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QUANTITATIVE METALLURGICAL

ANALYSIS

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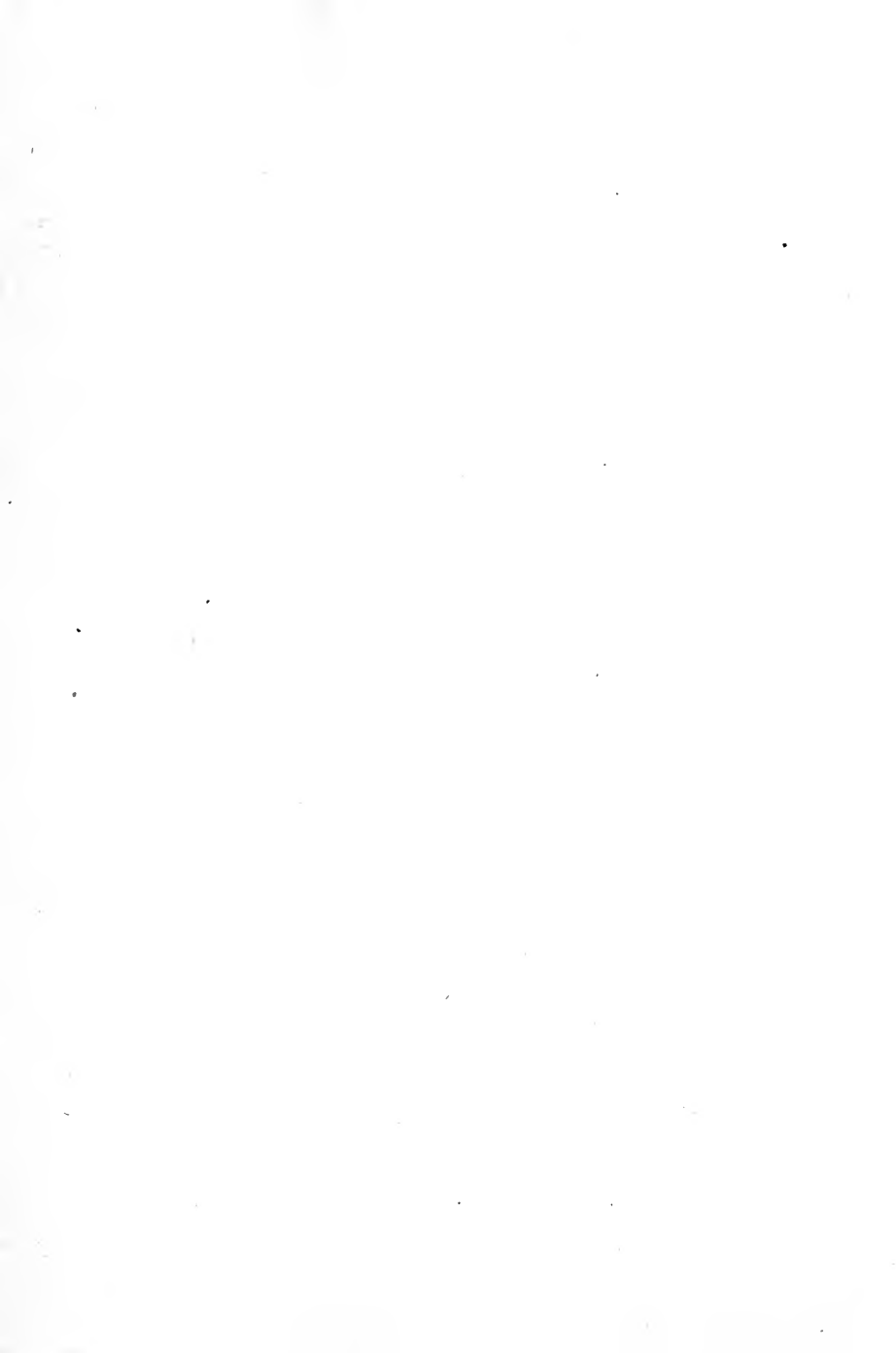
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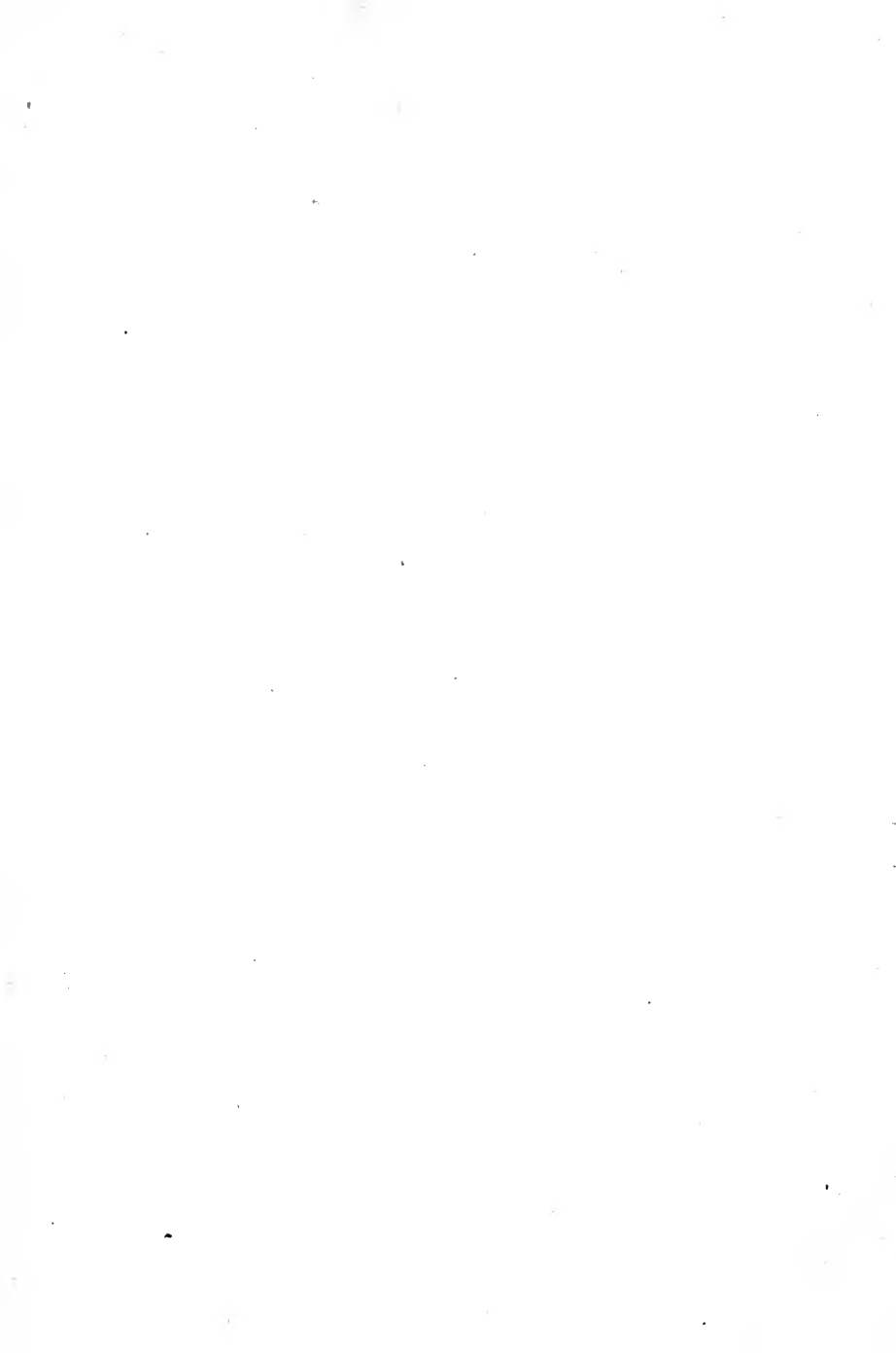
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QUANTITATIVE  
METALLURGICAL  
ANALYSIS





# QUANTITATIVE METAL- LURGICAL ANALYSIS

SELECTED METHODS FOR  
CHEMICAL ANALYSIS OF ORES,  
SLAGS, COAL, PIG IRON AND STEEL

Arranged by  
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Assistant Professor of Chemistry, University of Minnesota

The H. W. WILSON COMPANY  
MINNEAPOLIS  
1904

**GENERAL**

*BOOKS OF REFERENCE.*

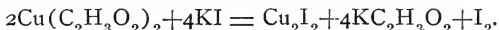
- C. R. Fresenius—Quantitative Analysis.
- F. Cairns—Quantitative Analysis.
- H. Furman—A Manual of Practical Assaying.
- A. A. Blair—The Chemical Analysis of Iron.
- N. W. Lord—Notes on Metallurgical Analysis.
- M. Troilius—Notes on the Chemistry of Iron.
- J. O. Arnold—Steel Works Analysis.
- F. C. Phillips, Ed.—Methods of Iron Analysis in the Laboratories about Pittsburg, Pa.



*VOLUMETRIC IODIDE METHOD FOR THE DETERMINATION OF COPPER IN COPPER ORES.*

MODIFIED BY A. H. LOW.

The method depends upon the following reaction:



Cuprous iodide precipitates and a proportionate amount of iodine is set free, which may be determined by titration with sodium thiosulphate. The reaction is:  $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ .

The standard solution required is that of sodium thiosulphate which may be prepared by dissolving 19.59 grams of the pure salt in a litre of water, and standardizing as follows:

Weigh out into two flasks of 200-300 c.c. capacity two portions of copper foil of about 0.2 gram each. Dissolve by warming with 5 c.c. of dilute nitric acid (sp. gr. 1.2). Boil for a few moments to partially expel the red fumes and then add 5 c.c. of strong bromine water and boil until the bromine is thoroughly expelled. The bromine is to insure the complete destruction or removal of the red fumes. Remove from the heat and treat the solution by one of the following methods to change the copper into the form of copper acetate. (a) Add a slight excess of ammonia water and boil until the excess of ammonia is expelled, as shown by a change of color of the liquid and a partial precipitation of the copper as hydroxide or oxide. Now add strong acetic acid in slight excess, perhaps 3 or 4 c.c. of the 80 per cent. acid in all, and boil again for a moment if necessary to redissolve the copper. (b) Add 20 c.c. of a cold saturated

solution of zinc acetate and heat the solution to boiling. (c) Add sodium carbonate till a permanent precipitate occurs and then acetic acid until the precipitate dissolves, and heat the solution to boiling. Free mineral acids decompose the iodide of potassium, therefore no free acid stronger than acetic should be present. The condition is attained by any one of the above methods. Cool the solution to the ordinary temperature, and dilute with water to about 50 c.c. Add 3 grams of potassium iodide and shake gently until the salt dissolves. Titrate the solution immediately with the thiosulphate until the brown color is nearly destroyed. Add 1 or 2 c.c. of starch solution, and continue the titration until the blue color disappears. Calculate the strength of the thiosulphate solution in terms of copper.

*Process*—Treat one gram of the pulverized ore in a covered casserole, under a hood, with 7 c.c. of concentrated nitric acid and gently heat for a few moments; add five c.c. of concentrated hydrochloric acid and again heat for a short time. Then add five c.c. of concentrated sulphuric acid and evaporate until dense fumes of sulphuric anhydride are evolved. Cool; add 50 c.c. of water and heat until the sulphates of copper, iron, etc., have dissolved. Filter into a small beaker, wash with a little hot water and endeavor to keep the volume of the filtrate down to about 50 or 60 c.c.

Place in the beaker two pieces of aluminium about  $1\frac{1}{2}$  inches square,  $\frac{1}{16}$  inch thick, with the four corners bent for  $\frac{1}{4}$  inch alternately up and down at right angles. Add five c.c. of concentrated sulphuric acid, cover the beaker and heat to boiling. Boil for eight or ten minutes. Unless the bulk of the solution is excessive, this will generally be sufficient to precipitate all of the copper. Transfer the solution to a flask of 200 to 300 c.c. capacity, rinsing in with hot water, as much of the copper as possible. Allow the copper in the flask to settle and decant the liquid through a filter, wash the copper two or three times, retaining it as completely as possible in the flask. Pour upon the aluminium in the beaker five c.c. of dilute nitric acid (sp. gr. 1.2) warm gently until the copper is dissolved. Then pour the solution through the filter, receiving the filtrate in the flask containing the main portion of the copper. At this stage do not wash either the aluminium or

the filter, but simply remove the flask and set the beaker in its place.

Heat the contents of the flask to dissolve the copper; add 5 c.c. of strong bromine water and boil for a moment to oxidize any arsenic present to arsenic acid. Remove the flask from the lamp and again place it under the funnel. Now wash the beaker, aluminium and filter with as little hot water as possible. Boil to remove the excess of bromine but avoid boiling to such a small bulk as to cause decomposition of bromides, etc.

Change the copper into the form of copper acetate, add about 3 grams of potassium iodide and titrate with the thiosulphate precisely as described above in the standardization of the thiosulphate.

#### References on sampling ores:

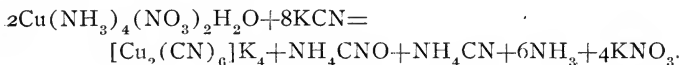
- Wm. Glenn, *Trans. Am. Inst. Min. Engs.*, Vol. XX, page 155.  
 Rattle and Nye, *Jour. An. & App. Chem.*, Vol. V, page 299.  
 N. W. Lord, Notes on Metallurgical Analysis.  
 A. A. Blair, *The Chemical Analysis of Iron.*

#### References on copper:

- H. Furman, *A Manual of Practical Assaying.*  
 A. H. Low, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 458.  
 A. H. Low, *Jour. Am. Chem. Soc.*, Vol. XXIV, page 1082.

