......
.000047	.0047	.0039	0.0031	0.0028
.000065	.0065	.0057	.0049	.0056

While in work of this character it would have been better to use chemicals which were entirely free from even the most minute traces of lithium, it may be well to add that blanks should always be made and that in this case the blank obtained of 0.0008 mg. is the largest blank determination ever found in any of the authors' work. From the above data it will be seen that 250 cc. of the original mineral water after subtracting the blank contained 0.0008 mg. of lithium or 0.003 mg. per liter. Several determinations of the lithium in two liters of other samples of the same water gave figures of less than 0.005 mg. of lithium per liter. The use of the combined amyl alcohol and spectroscopic method on some samples of soil gave the following results on the air-dried soils:

RESULTS ON AIR-DRIED SOILS FROM THE USE OF COMBINED AMYL ALCOHOL AND SPECTROSCOPIC METHOD

Number and weight of soil	Total lithium	Lithium	Lithium oxid
Grams.	mg.	Per cent.	Per cent.
No. 1:			
10	0.15	0.0015	0.0032
5	.08	.0016	.0034
No. 2:			
[1]10	.12	.0012	.0026
	.14	.0014	.0030
[1]5	.07	.0014	.0030
	.08	.0016	.0034
No. 3:			
5	.08	.0016	.0034
[1]5	.07	.0014	.0030
	.08	.0016	.0034
0.1	.0015	.0015	.0032

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[1] Two determinations by the spectroscope of the amount of lithium in the same sample.

As a regular practice in analytical work, the approximate determination of lithium in the mixed chlorids obtained in water analyses saves very much time by indicating whether it is worth while to extract the lithium for weighing. A similar test is regularly made on the solution in nitric acid of the oxids of the calcium and strontium. By making the solution to a definite volume it is easy to tell whether there is enough strontium present to separate and weigh. Though potassium is generally determined in all complete mineral water analyses, it is occasionally desired to obtain a close approximation of the amount present in some substance where the information is not worth the trouble and expense of a gravimetric determination. In many of these cases relatively large percentage errors are of no consequence. It is often, however, very desirable to be able to say that there is present 0.001 mg. or 0.03 mg. rather than report each amount as "trace" or "spectroscopic trace," which may be done if the lines are seen in the spectroscope without any idea as to the amount of the material required to produce the line. With the Krüss spectroscopic apparatus regularly employed, using a Bunsen burner, the following figures were obtained:

RESULTS, OBTAINED WITH SPECTROSCOPE, USING A BUNSEN BURNER

Metal	Amount necessary to give spectrum. (Mg. per cc.)	Metal	Amount necessary to give spectrum. (Mg. per cc).
Lithium.......	0.00002	Calcium.......	0.01
Rubidium......	.03	Strontium.....	.03
Caesium.......	.01	Barium.......	.05
Potassium.....	.005		

SUMMARY

1. Satisfactory results are obtained by the spectroscopic estimation of lithium according to the methods of Ballmann[1], Bell[2], or Foehr[3], when modified by applying them to the alkalies extracted with amyl alcohol by the Gooch method.

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[1] Zts. anal. Chem., 1875, 14: 297.
[2] Amer. Chem. J., 1885, 7: 35.
[3] Chem. Ztg., 1885, 9: 1013.

2. Contrary to the statement of Ranzoli[1], the quantitative spectroscopic method is not found preferable to the Gooch method for weighable amounts of lithium.

3. Approximate spectroscopic determinations regularly made of quantities of lithium, potassium, barium, strontium and calcium are very often of great service as a guide to the proper procedure in analyses.

[1] Gaz. chim. ital., 1901, 31 (I): 40.

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