### VOLUMETRIC DETERMINATION OF COPPER BY POTASSIUM CYANIDE SOLUTION.

The method depends upon the fact that the addition of potassium cyanide to an ammoniacal copper solution affords a colorless solution. The reaction is:



The standard solution required is potassium cyanide, which may be prepared as follows: Dissolve 30 grams of potassium cyanide in a half liter of water and thoroughly mix. To standardize, weigh out into two flasks, of 200 to 300 c.c. capacity, two portions of pure copper foil of about 0.3 gram each. Dissolve these in

5 c.c. of concentrated nitric acid; boil off the red fumes, dilute slightly, add 10 c.c. of ammonium hydroxide (sp. gr. .9), cool, dilute with water to about 100 c.c. and titrate with the potassium cyanide solution until within a few cubic centimeters of the end, when the bulk of the solution should be noted and distilled water added, if necessary, so that the final bulk will be about 180 c.c. Continue the titration slowly, the flask being shaken after each addition, until the blue or lilac tint can scarcely be discerned at the upper edge of the liquid, when viewed against a white background. Some chemists titrate to a faint rose or pink tint. Calculate the strength of the cyanide solution in terms of copper. casserole with 7 c.c. of concentrated nitric acid and gently heat

*Process*—Treat one gram of the pulverized ore in a covered for a few moments; add five c.c. of concentrated hydrochloric acid and again heat for a short while. Then add 5 c.c. of concentrated sulphuric acid and evaporate under a hood until *dense fumes* of sulphuric anhydride are evolved. Cool; add 50 c.c. of water and heat until the sulphates of copper, iron and so forth have dissolved. Transfer the contents of the casserole to a flask of 200 to 300 c.c. capacity, and add 6 grams of sheet zinc, and allow to stand until the copper is completely precipitated. If the action is too slow the flask may be gently heated. Next add 50 c.c. of water and 20 c.c. of concentrated sulphuric acid to rapidly dissolve the excess of zinc. When the solution of the zinc is complete dilute with water up to the neck of the flask; allow to settle, and decant the clear supernatant liquid; fill up with water and decant twice more. To the residue in the flask, add 5 c.c. of concentrated nitric acid, and boil to expel red fumes. Dilute with a little water, add 10 c.c. of ammonium hydrate (sp. gr. .9), cool, dilute with water to about 100 c.c. and filter if necessary. Wash the residue with a little water and titrate the copper solution with a standard cyanide solution. When near the end dilute to 180 c.c. and finish the titration as described above.

*ELECTROLYTIC DETERMINATION OF COPPER IN  
COPPER ORES.*

Treat one gram of the pulverized ore in a covered casserole, under a hood, with 7 c.c. of concentrated nitric acid and heat for a few moments, add 5 c.c. of concentrated hydrochloric acid and again heat for a short time. Then add 5 c.c. of concentrated sulphuric acid and evaporate until dense white fumes of sulphuric anhydride are evolved. Cool, add 50 c.c. of distilled water and heat until sulphates of copper, iron, etc., have dissolved. Filter into a weighed platinum dish and wash the residue with a little hot water. Connect the dish with the negative pole of a Bunsen battery of two cells or its equivalent. The current used should be of such a strength that it will decompose water at the rate of 3 to 4 c.c. of oxyhydrogen gas per minute. Place in the solution a platinum plate or spiral, connected with the positive pole of the battery. The copper is deposited upon the dish and generally requires from five to ten hours for complete deposition. When the precipitation of the copper appears to be complete, take about 2 or 3 c.c. of the solution out by means of a pipette and test it with a slight excess of ammonia. If copper is found, return the portion tested to the dish, and continue the electrolysis. If no blue color is produced with ammonia the copper is all deposited. Quickly remove the platinum spiral or plate and empty the dish, and wash it two or three times very carefully with distilled water, and then two or three times with alcohol, to wash out all of the water. Dry the dish and contents for a few seconds in the drying oven at about 105° C. Cool in a desiccator and weigh.

A platinum cone may be used for the negative electrode instead of the platinum dish. Have the copper solution in a beaker of about 75 c.c. capacity. Place in the solution the platinum cone and platinum spiral, connect the cone with the negative pole of the battery and the platinum spiral with the positive pole and continue the electrolysis as above.

*COLOR METHOD FOR COPPER.*

This method is often used for the estimation of copper in

substances containing less than 2 per cent. of copper, e.g. in slags from copper smelting operations, and in tailings from concentrating works. The method consists in converting the copper in a substance to be tested, into ammonia-copper-nitrate and comparing the blue color produced, with that produced by dissolving the same amount of a standard copper ore, in the same amount of acid and using the same amount of ammonia as is used in the sample to be tested.

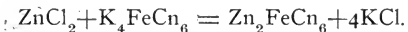
*Process*—Weigh out the same amount of sample and standard, and treat with acids as described in the cyanide process, and then precipitate it with zinc. The copper is washed by decantation, dissolved in about 2 c.c. of nitric acid and an excess of ammonia (about 4 c.c. sp. gr. .9) added. Dilute with water, and filter if necessary, into the comparison tubes.

Reference: T. Carnelly, *Chem. News*, Vol. XXXII, page 308.

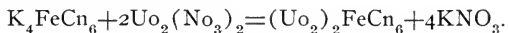
#### TECHNICAL DETERMINATION OF ZINC IN ORES— POTASSIUM FERROCYANIDE METHOD.

MODIFIED BY A. H. LOW.

*Preparation of Standard Ferrocyanide Solution*—Dissolve 22 grams of potassium ferrocyanide crystals in water and dilute to one liter. Weigh carefully about 0.1 gram of pure zinc and dissolve in six c.c. of strong hydrochloric acid, using a 400 c.c. beaker. Then add about 10 grams of ammonium chloride and 200 c.c. of boiling water. Titrate with the ferrocyanide solution. The reaction is:



Continue the titration until a drop, when tested on a porcelain plate with a drop of strong solution of uranium nitrate, shows a brown tinge. The reaction is:



When the titration is about finished, the reaction is much sharper if several drops are placed in the depression of the plate and tested with a drop of uranium nitrate. As this is near the



end of the titration the amount of zinc lost by it is insignificant. As soon as a brown tinge is obtained, note the reading of the burette and then wait a minute or two and observe if one or more of the preceding tests do not also develop a tinge. The end point is usually passed by a test or two and the burette readings must be accordingly corrected. A further correction must be made for the amount of ferrocyanide required to produce a tinge under the same conditions when no zinc is present. This is only one or two drops. One c.c. of the standard solution will equal about .005 gram of zinc or about one per cent. when 0.5 gram is taken for analysis.

*Assay of Ores.*

To 0.5 gram of the pulverized ore in a 250 c.c. pear-shaped flask, add about 2 grams of potassium nitrate and 5 c.c. of strong nitric acid. Heat until the acid is about half gone and then add 10 c.c. of a cold saturated solution of potassium chlorate in strong nitric acid and boil to complete dryness. Avoid overheating and baking. It is usually necessary to manipulate the flask in a holder over a naked flame to avoid loss by bumping. The boiling may be conducted rapidly, and toward the end it is best to heat the entire flask so as to expel every trace of liquid. The potassium nitrate serves simply as a diluent of the dry residue and insures the completeness of the subsequent extraction of the zinc. Cool sufficiently and add 30 c.c. of a prepared ammoniacal solution and heat to boiling. This solution is made by dissolving 200 grams of ammonium chloride in a mixture of 500 c.c. of strong ammonia water and 350 c.c. of water.

Boil the contents of the flask gently for about two minutes and then filter through a 9 c.m. filter and wash with a hot solution of ammonium chloride containing about 100 grams of the salt and 50 c.c. of strong ammonia water to the liter. Collect the filtrate in a 400 c.c. beaker. Place a bit of litmus paper in the filtrate (not necessary if much copper is present) and neutralize carefully with hydrochloric acid, finally adding 6 c.c. of the strong acid in excess. Dilute to about 150 c.c. and add 50 c.c. of a cold saturated solution of hydrogen sulphide. Heat nearly to boiling and titrate with standard potassium ferrocyanide solution. Make corrections of burette readings as in standardization.

*Notes.*—If the ore contains considerable arsenic give it a

preliminary treatment as follows:—To 0.5 gram of ore in the flask add 10 c. c. of strong hydrochloric acid and one c. c. of bromine. Warm gently for several minutes to decompose the ore without loss of bromine, and then boil rapidly to complete dryness. The arsenic will then be sufficiently expelled. Now add the potassium nitrate and nitric acid and proceed as above. If the ore contains much copper and cadmium it may be necessary to pass a current of hydrogen sulphide gas into the hot solution to precipitate them instead of using the water solution of the hydrogen sulphide. If the precipitate is very large it had better be filtered off and the filtrate titrated as usual.

Ores containing copper but no cadmium the copper can be best precipitated with test lead without the use of hydrogen sulphide as follows: After neutralizing the ammoniacal filtrate from the insoluble residue acidify with an excess of 10 c.c. of concentrated hydrochloric acid and add about 30 grams of test lead. Heat nearly to boiling and stir the lead about until the copper is all precipitated. Now dilute to 200 c.c. and titrate as described without removing the lead and precipitated copper.

References:

*Jour. An. & App. Chem.*, Vol. XI, page 491.

A. H. Low, *Jour. Am. Chem. Soc.*, Vol. XXII, page 198.

### DETERMINATION OF LEAD IN LEAD ORES.

#### VOLUMETRIC METHOD—ALEXANDER'S.

This method is based on the fact that ammonium molybdate when added to a hot solution of lead acetate will give a precipitate of molybdate of lead  $PbMoO_4$ , which is insoluble in acetic acid. An excess of ammonium molybdate will give a yellow color with a freshly prepared solution of tannin.

*Solution Required*—A standard solution of ammonium molybdate containing about nine grams of salt per liter. If the solution is not clear, add a few drops of ammonia.

*Indicator*—A freshly prepared solution of one part of tannin to 300 parts of water.

*Standardizing*—Weigh out .3 gram of pure dry sulphate of

lead, dissolve it in hot ammonium acetate, acidify with acetic acid and dilute with water to 250 c.c.; heat to boiling and run in from a burette the ammonium molybdate solution till the lead is all precipitated as white  $\text{PbMoO}_4$ . This is ascertained by placing drops of indicator on the porcelain plate and to them add a drop of the solution tested after each addition of molybdate. When the end is reached the excess of ammonium molybdate gives a yellow color with tannin. The excess necessary to affect the indicator (about 7 c.c.) must be determined and subtracted from the burette readings. In titrating it is essential to stir the solution very thoroughly, and when near the end to wait a few seconds before trying the drop test.

#### ASSAY OF LEAD ORE.

Dissolve one gram of the finely pulverized ore in 15 c.c. of concentrated nitric acid in a covered casserole by the aid of heat. Partly cool and add 10 c.c. of sulphuric acid of sp. gr. 1.41, and evaporate till fumes of sulphuric anhydride appear. Allow to cool and add 100 c. c. of water and heat to boiling for a few minutes. Allow to cool and then decant through a small filter, leaving as much of the lead sulphate, silica, etc., as possible in the casserole. Wash thoroughly with dilute sulphuric acid, then once with water. Dissolve the lead sulphate from the residue, in the casserole, in a strong hot solution of ammonium acetate, slightly acid with acetic acid. Pour this solution through the filter into a clean beaker and repeat this until all the lead sulphate is dissolved, then wash the contents of the casserole onto the filter with hot water. Acidify the filtrate with acetic acid, dilute to 250 c.c. with hot water and heat to boiling. The solution is now ready for titration, which is done as in standardizing.

Consult: H. Furman, A Manual of Practical Assaying.

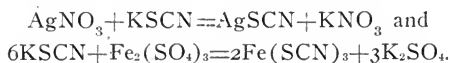
### *DETERMINATION OF ARSENIC IN ORES AND METALLURGICAL PRODUCTS.*

#### CANBY'S MODIFICATION OF PEARCE'S METHOD.

Mix 0.5 gram of the pulverized ore with about eight times its

weight of a mixture of equal parts of sodium carborate and potassium nitrate, in a large porcelain crucible. Heat gradually up to fusion, and keep so for five minutes or more. Cool, treat with boiling water, filter off the insoluble residue and wash it with hot water. Acidify the filtrate with dilute nitric acid and boil off the carbonic and nitrous acid gases. Add an emulsion of zinc oxide until it can be seen in some excess in the bottom of the beaker after stirring vigorously and then allowing a few moments to settle. Should an unusually heavy precipitate of gelatinous silica and alumina be produced, filter, wash and add more emulsion to the filtrate. Now add a slight excess of silver nitrate, stirring vigorously to precipitate the silver as silver arsenate,  $\text{Ag}_3\text{AsO}_4$ . Filter and wash with cold water. Now place the beaker in which the precipitation was made, under the funnel, and dissolve off the precipitate with dilute nitric acid, and wash with cold water. Cool the solution, and titrate the silver with standard solution of potassium or ammonium sulphocyanate, using 1 c.c. of a saturated solution of ferric sulphate as indicator.

With potassium sulphocyanate, the following are the reactions:



Add the sulphocyanate solution from a burette until a faint amber yellow color can be seen in the solution after vigorous stirring.

#### PREPARATION AND STANDARDIZATION OF THE SULPHOCYANATE SOLUTION.

Dissolve 5 or 6 grams of the potassium or ammonium sulphocyanate in a liter of water and mix thoroughly. The solution is standardized by dissolving 0.3 or 0.4 gram of pure silver in nitric acid, boiling to expel red fumes, diluting to about 100 c.c. and titrating with the sulphocyanate solution, using 1 c.c. of the ferric sulphate (or ferric alum) as indicator. Calculate the strength of the solution in terms of arsenic.

*Note Bennett's Modification of the Pearce Method*—Decompose the ore by fusion, treat with water and filter off the insoluble residue. Acidify the filtrate strongly with acetic acid; cover and boil rapidly for a few minutes to expel carbonic acid.

Cool and add a few drops of phenolphthalein, then sodium hydrate to *just* alkaline reaction, then one or two drops of acetic acid, which will discharge the purple red color if too much hydroxide has not been used. The volume of the solution should now be about 100 c.c. Add in slight excess while violently agitating with a stirring rod, a neutral solution of silver nitrate and allow to settle for a few minutes. Filter, wash the precipitate with cold water, dissolve it in dilute nitric acid and cool. Dilute to about 100 c.c. and titrate the silver with a standard sulphocyanate solution, using 1 c.c. of ferric sulphate as indicator. Calculate percent. As.

## References :

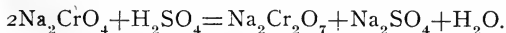
- A. H. Low, *Chem. News*, Vol. XLVIII, page 85.  
L. M. McCay, *Chem. News*, Vol. XLVIII, page 7.  
Canby, *Trans. Am. Inst. Min. Engrs.*, Vol. XVII, page 77.  
R. Pearce, *Proc. of the Colo. Sci. Soc.*, Vol. I.  
J. F. Bennett, *Jour. Am. Chem. Soc.*, Vol. XXI, page 431.

## DETERMINATION OF CHROMIUM IN CHROME IRON ORES.

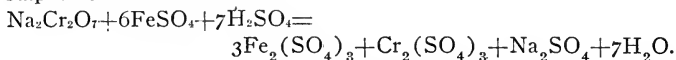
METHOD OF A. G. MCKENNA.

Weigh 0.5 gram of the finely ground ore in a nickel or iron crucible. Mix with the ore three or four grams of sodium peroxide. Hold the crucible over a Bunsen burner by means of a pair of tongs and heat until fusion begins. Keep the mass in a liquid condition at a low red heat for about five minutes. Cool, then place crucible and contents in a number four beaker and add hot water to cover the crucible. Cover the beaker with a glass cover and keep warm until the fusion dissolves. The chromate passes into solution, and the ferric hydroxide remains undissolved. Remove the crucible; and heat the solution to boiling for fifteen minutes. Allow the liquid to cool for a moment, then acidify with dilute sulphuric acid adding 10 c.c. in excess of the amount necessary to dissolve the ferric hydroxide. The sulphuric acid converts the sodium chromate to sodium bichromate.

The reaction is:



Dilute the solution with cold water to about 300 c.c. and add 70 c.c. of ferrous sulphate solution prepared as follows: Dissolve 25 grams of ferrous sulphate crystals in water to which has been added 10 c.c. of dilute sulphuric acid. Dilute the solution to 500 c.c. and mix thoroughly. The reaction between the sodium bichromate solution and ferrous sulphate in presence of sulphuric acid is as follows:



Now determine the excess of ferrous sulphate which has been added by means of a standard solution of potassium permanganate (or potassium bichromate).

Determine the exact strength of the ferrous sulphate solution as follows: Run out from a burette into a beaker about 30 c.c. of the ferrous solution; add about 10 c.c. of dilute sulphuric acid; dilute to about 150 c.c. and run in the permanganate from the other burette until the pink color becomes permanent. Calculate the amount of iron oxidized by the chromium from the chrome ore and then the weight of chromium in solution and the percentage in the ore.

#### References:

- E. H. Saniter, *Jour. Soc. Chem. Ind.*, 1896, page 155.  
 Gerth, *Chem. News*, Vol. VI, page 31.  
 Kennicutt & Patterson, *Jour. An. & App. Chem.*, Vol. III, page 132.  
 J. Massignon, *Jour. An. & App. Chem.*, Vol. V, page 465.  
 A. G. McKenna, *Proc. Eng. Soc. Western Pa.*, 1896 & 1897.  
 F. C. Phillips, Ed., *Methods of Analysis in the Laboratories Around Pittsburgh, Pa.*

### PARTIAL ANALYSIS OF SLAG.

*Silica*—Weigh out .5 to 1 gram of the pulverized slag into a casserole. Decompose with hydrochloric acid and a little nitric acid and evaporate to complete dryness. Heat the residue for about one hour in a drying oven at 130° C. to dehydrate the silica. Add 5 c.c. of hydrochloric acid, heat, add water, heat again and filter, wash with hot water, ignite, and weight  $\text{SiO}_2$ .

If  $\text{BaSO}_4$  is present treat with hydrofluoric acid and get the silica by loss in weight.

*Barium*—Treat another portion of from .5 to 1 gram with hydrochloric and a little sulphuric acid. Evaporate to dryness,

heat until fumes of sulphuric anhydride appear. Add water, and hydrochloric acid, heat, filter, wash with hot water ignite and weigh  $\text{SiO}_2 + \text{BaSO}_4$ . Subtract from this the  $\text{SiO}_2$  as determined above to get  $\text{BaSO}_4$ .

*Lime*—Method I—Heat the filtrate from the silica to boiling, add ammonia in slight excess, and then a strong solution of oxalic acid in excess to dissolve the iron and aluminum precipitate. Heat the solution to boiling to precipitate calcium oxalate. Allow to stand for a short time to settle, then filter and wash thoroughly with hot water. Place the funnel over a clean beaker, and by means of a glass rod make a hole in the filter, and wash the precipitate through the funnel into the beaker. Wash the filter paper with a little hot dilute sulphuric acid. If the sulphuric acid fails to dissolve the last traces of the calcium oxalate a little hydrochloric acid may be used, and the filter paper again washed with hot water.

The reaction is  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{C}_2\text{O}_4$ . Dilute the solution to about 100 c.c. Add about 15 c.c. of sulphuric acid, heat to about  $70^\circ\text{C}$ . and titrate the oxalic acid with standard permanganate solution. Calculate the per cent. of  $\text{CaO}$ .

*Note*—Tartaric acid may be used instead of oxalic acid to dissolve the hydroxides of iron and aluminum, and the calcium then precipitated with ammonium oxalate. This method is not satisfactory if the slag contains more than 0.5 per cent. of manganese.

*Method II*—Treat one gram of the pulverized slag with water and hydrochloric acid. Boil gently until the slag is decomposed. Dilute the liquid, nearly neutralize the acid with ammonia. Make a basic acetate precipitation, filter and determine the calcium in the filtrate as follows: concentrate the solution and precipitate the calcium with ammonium oxalate. Determine the lime volumetrically as in method I.

*Note*—If much manganese is present the calcium oxalate must be redissolved and reprecipitated before making the titration. Or the manganese may be precipitated with bromine and filtered off before adding the ammonium oxalate.

*Magnesia*—may be determined in the filtrate from the calcium oxalate by precipitation with hydrogen sodium phosphate in presence of an excess of ammonia.

*Iron, Lead, Copper, Manganese, Zinc*—Follow the methods

described in the notes on the analyses of various ores, taking separate portions for each.

#### *ANALYSIS OF BLAST FURNACE SLAG.*

Fuse 3 grams of the finely pulverized slag with 15 grams of anhydrous sodium carbonate and 0.5 gram of sodium nitrate in a platinum crucible. Allow to cool, decompose the fused mass with hot water. Acidify with hydrochloric acid and evaporate to dryness in a porcelain dish or casserole and heat the residue for about one hour at  $110^{\circ}$  -  $130^{\circ}$  C. to dehydrate the silicic acid. Moisten the residue with concentrated hydrochloric acid, warm gently, add water, heat and filter into a quarter liter graduated flask. Wash the silica well with hot water, ignite and weigh the  $\text{SiO}_2$ .

Dilute the solution in the flask to the containing mark and mix thoroughly.

*Note*—Some varieties of slag are soluble in hydrochloric acid and therefore do not require fusion with sodium carbonate and sodium nitrate, in which case treat the slag with hydrochloric acid and a little nitric acid, evaporate to dryness, dehydrate the silicic acid and continue as above.

*Determination of the Iron*—Take out 50 c.c. of the solution. Reduce the iron with stannous chloride and continue as directed on page 21. Calculate the per cent. of  $\text{Fe}_2\text{O}_3$ .

*Determination of the Phosphorus*—To 100 c.c. of the solution add ammonia until the mass sets to a stiff jelly, making sure that there is present an excess of ammonia. Next add strong nitric acid in sufficient amount to bring the solution to a clear amber color, and continue as directed on page 24.

*Determination of Alumina, Manganese, Lime and Magnesia*—Take 50 c.c. of the solution in a large beaker, add sodium carbonate until the fluid is nearly neutral and then to the clear red liquid add a solution of about five grams of sodium or ammonium acetate, dilute to about 500 c.c. with boiling distilled water. Heat to boiling for a minute or two, filter while hot and wash by decantation with hot water. Dissolve the precipitate in



hot dilute hydrochloric acid, add a little water, heat to boiling, add ammonia in slight excess, filter, and wash with hot water. Ignite and weigh  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . Calculate the per cent. of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . The per cent. of  $\text{Al}_2\text{O}_3$  is determined by subtracting the per cent.  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  previously determined from the above.

Add the filtrate and washings from the acetate precipitation to those from the precipitation by ammonia, evaporate the solution to about 200 c.c. When cold add bromine water until the solution is strongly colored, add ammonia in slight excess and heat moderately for some time, then filter off precipitate of  $\text{MnO}(\text{OH})_2$ , wash with hot water. Test filtrate with more bromine and ammonia, dry, ignite and weigh  $\text{Mn}_3\text{O}_4$ . Calculate the per cent.  $\text{MnO}$ .

Instead of igniting the precipitate of hydrated peroxide of manganese it may be dissolved in an excess of standard ferrous sulphate solution, containing a little sulphuric acid, and the excess of the ferrous salt determined with a standard solution of permanganate or bichromate of potash. See Ford-Williams process, page 30.

*Note*—The amount of calcium carried down with the manganese depends largely upon the relative quantities of calcium and manganese. When the amounts of each are over 0.02 gram a double precipitation of the manganese should be made.

When a slag contains a very large amount of manganese instead of precipitating with bromine, add ammonia to the solution in slight excess and enough ammonium sulphide to precipitate all of the manganese, allow the precipitate to settle. Filter the manganese sulphide by decantation and wash three times with a 5 per cent. ammonium nitrate solution containing 1 or 2 c.c. of ammonium sulphide, finally transfer the precipitate onto the filter paper, dry, ignite the filter paper in a weighed porcelain crucible, add the precipitate, heat at first over a small flame with the crucible cover off, finally increase the heat and at last heat over the blast lamp to constant weight. Weigh  $\text{Mn}_3\text{O}_4$ . Calculate per cent.  $\text{MnO}$ . Instead of weighing the manganese as  $\text{Mn}_3\text{O}_4$  the sulphide may be filtered off and determined as described on page 28.

Acidify the filtrate, from the manganese precipitate, with hy-

drochloric acid and concentrate to about 100 c.c., filter if necessary. Add ammonia in slight excess, then precipitate the calcium with ammonium oxalate as calcium oxalate,  $\text{CaC}_2\text{O}_4$ . Filter, wash, ignite and weigh  $\text{CaO}$ . Calculate the per cent. of  $\text{CaO}$ . The precipitate of calcium oxalate may be dissolved in dilute sulphuric acid and the  $\text{CaO}$  determined volumetrically by means of a standard permanganate solution. See page 13.

To the filtrate from the calcium oxalate add a volume of ammonia of sp. gr. .96, equal to one-third the volume of the solution. Then add hydrogen sodium phosphate drop by drop while stirring the solution with a glass rod, to precipitate the magnesium as ammonium magnesium phosphate. Allow to stand for some time, filter, wash with a mixture of one part of ammonia, sp. gr. .96, and three parts water, dry, ignite and weigh  $\text{Mg}_2\text{P}_2\text{O}_7$ . Calculate the per cent. of  $\text{MgO}$ .

*Determination of the Sulphur*—To the remaining 50 c.c. of the original solution add a few drops of hydrochloric acid, heat to boiling in a beaker and precipitate the sulphur with barium chloride as barium sulphate,  $\text{BaSO}_4$ . Calculate the per cent. of sulphur.

The above applies to the analysis of open hearth slags, refinery slags, tap cinder, mill cinder and converter slag. Basic slag, from the Thomas Bessemer Process, which often contains a high per cent. of phosphoric acid, requires that the process be slightly modified.

#### METHOD FOR THE COMPLETE ANALYSIS OF LEAD AND COPPER SLAGS, MATTES AND CINDERS.

Treat 1.5 grams of the pulverized material with about 20 c.c. of hydrochloric acid, (sp. gr. 1.2), a few drops of concentrated nitric acid and about 2 c.c. of concentrated sulphuric acid in a casserole. Evaporate until heavy white fumes of sulphuric anhydride are evolved. Cool and add about 25 c.c. of water. Heat for some time and again cool. Filter off the  $\text{SiO}_2$ ,  $\text{BaSO}_4$  and  $\text{PbSO}_4$ . Wash with dilute sulphuric acid (1 vol. of concentrated acid to 20 vol. of water) by decantation, leaving as much as pos-

sible of the residue in the casserole. Set the filtrate aside for the determination of Fe, Al, Cu, Zn, Mn, Ca and Mg.

Digest the residue in the casserole with a strong solution of ammonium acetate, to dissolve the lead sulphate, and filter on the filter used in the first operation. Wash with hot water containing a little ammonium acetate. Ignite the residue of  $\text{SiO}_2$  and  $\text{BaSO}_4$ , cool and weigh in a platinum crucible. Separate and determine the  $\text{SiO}_2$  and  $\text{BaSO}_4$  by either of the following methods:

(a) To the residue in the crucible add 4 or 5 drops of dilute sulphuric acid, and add 1 or 2 c.c. of hydrofluoric acid and evaporate under the hood to expel the silica as  $\text{SiF}_4$ . Ignite and weigh the residue of  $\text{BaSO}_4$  and calculate BaO. The weight of barium sulphate subtracted from the weight of barium sulphate plus silica gives weight of silica.

(b) Fuse the insoluble residue of silica and barium sulphate with 3 or 4 grams of sodium carbonate. Dissolve the fused mass in hot water and boil. Filter and wash with hot water until the washings are free from sulphates. Acidify the filtrate with hydrochloric acid and evaporate to dryness and determine the  $\text{SiO}_2$  in the usual manner. Dissolve the precipitate on the filter paper in dilute hydrochloric acid, wash the filter with hot water, heat the solution to boiling and precipitate the barium by adding dilute sulphuric acid. Allow to stand for some time, filter, wash and ignite. Weigh  $\text{BaSO}_4$ .

Determine the lead by either of the following methods:

(a) To the filtrate containing the lead acetate add acetic acid to acid reaction, dilute with water to 250 c.c., heat to boiling and titrate with standard ammonium molybdate solution, using tannin (1 to 300) for indicator. See page 8.

(b) To the filtrate containing the lead acetate add sulphuric acid, allow to stand for a short time and filter off the lead sulphate. Wash at first with dilute sulphuric acid (1 vol. of con.  $\text{H}_2\text{SO}_4$  to 20 vol. water) and then with alcohol to displace the sulphuric acid. Dry, ignite and weigh the  $\text{PbSO}_4$  in a porcelain crucible. Calculate the per cent. of lead.

To the filtrate containing the Cu, Fe, Al, etc., add a little hydrochloric acid, heat to about  $70^\circ$  and precipitate the copper as copper sulphide with  $\text{H}_2\text{S}$ . Filter, wash with hydrogen sul-

phide water, dry, transfer the precipitate to a weighed Rose crucible, burn the filter, add the ash to the contents of the crucible. Add a little sulphur, ignite in a current of hydrogen or coal gas. Allow the crucible and contents to cool in a current of the gas, and weigh as  $\text{Cu}_2\text{S}$ . Calculate per cent. of copper.

Instead of weighing as  $\text{Cu}_2\text{S}$ , the precipitate may be placed in a beaker, the filter ash added, and the precipitate dissolved in nitric acid, when the copper may be determined electrically, colorimetrically or by the volumetric method.

Boil the filtrate from the  $\text{CuS}$  to expel all the hydrogen sulphide, filter if necessary, add a little concentrated nitric acid and boil for a short time, to oxidize the iron. Cool, add sodium carbonate until the solution is nearly neutral. Add about 5 grams of sodium or ammonium acetate and then about a half liter of hot water, heat to boiling and boil for two or three minutes. Allow to settle for a few moments. Filter while hot and wash with hot water by decantation. Dissolve the precipitate in hot dilute hydrochloric acid, add a little water, heat to boiling, add ammonia in slight excess, filter and wash with hot water. Dissolve this precipitate of iron, alumina (and  $\text{P}_2\text{O}_5$ ) in hydrochloric acid and dilute with water to 250 c.c. Take 100 c.c. of the 250 for volumetric determination of iron. Take another 100 c.c. and precipitate the iron, aluminum and phosphorus with ammonia. Filter, wash and ignite and weigh  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ .

Combine the filtrate from the basic acetate precipitation with the filtrate from the first ammonia precipitation, acidify with acetic acid and boil. Conduct into the boiling solution a current of hydrogen sulphide for half an hour. Filter off the precipitate of  $\text{ZnS}$  and wash with water, containing hydrogen sulphide.

If the precipitate of zinc sulphide is not very large it may be dried and ignited in a porcelain crucible, with the addition of a little ammonium carbonate to assist in the conversion of the zinc sulphide into zinc oxide, cooled and weighed as  $\text{ZnO}$ .

If the precipitate of zinc sulphide is quite large dissolve it in hot dilute hydrochloric acid and precipitate the zinc as basic carbonate of zinc with sodium carbonate added in excess and the solution boiled. Filter, wash, dry, ignite in a porcelain crucible and weigh as zinc oxide. Calculate the per cent. of zinc.

Boil the filtrate from the precipitate of zinc sulphide with an

excess of bromine water for about half an hour. Add ammonia to alkaline reaction and a little more bromine water and heat the solution just below boiling until the precipitate is brown colored and flaky, and the solution colorless. Filter off the precipitated hydrated peroxide of manganese,  $MnO(OH)_2$ , wash thoroughly with hot water, test filtrate for manganese with more bromine and ammonia, heat for some time and filter if necessary, dry, ignite and weigh  $Mn_3O_4$ . Calculate the per cent. of manganese.

Instead of igniting the manganese precipitate, it may be transferred to a beaker and determined by the Williams method. See page 30.

See also methods for the determination of manganese in blast furnace slag, page 15.

In the filtrate from the manganese determine the calcium and magnesium in the usual manner.

*Determination of Sulphur*—Take a separate portion using the method described on page 31.

### COAL AND COKE ANALYSIS.

Pulverize 10 to 15 grams of the carefully sampled coal and transfer it to a tightly corked bottle.

*Moisture*—Dry one gram of the pulverized coal in an open porcelain or platinum crucible at  $104^{\circ}$ - $107^{\circ}$  for one hour. Cool in a desiccator and weigh covered.

*Volatile Combustible Matter*—Place one gram of the fresh, undried, powdered coal in a platinum crucible weighing twenty or thirty grams and having a tightly fitting cover. Heat over the full flame of the Bunsen burner for seven minutes. Cool and weigh. To find volatile combustible matter, subtract the per cent. of moisture from the loss found here.

*Ash*—Burn the portion of the powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined till free from carbon. Cool and weigh. Examine the ash for unburned carbon by moistening it with alcohol.

*Fixed Carbon*—This is found by subtracting the per cent. of ash from the per cent. of coke as found above.

*Sulphur—Eschka's Method*—Mix thoroughly one gram of the finely powdered coal with one gram of magnesium oxide, and one half gram of dry sodium carbonate, in a thin platinum dish having a capacity of 75 c.c.-100 c.c. The dish is heated on a triangle over an alcohol lamp, held in the hand at first. Gas must not be used on account of the sulphur it contains. The mixture is frequently stirred with a platinum wire and the heat raised very slowly, especially with soft coals. The flame is kept in motion and barely touching the dish, at first, till strong glowing has ceased, and is then increased gradually till in 15 minutes the bottom of the dish is at a low red heat. When the carbon is burned transfer the mass to a beaker and rinse the dish, using about 50 c.c. of water. Add 15 c.c. of saturated bromine water and boil for 5 minutes. Allow to settle, decant through a filter. Boil a second and third time with 30 c.c. of water and wash till the filtrate gives only a slight opalescence with silver nitrate and nitric acid. The volume of the filtrate should be about 200 c.c. Add one and a half cubic centimeters of concentrated hydrochloric acid. Boil till the bromine is expelled and add to the hot solution, drop by drop, especially at first, and with constant stirring 50 c.c. of a 2 per cent. solution of hot barium chloride. Digest on a water bath until the precipitate settles. Filter, wash, ignite, cool and weigh  $\text{BaSO}_4$  and calculate the per cent. of sulphur.

*Note*—For practical purposes the sulphur may be considered as existing in the coal in the form of pyrites, and that in the above analysis one-half of the sulphur passes off with the volatile combustible matter and the other half with the fixed carbon.

In calculating results of analysis, one-half of the sulphur may be subtracted from the volatile matter and the other one-half from the fixed carbon. If a determination of phosphorus is desired, it may be found in the ash after burning the coal or coke and can be determined by any of the well known methods and the per cent. deducted from the per cent. of ash.

If the calculations are made as indicated above, the sum total of moisture, volatile matter, fixed carbon, ash, sulphur and phosphorus should equal one hundred per cent.

**Reference :**

*Jour. Am. Chem. Soc.*, Vol. XXI, page 1116.

*DETERMINATION OF IRON IN IRON ORES.**Standardization of Potassium Permanganate Solution:*

Dissolve about eight grams of potassium permanganate crystals in about 500 c.c. of water, with frequent agitation to insure complete solution, if possible. After this, allow the solution to stand for two or three days. Filter through a layer of asbestos, dilute to about 2000 c.c. and mix thoroughly.

Weigh out and place in number 2 beakers two portions of standard iron ore of about 0.5 gram each. Pour over each of these 10 c.c. of hydrochloric acid (sp. gr. 1.2), and as much stannous chloride solution as will nearly reduce the iron, cover the beakers with glass covers, heat at a temperature just below boiling until the undissolved residue is white or nearly so.

The stannous chloride solution should be of such strength that about 3.5 c. c. will reduce one-half gram of the average iron ore. It may be prepared by dissolving pure tin in hot concentrated hydrochloric acid leaving an excess of the acid and then properly diluting with distilled water, or

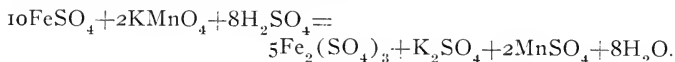
By dissolving 100 grams of stannous chloride salt in 70 c.c. of concentrated hydrochloric acid and diluting with distilled water to one half liter.

If a dark residue remains, collect it on a filter, wash free from hydrochloric acid, and ignite the filter in a platinum crucible. Mix the ash with a small amount of sodium carbonate and heat to fusion. Cool and dissolve the fused mass in boiling water in the crucible. Unite solution and precipitate (if any) with the acid extraction. Heat the solution then to boiling, wash off the cover and sides of the beaker and add stannous chloride solution to the *hot* solution until it is colorless, but avoid adding more than a drop or two in excess. In case a larger amount has been added, add permanganate solution until a tinge of ferric iron is produced. Destroy this as above. Dilute with 100 c.c. of water and cool completely; when cold add rapidly about 30 c.c. of mercuric chloride solution (50 grams per liter). Allow the solution to stand 3 minutes, dilute with water to about 300 c.c.

Next add about 10 c.c. of a solution prepared as follows: 160 grams of manganous sulphate dissolved in 1750 c.c. of water, to which is added 330 c.c. of phosphoric acid syrup (sp. gr. 1.7) and 320 c.c. of concentrated sulphuric acid.



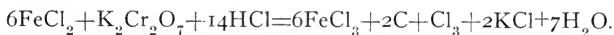
Titrate the solution as quickly as possible with the potassium permanganate to the appearance of a faint pink color, which remains permanent for a short time. The reaction for the oxidation of the iron from ferrous sulphate to ferric sulphate by the permanganate in presence of sulphuric acid is as follows:



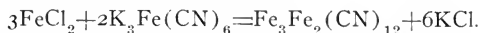
Calculate the strength of the permanganate in terms of metallic iron.

*Standardization of Potassium Bichromate Solution:*

Dissolve about 12 grams of potassium bichromate in approximately 2000 c.c. of water. Mix thoroughly and standardize by means of standard iron ore. Decompose and reduce the ore just the same as in the standardization of permanganate solution. Omit the addition of the manganous sulphate mixture. Titrate the reduced iron solution with the potassium bichromate solution. The reaction is:



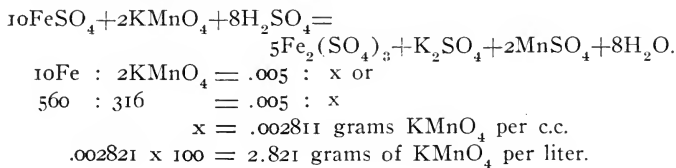
The end point in the titration is reached when a drop or two of the iron solution and a drop of very weak solution of freshly prepared potassium ferricyanide gives no blue color when brought together on a porcelain tile. Reaction:



Calculate the strength of the potassium bichromate solution in terms of metallic iron.

It is advantageous, when one has a great many determinations of iron to make to dilute the standard solution so that each c.c. is equivalent to one per cent. or two per cent. of metallic iron, when 0.5 gram is taken for analysis. E.g., suppose it is desired to have a permanganate solution of such a strength that each c.c. will represent 1 per cent. of metallic iron when 0.5 gram is taken.

The calculation is as follows:





Still another practice in commercial work is to weigh out the ore in such proportions, that the burette readings of the standard solution give the percentage at once without calculation. Thus, if the standard ore contains 64.43 per cent. iron, the weight of ore would be so taken that the readings of the burette would be 32:215 c.c. If, however, it should be so taken that the reading is 32.8 c.c., then the weight would be diminished in the proportion of 32.215 to 32.8. For the obtaining of the percentage the burette reading is doubled.

*The Process:*

Pulverize the ore in an agate mortar to a fine powder. If necessary dry the ore in a drying oven until its weight is constant. Weigh out duplicate samples of 0.5 gram each. Place each sample in a number 2 beaker and add 10 c.c. of hydrochloric acid (sp. gr. 1.2) and heat on the iron plate. If the ore contains organic matter add a little potassium chlorate and boil till the smell of liberated chlorine has disappeared. Add stannous chloride and continue as in the standardization of the permanganate solution with standard iron ore. Or, if it is desired to use the bichromate method, continue as in the standardization of potassium bichromate with standard iron ore. Two results on the same sample should agree within 0.1 per cent.

References:

- R. W. Mahon, *Am. Chem. Jour.*, Vol. XV, page 360.  
*Jour. Am. Chem. Soc.*, Vol. XVII, page 405.  
*Jour. An. & App. Chem.*, Vol. V, page 325.

*DETERMINATION OF PHOSPHORUS IN IRON ORES.*

EMMERTON'S VOLUMETRIC METHOD—Dissolve 3 grams of the pulverized ore in 40 c.c. of concentrated hydrochloric acid, and evaporate to about 20 c.c., avoiding a temperature so high as to convert the ferric chloride into ferric oxide. Add 10 c.c. of concentrated nitric acid and evaporate down to about 10 c.c. If the nitric acid solution is allowed to go to dryness, it affords ferric oxide, insoluble in nitric acid, which always retains some phosphate. This can only be brought into solution by hydrochloric acid, which must be removed by addition of more nitric acid and evaporating. Dilute with about 20 c.c. of distilled water and filter into an Erlenmeyer flask of about 400 c.c. capacity and wash with the least pos-

sible amount of water. It is not always possible to get the whole of the phosphorus in solution by the above process, therefore the residue should be treated by one of the following methods in order to obtain any insoluble phosphorus which may be present.

(a) Ignite the residue in a platinum crucible, fuse it with 5 to 6 parts of sodium carbonate, dissolve the fused mass in water and hydrochloric acid, evaporate to dryness in order to dehydrate any silicic acid that may be present. Moisten the residue with concentrated nitric acid, heat after adding a small amount of water, and filter into the flask containing the soluble phosphorus, (or into another flask if it is to be determined separately).

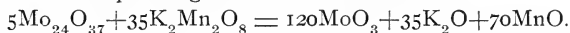
(b) Ignite the residue in a platinum crucible, add 3 or 4 drops of dilute sulphuric acid and about 5 c.c. of hydrofluoric acid, and evaporate under the hood to complete dryness and finally ignite to redness. Fuse the residue with 5 to 6 parts of sodium carbonate, dissolve the fused mass in water and nitric acid and add it to the solution in the flask containing the soluble phosphorus.

(c) Place residue and filter paper in a platinum crucible and ignite. When the paper is burned off break up the residue with a platinum rod and ignite at a red heat for about two minutes. Pulverize the ignited residue in an agate mortar. Transfer the residue to beaker, add water and a little nitric acid and boil gently for about 5 minutes. Filter into the flask containing the soluble phosphorus.

To the solution add ammonia, shaking the flask after each addition, until the mass sets to a stiff jelly. Then add strong nitric acid gradually, shaking well after each addition, until the precipitate dissolves and then add a little in excess to get a clear amber color. The solution at this point should be about 200 to 250 c.c. in bulk. Put a thermometer into the liquid and heat carefully until the temperature reaches 85°C. Add at once 50 c.c. of ammonium molybdate solution to precipitate the phosphorus as phosphomolybdate of ammonium,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ . Close the flask with a rubber stopper, wrap it in a thick cloth or towel and shake or whirl for five minutes, then allow to stand for five minutes for the precipitate to settle. Filter and wash the precipitate five times with water containing 10 c.c. concentrated nitric acid per liter and then five times with water, containing ten grams of potassium nitrate per liter. Put the funnel containing the yellow

precipitate in the neck of a flask of about 400 c.c. capacity in which has been placed 15 grams of granulated zinc.

Pour over the precipitate on the filter dilute ammonia (one vol. ammonia, sp. gr. .96, and three volumes of water) and receive the solution in the flask containing the granulated zinc. Next pour into the flask 100 c.c. of dilute sulphuric acid (1 vol. acid to 5 vol. of water) and heat on the iron plate for about 15 minutes. The color of the solution passes through pink, plum, pale olive green to dark green. The  $\text{MoO}_3$  is reduced by the zinc and sulphuric acid to a mixture of oxides corresponding to the formula  $\text{Mo}_{24}\text{O}_{37}$ . Filter through a folded filter. The zinc is decanted on to the filter paper with the liquid to keep up the reducing action. Wash two or three times with water. Titrate with standard potassium permanganate solution, to the appearance of the pink color due to the slight excess of permanganate. The reaction is:



The strength of the permanganate solution in terms of  $\text{MoO}_3$  is 88.16 per cent. of its strength against iron. The yellow precipitate of phosphomolybdate of ammonium contains  $12\text{MoO}_3$  to 1 of P, the phosphorus being 1.794 per cent. of the  $\text{MoO}_3$ . Therefore 88.16% of the strength of the solution in terms of iron gives its strength in terms of  $\text{MoO}_3$  and 1.794% of this gives its strength in terms of phosphorus.

Let Fe = the iron value of the permanganate.

Let P = phosphorus value.

Then  $P = \text{Fe} \times .015816$ .

Two results on the same sample should agree within .001%.

It is advisable to check the strength of the standard permanganate in terms of phosphorus as calculated above by means of a standard iron ore of known phosphorus content, or by means of some of the pure yellow precipitate dried at  $110^\circ\text{C}$ . It contains 1.63 per cent. phosphorus.

#### References:

- Emmerton, *Trans. Am. Inst. Min. Engs.*, Vol. XV, page 93.  
 Dudley & Pease, *Jour. Am. Chem. Soc.*, Vol. XVI, page 224.  
 Blair & Whitfield, *Jour. Am. Chem. Soc.*, Vol. XVII, page 747.  
 G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 955.  
 W. A. Noyes, *Jour. Am. Chem. Soc.*, Vol. XVI, page 553.  
 W. A. Noyes, *Jour. Am. Chem. Soc.*, Vol. XVII, page 129.  
 Mixer & Du Bois, *Jour. Am. Chem. Soc.*, Vol. XIX, page 614.  
 H. C. Babbitt, *Jour. Am. Chem. Soc.*, Vol. VII, page 165.  
 E. D. Campbell, *Jour. Am. Chem. Soc.*, Vol. VII, page 2.  
 Dudley & Pease, *Jour. Am. Chem. Soc.*, Vol. VII, page 519.  
 P. W. Shimer, *Jour. Am. Chem. Soc.*, vol. XXI, page 723.

*Reduction of the MoO<sub>3</sub> in a Reductor:*

Obtain the yellow precipitate and dissolve it in ammonia just as described on page 25 and the solution is allowed to run into a clean beaker. Wash the filter paper with water until the solution measures about 60-70 c.c. Add to the liquid in the beaker 10 c.c. concentrated sulphuric acid and pass it through the reductor which has just been cleaned by passing through it distilled water and then 100 c.c. of warm dilute sulphuric acid, strength: 25 c.c. concentrated sulphuric acid per liter of distilled water. After passing the molybdate solution through the reductor, wash with about 200 c.c. of the warm dilute sulphuric acid, and finally with about 50 c.c. hot water.

**References:**

Jones' Reductor, *Trans. Am. Inst. Min. Engs.*, Vol. XVII, page 441  
Dudley & Pease, *Jour. An. & App. Chem.*, Vol. VII, page 109.

*Acidimetric Method*—Follow Emmerton's method until the yellow precipitate of ammonio-phospho-molybdate is obtained and then continue as follows: Filter the yellow precipitate on a 9 c.m. filter and wash by decantation with water containing 10 c.c. concentrated nitric acid per liter and then five times with water containing 10 grams potassium nitrate per liter. Place precipitate and filter in the flask containing the bulk of the precipitate. Dissolve the precipitate in an excess of standard solution of caustic soda or caustic potash. With potash the reaction is:



Add water and a few drops (.5 c.c.) of phenol phthalein indicator and titrate the excess of caustic alkali with a standard solution of nitric acid.

*Solutions Required:*

*Standard Caustic Potash*—Strength, 8.3334 grams of potassium hydroxide per liter. This solution may be prepared from normal caustic potash solution by taking 148.39 c.c. and diluting to one liter with distilled water. One cubic centimeter of this solution will equal .0002 gram of phosphorus.

*Standard Caustic Soda*—Strength, 5.9355 grams of sodium hydroxide per liter. This solution can be prepared from normal

caustic soda by diluting 148.39 c.c. to one liter. This solution is of such a strength that one c.c. equals .0002 gram phosphorus.

*Standard Nitric Acid*—This solution has the same strength, volume for volume, as the caustic soda or caustic potash. It can be prepared by diluting 148.39 c.c. of normal nitric acid to one liter. It contains 9.3484 grams of nitric acid to the liter.

*Phenol Phthalein*—One gram dissolved in 100 c.c. of 60% alcohol.

*Calculation of Analysis*—The difference between the number of c.c. of caustic alkali used and the number of c.c. of standard acid multiplied by .0002 gives the weight of phosphorus found.

Weight of Phosphorus  $\times$  100

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Amount of ore taken = per cent. phosphorus.

It is advisable to check the strength of the standard acid and alkali in terms of phosphorus as calculated above, against a standard iron ore of known phosphorus content, or by means of some of the pure yellow precipitate dried at 110°C. It contains 1.63 per cent. phosphorus.

References :

- J. O. Handy, *Jour. An. & App. Chem.*, Vol. VI, page 204.  
 Manby, *Jour. An. & App. Chem.*, Vol. VI, page 82.  
 M. Rothberg, *Jour. An. & App. Chem.*, Vol. VI, page 241.  
 F. Hundeshagen, *Zeit. Anal. Chem.*, Vol. XXV, page 489.

*Wood's Method*—Direct weighing of the phosphomolybdate of ammonium.

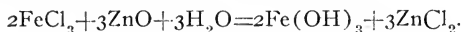
Follow Emmerton's method until the yellow precipitate is obtained then filter on a 9 c.m. filter which has been previously dried at 110°C. and weighed. Wash with a two per cent. nitric acid solution until free from iron, then wash once or twice with alcohol. Dry in the air bath at 110° C. and weigh. 1.63 per cent of the dried precipitate is phosphorus.

*Note*—The yellow precipitate must contain no silica. With ores containing soluble silicates, evaporate the acid solution to complete dryness, to render the silica insoluble, moisten with hydrochloric acid, add water, heat, and filter off the insoluble residue.

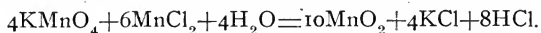
Reference : E. F. Wood, *Zeit. Anal. Chem.*, Vol. XXVIII, pages 141-172.

*DETERMINATION OF MANGANESE IN IRON ORES.*

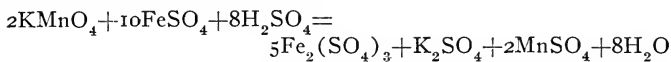
**VOLHARD'S METHOD, MODIFIED BY G. C. STONE**—Grind the ore to a fine powder. Weigh out two portions of about one gram each and place in number 2 beakers. Pour into each 10 c.c. of concentrated hydrochloric acid. Cover the beakers with glass covers and heat until ore is decomposed. Add a little potassium chlorate and boil a minute or two. Remove covers and evaporate off excess of acid. Cool and add cold water. At this point if there is any doubt as to the decomposition of the ore, filter off and test insoluble residue for manganese. If not, the filtration may be omitted. Wash contents of the beaker into a half liter flask with cold water. Nearly neutralize with carbonate of soda; the solution should remain clear and should be of a deep red color. Next add an emulsion of zinc oxide until the precipitate curdles and settles readily. Add a little more of the emulsion to make sure that the precipitation is complete. The reaction is:



Dilute to the mark with cold water, mix thoroughly, pour into a beaker and allow the precipitate to settle. Take portions of 200 cc. each of the supernatant liquid and transfer to 400-500 c.c. flasks; heat nearly to boiling and titrate one after the other with standard potassium permanganate solution, adding it in small portions at a time, and shaking the flask over a Bunsen flame, after each addition. Keep the temperature as near the boiling point as possible, while making the titration. The greater part of the permanganate solution should be added at once and the solution vigorously shaken and then the precipitate allowed to settle. The following is the reaction which takes place:



In the above equation we see that two molecules of potassium permanganate oxidizes three molecules of manganous chloride, while in the following equation:



we see that two molecules of potassium permanganate oxydizes ten molecules of ferrous sulphate, therefore the oxydizing power of  $\text{KMnO}_4$  in the former case is only  $\frac{3}{10}$  as great as in the latter.

So the value of the permanganate in terms of manganese is to its value in terms of iron as 3:10 or  $\frac{55}{56} \times \frac{3}{10} = \frac{165}{560}$ . The value of the standard permanganate solution in terms of iron multiplied by  $\frac{165}{560}$  gives strength of permanganate solution in terms of manganese.

## References :

*Jour. Am. Chem. Soc.*, Vol. XVIII, page 385.

*Liebig's Annalen*, 197, page 318.

*Chem. News*, Vol. XL, page 207.

G. C. Stone, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 228.

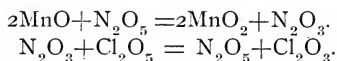
G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 498.

FORD-WILLIAMS METHOD—This is a good method to use when the ore contains only a small amount of manganese.

Pulverize the ore to a fine powder. Weigh out duplicate samples of one to five grams each. With ores high in manganese use one gram; with ores low in manganese weigh about five grams. Place each sample in a number 4 beaker, add 10 c.c. concentrated hydrochloric acid for each gram of ore taken. Cover the beaker and heat on the iron plate until the residue is white or nearly so. Then add 25 to 50 c.c. strong nitric acid and boil about five minutes to expel hydrochloric acid. If there is a large insoluble residue, filter it on an asbestos filter and wash with strong nitric acid. If the insoluble residue is small, the filtration may be omitted.

Now add 75 c.c. of strong nitric acid and heat. When the solution is warm add about 5 grams of potassium chlorate, bring the solution to a boil and continue the boiling about 10 minutes. If the sample contains much silica, add a few drops of hydrofluoric acid (more or less according to the amount of silica present) and boil for a few minutes. Allow it to cool somewhat, add 25 c.c. more nitric acid and five grams more of potassium chlorate and again boil for about 10 minutes. If the nitric acid has the faintest yellow color, it indicates the presence of nitrous acid. Nitrous acid reduces  $\text{MnO}_2$  to  $\text{MnO}$ , which is soluble. This acid may be removed by blowing a current of air through the  $\text{HNO}_3$ .

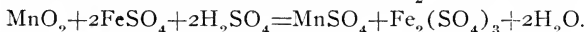
Manganous nitrate in the strong nitric acid solution is, by a complex reaction, oxidized to insoluble manganese dioxide on the addition of potassium chlorate. The following is probably the reaction :



Cool the solution quickly and filter on an asbestos filter, using a filter pump. Wash two or three times with strong nitric acid, suck the precipitate as dry as possible and then wash two or three times with cold water to rid of all the nitric acid. Transfer the precipitate with the asbestos filter to the beaker in which the precipitation was made. Measure into the beaker 100 c.c. of a standard solution of ferrous sulphate prepared as follows:

10 grams of crystallized salt,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 900 c.c. water and 100 c.c. Con.  $\text{H}_2\text{SO}_4$ , thoroughly mixed.

The reaction between the precipitate of  $\text{MnO}_2$  and this solution is:



Stir until the whole of the precipitate has been dissolved. Dilute the solution with water and titrate the excess of ferrous sulphate with a standard potassium permanganate solution. If the strength of the permanganate solution in terms of iron is known, its strength in terms of manganese can be calculated from the above reaction. We see that two Fe is equivalent to one Mn and we can make the following proportion:

$$\begin{aligned} 112 : 55 &= \text{Strength of permanganate in terms of Fe} : x \\ x &= \text{Strength of permanganate in terms of Mn.} \end{aligned}$$

Find the value of the ferrous sulphate solution in terms of the permanganate solution by taking 50 c.c. of the ferrous sulphate solution, placing it in a beaker, adding water and titrating to a faint pink color with permanganate.

*Example:*

Amount of ore taken for analysis, 2 grams.

Strength of the permanganate in terms of Mn, .002 gram.

50 c.c. Ferrous Sulphate solution = 15 c.c. permanganate.

Then 100 c.c. Ferrous Sulphate solution = 30 c.c. permanganate. After treating the precipitate of  $\text{MnO}_2$  with 100 c.c. of ferrous sulphate solution it required 10 c.c. of the standard permanganate solution to give a permanent pink color. As 100 c.c. of the ferrous sulphate solution = 30 c.c. of the permanganate solution, there would be the equivalent of 30—10 c.c. or 20 c.c. of permanganate in ferrous sulphate oxydized by the  $\text{MnO}_2$ .

One c.c. of the permanganate being equal to .002 gram of man-



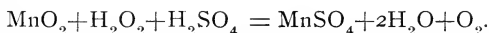
ganese, 20 c.c. is equal to .04 gram Mn, and 2 grams of the sample having been taken

$$\frac{.04 \times 100}{2} = 2 \text{ per cent. manganese.}$$

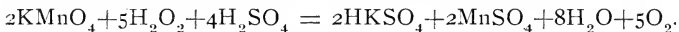
References :

- Ford, *Jour. Am. Chem. Soc.*, Vol. XX, page 504.  
 Ford, *Trans. Am. Inst. Min. Engs.*, Vol. IX, page 397.

*Julian's modification* of the above methods is as follows: Obtain the manganese dioxide precipitate exactly as given above; when the manganese is all oxidized to dioxide, cool, and dilute to 400-450 c.c. Now add from a burette an excess of standard hydrogen peroxide, to completely dissolve the precipitate. The reaction is:



Immediately titrate the excess of hydrogen peroxide with a standard potassium permanganate solution. The reaction is:



The hydrogen peroxide solution is prepared by thoroughly mixing one pound of hydrogen peroxide with about eight liters of water and 100 c.c. of concentrated sulphuric acid. It is standardized by means of a standard potassium permanganate solution.

References :

- F. Julian, *Jour. Am. Chem. Soc.*, Vol. VII, page 113.  
 F. Julian, *Berg. u. Huttenmann Zeit.*, 1897, pages 56, 410.  
*Jour. Soc. Chem. Industry*, 1898, page 185.

### DETERMINATION OF SULPHUR IN IRON ORES.

Weigh one gram of the finely pulverized ore into a large platinum crucible; add about eight grams of chemically pure carbonate of soda and about one half gram of potassium nitrate; mix thoroughly and heat carefully until the mass appears liquid and in a quiet state of fusion. Cool and treat with hot water until the fused mass is decomposed. If the solution is red or green it indicates the presence of manganese; add a few drops of alcohol, which will precipitate the manganese as manganese dioxide. Filter and wash with hot water. Acidulate the filtrate with hydrochloric

acid and evaporate to complete dryness. Treat the residue with water and a few drops of hydrochloric acid, heat and filter. Wash with hot water; heat the filtrate to boiling and precipitate the sulphur with a hot solution of barium chloride. Allow the precipitate to settle, filter, wash with hot water, ignite and weigh as barium sulphate. Calculate the per cent. of sulphur in the ore.

*Aqua Regia Method*—Weigh out from one to five grams of the finely pulverized ore. If high in sulphur, one gram; if low in sulphur, five grams. Place in a beaker and add about 20 c.c. of aqua regia for every gram of ore taken. Cover the beaker and warm for some time, then remove cover and evaporate to dryness. Allow to cool. Moisten the residue with hydrochloric acid; add water, heat, and filter. Dilute the filtrate to about 200 c.c.; heat to boiling; add solution of barium chloride to precipitate the sulphur as barium sulphate. Allow the precipitate to settle, filter, wash with hot water, ignite and weigh. Calculate per cent. of sulphur in the ore.

#### DETERMINATION OF SILICA IN IRON ORES.

*Method I*—Dissolve one gram of the pulverized ore in hydrochloric acid; evaporate to dryness. Moisten the residue with concentrated hydrochloric acid; add water, heat, filter, wash and ignite and weigh the insoluble residue in a platinum crucible. Treat the residue with hydrofluoric acid and a few drops of sulphuric acid; evaporate to dryness; ignite and weigh. In almost all iron ores the loss in weight would represent the silica. If, however, the insoluble residue contains calcium, magnesium, sodium, or potassium, the loss in weight would not represent the silica, but should be increased by the amount of  $\text{SO}_3$  found in the insoluble residue in combination with these elements.

To determine the  $\text{SO}_3$ , fuse the residue with a little carbonate of soda, dissolve in hot water, acidulate with hydrochloric acid, heat to boiling, and add a solution of barium chloride. Filter off the precipitate, ignite and weigh as barium sulphate. Calculate the amount of  $\text{SO}_3$  and add its weight to the loss by volatilization with the hydrofluoric acid.

*Method II*—Weigh one gram of the ore into a platinum cruci-

ble, and mix with about eight times its weight of carbonate of soda; fuse thoroughly; dissolve the fused mass in hot water; acidulate with hydrochloric acid; evaporate to dryness in a casserole; heat the residue for a short time at a temperature of  $110^{\circ}$  to  $130^{\circ}$  C. Moisten the residue with concentrated hydrochloric acid; add water, heat and filter. Wash alternately with dilute hydrochloric acid and water, ignite and weigh the silica.

If greater accuracy is desired the silica may be treated with hydrofluoric acid and sulphuric acid; the loss after evaporation and ignition is weight of silica.

The filtrate from the silica may be used for the determination of alumina.

*Method III*—Treat about one gram of the ore in a number two beaker with 20 c.c. of concentrated hydrochloric acid. Cover the beaker and heat until the ore is decomposed. Remove the cover and evaporate to dryness. Moisten the residue with concentrated hydrochloric acid, add water, heat and filter. Wash with water, ignite the residue in a platinum crucible, and fuse with eight parts of sodium carbonate. Cool; treat the fused mass with dilute hydrochloric acid, evaporate to dryness; heat for some time at a temperature of from  $110^{\circ}$  to  $130^{\circ}$  C. Moisten the residue with concentrated hydrochloric acid, add water, heat and filter. Wash with hot water, ignite and weigh the silica.

The combined filtrates from the silica may be used for the determination of alumina.

Reference: W. F. Hellebrand, *Jour. Am. Chem. Soc.*, Vol. XXIV, page 435.

#### DETERMINATION OF ALUMINA IN IRON ORES.

About 1. gram of the finely pulverized ore is dissolved in 15 c.c. of concentrated hydrochloric acid, the siliceous residue filtered off and ignited in a platinum crucible and the silica volatilized as silicon tetrafluoride,  $\text{SiF}_4$ ; with hydrofluoric acid. The residue from the silica is then fused with anhydrous sodium carbonate, and the fusion decomposed with water and hydrochloric acid, and added to the original filtrate. A solution of hydrogen sodium phosphate, somewhat in excess of the required amount to precipitate the aluminum is then added (about 20 c.c. of a 10% solution).

The solution is neutralized with ammonia water using a drop or two of methyl orange for the indicator and then just sufficient hydrochloric acid is added to dissolve the precipitated phosphate. It should require about 3.5 c.c. of the concentrated hydrochloric acid. A solution of sodium thiosulphate sufficient to neutralize the acid is then added. This will require about 15 grams of the thiosulphate which should be dissolved in about 75 c.c. of distilled water before being added. Sulphur is precipitated and the iron reduced to the ferrous state. The solution is next diluted with water to 400 or 500 c.c., heated to boiling, 15 c.c. of acetic acid (sp. gr. 1.04) added, and boiled for about one-half hour, or until  $\text{SO}_2$  is expelled. The precipitate is filtered, washed, ignited in a porcelain crucible and weighed as  $\text{AlPO}_4$ . Calculate per cent.  $\text{Al}_2\text{O}_3$ .

#### *DETERMINATION OF TITANIUM IN IRON ORES.*

One gram of the finely pulverized ore intimately mixed in a large platinum crucible with 12 grams of potassium di-sulphate and 2 grams of sodium fluoride is gradually heated by a low flame until the di-sulphate is melted. Heating is continued, keeping the mass just liquid and the temperature at the point at which slight fumes of sulphuric anhydride are given off when the lid of the crucible is raised, until all the particles of the ore have disappeared. Remove the flame, and, as the melt cools, incline the crucible in different directions, so that the fused mass may solidify well up on the sides. When cool add 2 or 3 c.c. concentrated sulphuric acid, and carefully heat until the mass is just liquid. Discontinue heating, and place a platinum rod in the solidifying melt. When cold, fuse the mass where it is in contact with the crucible, and remove it by means of the platinum rod to a beaker containing 150-200 c.c. of a 5 per cent. solution of sulphuric acid. In the beaker also place the crucible and cover. Gently warm, but do not raise the temperature of the beaker and its contents beyond that which can be comfortably endured by the palm of the hand. The melt should completely dissolve to a clear solution. Determine the titanium in the solution by one of the following methods.

*Gooch's Method*—Add 50 c.c. of sulphurous acid and *gently* warm for a few minutes. The solution is cooled and neutralized with ammonia until the precipitate which forms dissolves with difficulty. Add 10 c.c. of sulphurous acid, 20 grams of sodium acetate (in solution), and one-sixth the total volume of acetic acid (sp. gr. 1.04). The solution is heated to boiling, the titanium being precipitated in a flocculent condition. Boiling is continued for two or three minutes. If filtered immediately, the filtrate, upon evaporation, is sometimes found to contain traces of titanous acid; this, however, may be obviated by digesting the previously boiled precipitate on the steam bath for half an hour.

After allowing the precipitated titanous acid to settle, filter, wash with hot water containing 5 per cent. of acetic acid, and finally with hot water. The titanous acid precipitate is generally contaminated more or less with iron, alkali sulphates, alumina, phosphoric acid, etc. In order to eliminate these impurities, the precipitate is thoroughly ignited in a platinum crucible to burn out the carbon of the filter paper, and then fused with sodium carbonate (avoid presence of potassium carbonate) and a little sodium nitrate, in order to form soluble phosphate and aluminate of sodium; the titanium, at the same time is converted into insoluble sodium titanate, and the iron into insoluble ferric oxide. A liberal amount of the flux and an hour's fusion with the strong flame of a blast lamp are necessary to effect these changes completely. After fusion, the melt is boiled with a solution of sodium carbonate, filtered and washed with water containing a little sodium carbonate. The insoluble sodium titanate and ferric oxide are collected on a filter, dried in an air-bath, and transferred to a platinum crucible. The filter paper is burned on a platinum wire, and the residue also added to the crucible. The contents of the crucible are fused with a little sodium carbonate, and the cooled mass treated in the crucible with sulphuric acid, heat being gradually applied until fumes of sulphuric anhydride are evolved. After cooling, the liquid or pasty mass is dissolved in a mixture of 100 c.c. water and 20 c.c. sulphurous acid. Then, after neutralizing with ammonia until the precipitated titanous acid dissolves with difficulty, 5 to 10 grams of sodium acetate (in solution) and 25

c.c. of acetic acid (sp. gr. 1.04) are added. The solution is boiled for several minutes; digested on the steam bath for half an hour at a temperature just below boiling; the precipitated titanic hydrate filtered; washed with hot water containing 5 per cent. of acetic acid, and finally with hot water; ignited and weighed as titanic oxide ( $\text{TiO}_2$ ).

*Bettel's Method*—To the solution add sodium carbonate so long as it can be added without forming a permanent precipitate. Then add 3 c.c. of dilute sulphuric acid and 100 or 150 c.c. of a strong solution of sulphurous acid; dilute with cold water to about 700 c.c. Cover with a watch glass and slowly heat to boiling. Continue the boiling for about two hours. Add hot water and a little sulphurous acid from time to time during the boiling so as to keep the bulk of the solution to about 700 c.c. During the boiling, sulphur dioxide should always be present to keep the iron reduced to the ferrous form, otherwise more or less iron would be precipitated along with the titanium dioxide. Allow the precipitate to settle. (Do not use filter pump.) Filter, wash with water containing a little sulphurous acid and a little ammonium sulphate. Dry, ignite in a platinum crucible, partly cool, add a few pieces of solid ammonium carbonate and again ignite to remove traces of sulphuric anhydride. Cool and weigh as  $\text{TiO}_2$ .

This may contain traces of iron oxide, calcium sulphate or phosphoric acid, therefore if very accurate results are desired, weigh into the crucible six or eight parts of carbonate of soda and mix it with the  $\text{TiO}_2$  and fuse thoroughly. Cool, dissolve the fused mass in hot water, filter and wash with hot water. Ignite the precipitate of titanate of soda ( $\text{Na}_2\text{O} \cdot \text{TiO}_2$ ) in a platinum crucible and fuse it with about 15 times its weight of potassium bisulphate, observing the same precautions as in first fusion. Cool, place in a beaker, add cold water. When decomposed, filter, if necessary and wash with cold water. Determine the titanium in the filtrate by either of the following methods:

(a) Dilute and precipitate titanium di-oxide by boiling in presence of sulphurous acid. Filter, ignite and weigh  $\text{TiO}_2$ .

(b) To the solution add about 50 c.c. sulphurous acid, and about 10 grams of sodium acetate and 40 c.c. strong acetic acid, heat to boiling for about 15 minutes. Allow the precipitate to

settle, filter, wash with hot water containing a little acetic acid, dry, ignite and weigh  $TiO_2$ .

*Weller's Color Method.*

Dilute the solution to 500 c.c. with 5 per cent. sulphuric acid and mix thoroughly. Put 50 c.c. of the solution into a comparison tube. Put into a second comparison tube as much of a standard ferric sulphate solution, containing 5 per cent sulphuric acid, as will contain an amount of iron equal to that in 0.1 gram of the ore and dilute to 50 c.c. with 5 per cent. sulphuric acid.

Add to each tube 5 c.c. of hydrogen peroxide and then add to the second tube from a burette a standard solution of titanium sulphate until the yellow color produced matches that in the first tube. From the volume of the standard solution used calculate the percent of  $TiO_2$  in the ore.

To prepare the standard titanium sulphate solution fuse 0.5 gram of pure  $TiO_2$  in a platinum crucible with 5 grams of potassium bisulphate. Cool and dissolve the fusion in 5 per cent. sulphuric acid. Dilute the solution to 500 c.c. with the 5 per cent. acid.

This method is very satisfactory for the determination of titanium in ores containing less than about 4 per cent. For ores containing more than 4 per cent the Gooch method is recommended.

References :

Gooch, *Proc. Am. Acad. Arts and Sciences*, New Series, Vol. XII, page 435.

A. A. Blair, *The Chemical Analysis of Iron.*

F. J. Pope, *Trans. Am. Inst. Min. Engrs.*, Vol. XXIX, page 372.

J. O. Arnold, *Steel Works Analysis.*

H. L. Wells and W. L. Mitchell, *Jour. Am. Chem. Soc.*, Vol. XVII, page 878.

W. Bettel, See Crooke's *Select Methods*, page 194.

J. W. Bain, *Jour. Am. Chem. Soc.*, Vol. XXV, page 1073.

Weller, *Ber. d. Chem. Ges.*, Vol. XV, page 2593.

*DETERMINATION OF MOISTURE IN IRON ORES.*

Weigh out one or two grams of ore in a bulb tube and ignite in a slow current of dry air. Collect the water in a weighed calcium chloride tube which is connected with the bulb ignition tube. The increase in weight of the calcium chloride tube gives the amount of moisture in the sample. Calculate the per cent.

*DETERMINATION OF CARBONIC ACID IN IRON ORES.*

Take for this determination from one to five grams of the pulverized ore, the amount taken depending upon the amount of carbonic acid expected. Decompose the carbonate in a flask which is connected with a weighed caustic potash absorption bulb. The increase in weight of the absorption bulb gives the weight of carbon dioxide in the sample.

*DETERMINATION OF FERROUS IRON IN IRON ORES.*

Weigh into a large platinum crucible one gram of the finely pulverized ore and heat on a water bath with about 20 c.c. concentrated hydrochloric acid and about 20 c.c. of hydrofluoric acid. A water bath constructed for this process is provided with a grooved ring in which a funnel stands. A little water placed in the groove forms a tight joint. It is also provided with a tube in the side through which carbon dioxide can be passed to exclude the air during the process, and thus prevent any oxidation of the ferrous iron. Stir the contents of the crucible from time to time with a long platinum wire. When the ore is dissolved transfer the contents of the crucible to a beaker. Add water and determine the ferrous iron present by means of a standard solution of potassium bichromate. Calculate the per cent. of FeO.

*COMPLETE ANALYSIS OF IRON ORES.*

(Method suitable for all iron ores excepting those containing considerable titanitic acid.)

Treat five grams of the finely ground ore in a number three beaker with about 50 c.c. strong hydrochloric acid and one or two c.c. strong nitric acid. Heat the mixture until the ore is decomposed. Evaporate to dryness in order to render insoluble any silica which may have been dissolved. Moisten the residue with concentrated hydrochloric acid, add water, heat, filter into a 250 c.c. flask. Wash with water, ignite the siliceous residue in a platinum crucible and fuse it with about eight times its weight of carbonate of soda. Decompose the fused mass with water, acidify with hydrochloric acid, evaporate to



dryness; heat in a drying oven for an hour at  $110^{\circ}$  to  $120^{\circ}\text{C}$ . Cool, moisten with concentrated hydrochloric acid, add water, heat, filter into the 250 c.c. flask containing the first filtrate. Wash with hot water, ignite and weigh the  $\text{SiO}_2$ . Dilute the solution in the flask to the containing mark and mix thoroughly.

*Determination of the Iron*—Take out 50 c.c. of the solution. Reduce the iron with stannous chloride and continue as directed on page 21. Calculate the per cent. of  $\text{Fe}_2\text{O}_3$ .

*Determination of the Phosphorus*—To 100 c.c. of the solution add ammonia until the mass sets to a stiff jelly, making sure that there is present an excess of ammonia. Next add strong nitric acid in sufficient amount to bring the solution to a clear amber color, and continue as directed on page 24.

*Determination of Alumina, Manganese, Lime and Magnesia*—Take 50 c.c. of the solution in a large beaker, add sodium carbonate until the fluid is nearly neutral and then to the clear red liquid add a solution of about 5 grams of sodium or ammonium acetate; dilute to about 500 c.c. with boiling distilled water. Heat to boiling for a minute or two, filter while hot and wash by decantation with hot water. Dissolve the precipitate in hot dilute hydrochloric acid, heat to boiling then add ammonia water to alkaline reaction. Filter and wash the precipitate with hot water. Ignite and weigh  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ . Calculate the per cent. of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . The per cent. of  $\text{Al}_2\text{O}_3$  is determined by subtracting the per cent.  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  previously determined from the above. Add the filtrate and washings from the acetate precipitation to those from the precipitation by ammonia. Evaporate the solution to about 75 c.c. When cold add bromine water until the solution is strongly colored, add ammonia in excess and heat moderately for some time, then filter, wash with hot water. Test filtrate for manganese with more bromine and ammonia, heat for some time and filter if necessary, dry, ignite and weigh  $\text{Mn}_3\text{O}_4$ . Calculate the per cent.  $\text{MnO}_2$ .

Instead of igniting the precipitate of hydrated peroxide of manganese, it may be dissolved in an excess of standard ferrous sulphate solution, containing a little sulphuric acid, and the excess of the ferrous salt determined with a standard solution of permanganate or bichromate of potash. See Ford-Williams process, page 30.

Acidify the filtrate, from the manganese precipitate, with hydrochloric acid and concentrate to about 100 c. c. Add ammonia in slight excess, then precipitate the calcium with ammonium oxalate as calcium oxalate,  $\text{CaC}_2\text{O}_4$ . Filter, wash, ignite and weigh  $\text{CaO}$ . Calculate the per cent. of  $\text{CaO}$ .

To the filtrate from the calcium oxalate add a volume of ammonia of sp. gr. .96, equal to one third the volume of the solution. Then add hydrogen sodium phosphate drop by drop while stirring the solution with a glass rod, to precipitate the magnesium as ammonium magnesium phosphate. Allow to stand for some time, filter, wash with a mixture of one part of ammonia, sp. gr. .96, and three parts water, dry, ignite and weigh  $\text{Mg}_2\text{P}_2\text{O}_7$ . Calculate the per cent. of  $\text{MgO}$ .

*Determination of the Sulphur*—To the remaining 50 c.c. of the original solution add a few drops of hydrochloric acid, heat to boiling in a beaker and precipitate the sulphur with barium chloride as barium sulphate,  $\text{BaSO}_4$ . Allow the precipitate to settle, filter, wash, ignite and weigh  $\text{BaSO}_4$ . Calculate the per cent. of sulphur.

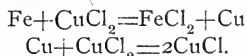
*Determination of Carbon Dioxide, Moisture and Ferrous Iron.* See page 37.

### DETERMINATION OF TOTAL CARBON IN IRON AND STEEL.

BY OXIDATION OF THE CARBON WITH CHROMIC ACID AND SULPHURIC ACID AFTER THE REMOVAL OF THE IRON.

Treat about one gram of the pig iron or cast iron drillings in a number two beaker with a hundred c.c. of saturated solution (300 grams per liter) of copper potassium chloride and 7.5 c.c. of strong hydrochloric acid. For steel, treat about 3 grams in a number three beaker with 200 c.c. of the copper potassium chloride and 15 c.c. of strong hydrochloric acid. Stir the solution vigorously for a few minutes, place the beaker in a warm place, but not where the temperature can rise above  $60^\circ$  or  $70^\circ\text{C}$ .

Continue to stir at frequent intervals until the precipitated copper is dissolved. Reactions are:



Allow the undissolved residue to subside and then filter through an ignited asbestos filter. The filter may be made by placing a small perforated platinum or porcelain disc in the bottom of a small funnel, and upon it is placed in the usual manner the asbestos which has been previously ignited. Wash the residue at first with a little dilute hydrochloric acid and then with hot water.

#### OXIDATION OF THE CARBONACEOUS RESIDUE.

##### *Apparatus required:*

I. A flask, A, (see Fig. 1), having a capacity of about 300 c.c.

D B C

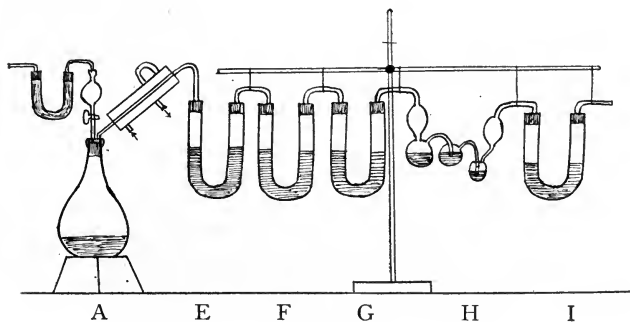


Fig. 1

provided with a double perforated rubber stopper. Through one of the holes is passed a separating funnel, B, with glass stopcock. The funnel should have a capacity of about 100 c.c. Through the other hole of the stopper is passed a condenser, C, through which a stream of water continually passes while the combustion is being made.

II. An apparatus, D, for the purification of the air. This consists of a U tube filled partly with pieces of solid potassium hydroxide and partly with granular calcium chloride.

III. A series of connected U tubes in which the carbon dioxide is dried and purified before entering the weighed absorption apparatus.

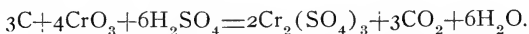
E contains a solution of silver sulphate and concentrated sulphuric acid.

F, a U tube filled with pumice stone which has been saturated with a concentrated solution of copper sulphate, and then heated to dehydrate the salt.

G, a U tube filled with granular calcium chloride.

IV. An apparatus, H, for the absorption of carbon dioxide, containing a solution of potassium hydroxide, sp. gr. 1.27 (two parts KOH to three parts  $H_2O$ ). This absorption apparatus is connected with a tube, I, partly filled with granular calcium chloride and partly with soda lime. This tube is to protect H from carbon dioxide and moisture of the air.

*Process*—Transfer the asbestos filter and carbonaceous residue to the combustion flask A. If necessary clean the funnel with a little ignited asbestos and place it in the flask with the residue. Weigh the apparatus for the absorption of the carbonic acid gas and connect it properly with the tubes G and I. Add through the separating funnel 10 c.c. of a saturated solution of chromic acid, and then slowly add 100 c.c. of concentrated sulphuric acid, which has been heated nearly to the boiling point with a little chromic acid, and then cooled. Pass a slow current of air through the whole apparatus and very gradually raise the temperature of the liquid in the flask nearly to the boiling point. The reaction is:



When the oxidation is complete, gradually lower the light while a current of air continues to pass. Extinguish the light and when about one liter of air has passed through the apparatus after the extinguishing of the flame, detach and weigh the carbon dioxide absorption apparatus. The increase in weight is  $CO_2$ . Calculate per cent. carbon. Results should agree within .01 per cent.

*DETERMINATION OF TOTAL CARBON IN IRON AND STEEL.*

BY COMBUSTION OF THE CARBON IN THE SHIMER CRUCIBLE AFTER THE REMOVAL OF THE IRON.

Separate the iron from the carbon as directed in the preceding experiment. Dry the carbonaceous residue in an air bath for about half an hour at  $100^{\circ}\text{C}$ . When dry, transfer it to the Shimer crucible with the carbon side down. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The carbon should all be kept within one-fourth of an inch of the bottom of the crucible, otherwise a part of the carbon might escape combustion.

Partly fill the crucible with ignited asbestos.

The Shimer crucible is a special water-jacketed platinum crucible closed by a hollow water-cooled metal stopper made gas-tight by means of a rubber band. See Fig. 2. Place the rubber band around the crucible stopper and insert it in the crucible.

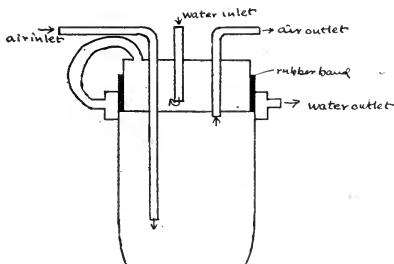


Fig. 2

The crucible is supported by passing it about half-way through a heavy piece of asbestos board. The crucible is connected, by means of the water inlet tube, with a water supply for cooling the stopper. Under the crucible is an upright Bunsen burner or blast lamp. If the carbonaceous matter is mainly graphite it will require the strong heat of a blast lamp to make the combustion.

Connected with the air inlet tube is Geissler's bulb containing

solution of potassium hydroxide (sp. gr. 1.27) for purification of the air. Between the Geissler bulb and the crucible is a small guard bottle to retain any drops of the potassium hydroxide that may be forced over from the Geissler apparatus.

An aspirator to furnish air pressure is connected with the Geissler bulb. Next to the crucible and connected to it by means of the air outlet tube is a short brass tube containing cupric oxide in its central portion and provided with wet wick at the ends for cooling purposes. Next to the cupric oxide tube is a glass tube filled with glass beads, wet with distilled water, for retaining hydrochloric acid and chlorine.

Next to the glass bead tube is attached a large calcium chloride tube.

The calcium chloride tube is connected with a weighed Geissler bulb containing potassium hydroxide (sp. gr. 1.27) and the Geissler bulb with a guard tube of calcium chloride.

Be sure that the water is running from the stopper and that the cupric oxide tube is red hot for from one and one-half to two inches in its central part, then turn on the air at the speed of about three bubbles per second and bring a small blast-lamp flame immediately under the crucible, so as to heat the bottom to a bright red heat, extending at least one-fourth inch from the bottom. A large flame should be avoided. Time required for making combustion about twenty-five minutes.

#### References:

- P. W. Shimer, *Jour. Am. Chem. Soc.*, Vol. XXI, page 557; and Vol. XXIII, page 227; and Vol. XXV, page 997.  
G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XXIV, page 1206.  
J. V. R. Stehman, *Jour. Am. Chem. Soc.*, Vol. XXV, page 237.

## DETERMINATION OF GRAPHITIC CARBON IN IRON.

### METHOD I.

Dissolve one gram of pig iron in 15 c.c. of nitric acid of sp. gr. 1.2. Collect the undissolved material upon an ignited asbestos filter and wash with hot water. Treat the residue on the filter with a hot solution of potassium hydrate of 1.1 specific gravity. Wash thoroughly with hot water, then with a little dilute hydrochloric acid and finally with hot water. Burn the carbon with chromic and sulphuric acids. See page 41.

A very satisfactory result may be obtained as follows: Place the asbestos filter and graphite in a platinum crucible. Dry the crucible and contents at 100°C., cool and weigh. Heat over a Bunsen burner until the graphite is all burned off and weigh again. The loss of weight gives graphite.

#### METHOD II.

Dissolve 2 grams of pig iron in 50 c.c. of dilute nitric acid (sp. gr. 1.2) in a number four beaker, heat gently to boiling and then boil for about five minutes. Next add about 5 c.c. hydrofluoric acid, being careful not to allow it to touch the glass. Immediately give the beaker an oscillatory motion, heat a few moments, dilute with water and filter onto a filter paper which has been dried at 100°C. and then weighed. Wash at first with hot water and then two or three times with dilute hydrochloric acid. Wash again with water and then twice with ammonia and finally several times with water. Dry the filter paper and graphite at 100°C. and weigh. Calculate per cent. graphite. If extreme accuracy is required, place the dried and weighed paper and graphite in a platinum crucible and thoroughly burn off paper and graphite and weigh the siliceous residue. This weight of silica should be multiplied by 1.06 and the product deducted from the weight of graphite as found above.

#### References:

- P. W. Shimer, *Jour. Am. Chem. Soc.* Vol. XVII, page 873.
- G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XXII, page 47.
- F. L. Crobough, *Jour. Am. Chem. Soc.*, Vol. XVI, page 104.
- G. T. Dougherty, *Chem. News*, Sept. 8, 1899.
- T. M. Drown, *Trans. Am. Inst. Min. Engrs.*, Vol. II, page 224.

### DETERMINATION OF COMBINED CARBON.

#### EGGERTZ COLORIMETRIC METHOD.

The method depends upon the fact that when samples of similar varieties of steel or iron are dissolved in nitric acid (sp. gr. 1.2) the depth of the brown color produced is directly proportional to the amount of chemically combined carbon in the samples. The combined carbon in a sample of steel may be

determined by comparing the color produced upon dissolving a known weight of the sample in nitric acid with the color produced by dissolving a weighed quantity of similar steel whose percentage of combined carbon has been very accurately determined by the combustion method. See page 40.

*Process*—Clean, dry and number several test tubes. Weigh into one .2 gram of standard steel and into the other the same amount of each sample to be tested. Add to each tube the required amount of nitric acid of sp. gr. 1.2.

For steels containing less than .3% combined carbon use 3 c.c.  $\text{HNO}_3$  sp. gr. 1.2.

For steels containing .3-.5% combined carbon use 4 c.c.  $\text{HNO}_3$  sp. gr. 1.2.

For steels containing .5-.8% combined carbon use 5 c.c.  $\text{HNO}_3$  sp. gr. 1.2.

For steels containing .8-1% combined carbon use 6 c.c.  $\text{HNO}_3$  sp. gr. 1.2.

For steels containing 1% and over combined carbon use 7 c.c.  $\text{HNO}_3$  sp. gr. 1.2.

Place a small funnel in the mouth of each test tube. Heat them in a water bath, shaking them from time to time, until all of the carbonaceous matter is dissolved. Remove each test tube and place it in a cold water bath as soon as the solution becomes clear. When cold pour the solution of the standard steel into an Eggertz graduated comparison tube. Wash out the test tube with a few drops of nitric acid (sp. gr. 1.2). Dilute the solution with water to about twice the volume of the acid which was used in making it. To save time in making calculation it is best to dilute the solution to some convenient multiple of the carbon contents of the steel. Suppose that the standard steel contains .35 per cent. combined carbon, dilute the solution to 7 c.c. Then each c.c. equals .05 per cent. carbon. Next pour the solution of a sample to be tested into another Eggertz tube, and dilute it until the color is the same as in the standard. Suppose that 8 c.c. is the dilution of the sample, then it contains .4 per cent. of combined carbon.

**References:**

*Trans. Am. Inst. Min. Engs.*, Vol. I, page 240.

*Trans. Am. Inst. Min. Engs.*, Vol. XVI, page 111.

*Chem. News*, Vol. XLVII, page 285.

*G. Auchy, Jour. Am. Chem. Soc.*, Vol. XXV, page 999.



*DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.*

Treat about two grams of the borings with 75 c.c. of nitric acid (sp. gr. 1.135), 1 part concentrated  $\text{HNO}_3$ , and 3 parts water, in a 400-500 c.c. Erlenmeyer flask and heat gently. When the first action is over boil for one or two minutes. Add 10 c.c. of potassium permanganate solution (containing  $12\frac{1}{2}$  grams of  $\text{KMnO}_4$  per liter), and boil until the pink color disappears. A precipitate of manganese oxide is formed. Remove the flask from the heat and add a little ferrous sulphate (free from phosphate) or sugar and shake the flask until the precipitate of manganese dioxide dissolves. Use as little excess of the ferrous sulphate or sugar as possible. If the sample contain much graphite it is best to filter it off. To the solution add ammonia until the mass sets to a stiff jelly. Then add  $\text{HNO}_3$ , Con. to get amber color. Heat the solution in the flask to  $85^\circ\text{C}$ . and add about 50 c.c. ammonium molybdate solution, to precipitate the phosphorus as ammonio-phospho-molybdate. Determine the phosphorus in the yellow precipitate by the Emmerton method, page 24, or by the acidimetric method, page 26.

Different chemists working on the same sample should agree within .005 per cent.

**References :**

Dudley & Pease, *Jour. Am. Chem. Soc.*, Vol. VII, pages 108 & 519.  
Clemens Jones, *Jour. An. & Appl. Chem.*, Vol. IV, page 268.

*DETERMINATION OF MANGANESE IN IRON AND STEEL.*

## VOLHARD'S METHOD.

Take one gram of the borings. Dissolve the sample in 15 c.c. of nitric acid (sp. gr. 1.2) in a casserole. When solution is complete add 10 c.c. dilute sulphuric acid and evaporate to dryness, and heat the residue until heavy white fumes of sulphuric acid are evolved to destroy carbonaceous matter. Allow the dish to cool, all 100 c.c. water, and heat until the ferric sulphate

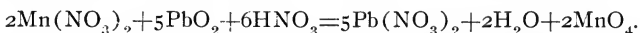
is dissolved. Wash the contents of the casserole into a half liter flask with cold water, nearly neutralize with carbonate of soda, and proceed from this point as directed in the analysis of iron ores. Page 28. Different chemists, working on the same sample, should agree within .01 per cent.

DETERMINATION OF MANGANESE IN IRON AND STEEL BY FORD-  
WILLIAMS METHOD.

Weigh one to five grams of the iron or steel and dissolve in nitric acid (sp. gr. 1.2). Use about 15 c.c. of the acid for every gram of iron or steel taken. In case of pig iron, filter off the graphite through an asbestos filter. Evaporate to about 10 c.c. Now add 75 c.c. of strong nitric acid and heat. When solution is warm add about 5 grams of potassium chlorate and boil. From this point proceed as in the analysis of iron ores; page 29.

THE COLOR METHOD FOR MANGANESE IN IRON AND STEEL.

Weigh out .2 gram of each sample and the standard. If the samples to be analyzed be pig iron, then use a pig iron standard, and if the sample is steel, a steel standard. Place the weighed portions in 10 inch test tubes properly numbered. Pour into each 20 c.c. of nitric acid (sp. gr. 1.2). Place in the mouth of each test tube a small funnel. Heat in the water bath at 100°C. until solution is complete, add 10 c.c. of water, heat in a calcium chloride bath (which boils at 115°C.) to boiling, add about 3 grams of lead dioxide (PbO<sub>2</sub>) and continue boiling for just five minutes. The reaction is:



Place the tubes in cold water, and when the insoluble matter settles, decant the clear solutions into the reading tubes and compare.

DETERMINATION OF SULPHUR IN IRON AND STEEL.

*Method I*—Weigh 5.4936 grams of the drillings into a number 3 beaker. Add slowly a mixture of 50 c.c. concentrated nitric

acid and one c.c. concentrated hydrochloric acid. Heat gently if the reaction does not begin in the cold, but remove from the heat and place the beaker in cold water if the reaction is too violent. If any of the sample resists solution add a few drops of concentrated hydrochloric acid from time to time. Add a little carbonate of soda, and evaporate to *complete* dryness.

The carbonate of soda is added to form sodium sulphate and thus prevent loss of sulphur trioxide, from the decomposition of the iron sulphate in case the residue is overheated. Add 30 c.c. of concentrated hydrochloric acid and evaporate to about 5 c.c. Add water, heat, and filter off the silica. Heat the filtrate to boiling and add 10-20 c.c. of a hot solution of barium chloride (1 to 10). Allow the precipitate to settle, filter, wash with a little dilute hydrochloric acid and then with hot water, ignite and weigh barium sulphate. The weight of the precipitate in milligrams divided by four and multiplied by ten gives the per cent. of sulphur.

*Method II—Evolution Method*—The process consists in liberating the sulphur from the iron or steel by means of dilute hydrochloric acid, in the form of hydrogen sulphide and absorbing the gas in an ammoniacal solution of cadmium chloride, as cadmium sulphide. The sulphur is afterward liberated from the cadmium sulphide as hydrogen sulphide by means of hydrochloric acid and the hydrogen sulphide titrated with a standard solution of iodine.

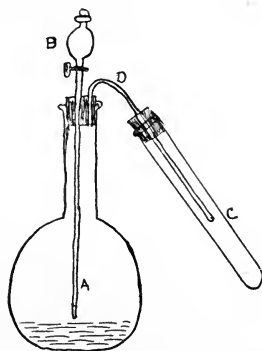
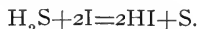


Fig. 3.

*Apparatus required*—A flask, A, of about 300 c.c. capacity, provided with a doubly perforated rubber stopper. See Fig. 3. Through one of the holes is passed a separating funnel, B, and through the other hole is passed a bent tube, D, extending to within two or three inches of the bottom, of an eight inch test tube, C.

*Solutions Required*—I. Ammoniacal Solution of Cadmium Chloride; prepared as follows: Dissolve 13 grams of cadmium chloride in water, add 65 c.c. of strong ammonia and dilute to a volume of one liter.

II. Standard Iodine Solution, of such strength that one c.c. is equivalent to .0005 gram of sulphur. The reaction between the hydrogen sulphide and the iodine is:



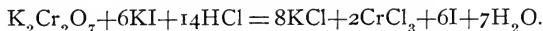
Then

$$\text{At. wt. of S} : 2 \text{ (at. wt. of I)} = .0005 : x.$$

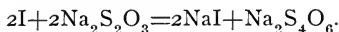
$$32 : 253.7 :: .0005 : x.$$

$X = .003965$  gram of iodine, the amount required to be present in each cubic centimeter of the iodine solution, or 3.965 grams per liter. The solution may be prepared from decinormal solution of iodine by taking 313.3 c.c. and diluting with water to one liter.

The solution may be prepared from iodine as follows: Weigh four grams of iodine and place it in a mortar with about six grams of potassium iodide and triturate with *small* portions of water until all is dissolved. Dilute the solution to one liter volume and mix thoroughly. Standardize the solution by means of a standard solution of sodium thiosulphate, containing about eight grams of the salt per liter; the exact strength of which may be determined by means of a standard potassium bichromate or permanganate solution as follows: Take 10 c.c. of the potassium bichromate solution in a number 4 beaker, add a little water and about one gram of potassium iodide. Add a little hydrochloric acid and stir a few moments. The reaction is:



Dilute with water and titrate the liberated iodine with the thiosulphate solution using starch indicator, toward the end of the reaction. The reaction is:



Calculate the strength of the thiosulphate solution. Now fix the strength of the iodine solution from the standard thiosulphate solution by titration, using the starch indicator. Dilute the iodine solution with water to the strength 1 c.c. = .0005 gram sulphur.

*Process*—Weigh into flask A 5 grams of the drillings. Place in the test tube C, about 10 c.c. of the cadmium chloride solution and add water until the test tube is about two-thirds full. Connect the test tube with the generating flask A. Slowly add by means of the separating funnel, 75 to 100 c.c. of dilute hydrochloric acid (sp. gr. 1.1) to the drillings. When about all of the drillings are dissolved heat to boiling a few minutes, and before removing the heat disconnect the test tube.

Pour the contents of the test tube into a large beaker, dilute to about 400 c.c. Acidify the solution with hydrochloric acid and titrate with the standard iodine solution, using the starch indicator. Do not wait for the precipitate of cadmium sulphide to dissolve before commencing the titration.

Each cubic centimeter of the iodine solution required equals .01 per cent. of sulphur. Results on the same sample, obtained by different analysts, should agree within .005 per cent.

#### References :

- Am. Chem. Jour.*, Vol. XXVII, page 500.
- G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 406.
- G. Auchy, *Jour. Am. Chem. Soc.*, Vol. XXIII, page 147.
- F. C. Phillips, *Jour. Am. Chem. Soc.*, Vol. XVIII, page 1079.
- F. C. Phillips, *Jour. Am. Chem. Soc.*, Vol. XVII, page 891.
- A. A. Blair, *Jour. Am. Chem. Soc.*, Vol. XIX, page 114.
- T. M. Drown, *Trans. Am. Inst. Min. Engrs.*, Vol. X, page 187.
- T. M. Drown, *Trans. Am. Inst. Min. Engrs.*, Vol. II, page 224.
- T. M. Drown, *Trans. Am. Inst. Min. Engrs.*, Vol. XII, page 507.
- C. B. Dudley, *Jour. Am. Chem. Soc.* Vol. XV., page 514.

#### BAMBER'S METHOD FOR SULPHUR IN PIG IRON.

Dissolve 5 grams in strong nitric acid, add two to five grams of potassium nitrate, evaporate to dryness in a platinum or porcelain dish, and ignite. Treat with water, with the addition of a little sodium carbonate, filter, and wash with water containing a little sodium carbonate. Acidulate with a little hydrochloric acid, evaporate to dryness, redissolve in water with a few drops of hydrochloric acid, and precipitate, boiling with barium chloride.

Method suitable for pig iron containing sulphur in such a form that it is not acted upon by  $\text{HNO}_3$ ,  $\text{HCl}$  or aqua regia.

WIBORGH'S COLOR METHOD FOR SULPHUR IN IRON AND STEEL.

Weigh .8 to 1 gram of the drillings into the generating flask A, (See Fig. 4) and fill the flask about one-third full of water. The cylinder B, is then adjusted, and the water in the flask heated to boiling. A rubber washer, C, is then placed on top of the cylinder, followed by the prepared cloth, D, (saturated with a solution of cadmium chloride), the second rubber washer, E, and the wooden ring, F, the whole being firmly clamped together by two steel clamps, G.

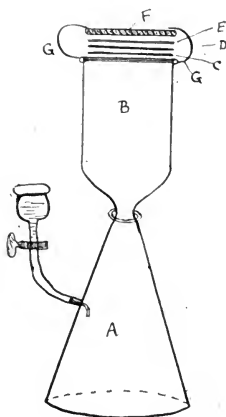


Fig. 4.

*Be sure that the top of the cylinder is in a horizontal position.* Heat the flask, and as soon as the cloth is moistened and the air driven out of the apparatus, admit about 12 c.c. of dilute sulphuric acid (1 to 4) through the side tube H, and apply gentle heat, till the sample is in solution. The cloth is then removed, dried on a blotting or filter paper and compared with the standard colors.

References:

*Jour. Am. Chem. Soc.*, Vol. VI, page 301.

F. P. Treadwell, *Analytischen Chemie.*, Vol., II, page 227.

*DETERMINATION OF SILICON IN PIG IRON, CAST  
IRON AND STEEL.*

**DROWN'S METHOD**—Treat one gram of the pig or cast iron drillings in a four inch casserole with 30 c.c. of silicon mixture (1 part concentrated  $H_2SO_4$  and 2 parts  $HNO_3$ , sp. gr. 1.2). For steel treat about 5 grams of the drillings with 100 c.c. of silicon mixture. Cover the dish with a glass cover. At first keep the dish well covered, but after the violent action ceases, pull the cover a little to one side and evaporate until fumes of sulphur tri-oxide appear. Cool, add from 150 to 200 c.c. of water and a little hydrochloric acid. Heat to dissolve the ferric sulphate, filter hot, wash with dilute hydrochloric acid, and then with hot water, ignite, cool and weigh  $SiO_2$ . Calculate the per cent. of silicon.

The silica should be perfectly white. If it is colored with oxide of iron, after weighing it, add two or three drops of concentrated sulphuric acid and four or five c.c. of hydrofluoric acid. Evaporate to dryness, ignite, cool and weigh again. The loss of weight gives the amount of silica.

Calculate the per cent. of silicon.

Chemical analyses of the same sample made by different chemists should agree within .01 per cent.

*Chromic Acid Modification of Drown's Method for Silicon in Pig Iron*—Treat one gram of the pig iron in a 4 inch casserole with 10 to 20 c.c. of water and 25 c.c. of silicon mixture (1 part  $H_2SO_4$ , sp. gr. 1.84 and 2 parts  $HNO_3$ , sp. gr. 1.2). Heat gently until the violent action ceases. When dissolved, evaporate rapidly until the iron sulphate becomes insoluble, and commences to sputter against the cover glass. Remove from the lamp and while hot add 15 c.c. of a water solution of chromic acid (120 gr. per liter). Boil again as before until the chromic acid crystallizes out. Remove from the lamp and add hot water, slowly at first, boil for a few minutes or until dissolved and clear. Filter, wash the chromic acid out of the filter with hot water, wash once with hydrochloric acid (sp. gr. 1.06) and then wash three or four times with hot water. Ignite, cool, and weight  $SiO_2$ . Calculate the per cent. of Si.

*Precautions*—The evaporation with the chromic acid must not be carried too far, otherwise insoluble salts are formed. On the other hand if the heat is not continued long enough, the graphite

will not all be oxidized. The small amount of graphite occasionally remaining is very rapidly burned off in the ignition. A slight green tint in the ash does not materially affect the result. This treatment with chromic acid not only removes the carbon, but renders the filtration much more rapid. Time required, from 20 to 30 minutes.

References :

- T. M. Drown, *Trans. Am. Inst. Min. Engrs.*, Vol. VII, page 346.  
D. H. Brown, *Jour. Anal. & App. Chem.*, Vol. VI, page 452.

*DETERMINATION OF ALUMINUM IN IRON  
AND STEEL.*

Treat 1 gram of the iron or steel in a number 3 beaker, with a mixture of 15 c.c. of nitric acid (sp. gr. 1.2) and 10 c.c. of hydrochloric acid (sp. gr. 1.1). Cover the beaker with a glass cover and heat until sample is dissolved. Remove the cover and evaporate to dryness. Take up in 15 c.c. of concentrated hydrochloric acid, dilute, filter on ashless filter paper, and wash with water. Add 20 c.c. of a 10% solution of hydrogen sodium phosphate and continue as in the determination of alumina in iron ores. See page 33.

Calculate per cent. aluminum.



# INTERNATIONAL ATOMIC WEIGHTS

	<b>O=16</b>		<b>H=1</b>	
Aluminium....Al	27.1	26.9	Molybdenum..Mo	96.0 95.3
Antimony.....Sb	120.2	119.3	Neodymium...Ne	143.6 142.5
Argon.....A	39.9	39.6	Neon.....	20. 19.9
Arsenic.....As	75.0	74.4	Nickel.....Ni	58.7 58.3
Barium.....Ba	137.4	136.4	Nitrogen.....N	14.04 13.93
Bismuth.....Bi	208.5	206.9	Osmium.....Os	191 189.6
Boron.....B	11	10.9	Oxygen.....O	16.00 15.88
Bromine.....Br	79.96	79.36	Palladium....Pd	106.5 105.7
Cadmium.....Cd	112.4	111.6	Phosphorus...P	31.0 30.77
Cæsium.....Cs	133	132	Platinum.....Pt	194.8 193.3
Calcium.....Ca	40.1	39.8	Potassium....K	39.15 38.86
Carbon.....C	12.00	11.91	PraseodymiumPr	140.5 139.4
Cerium.....Ce	140	139	Radium.....Ra	225 223.3
Chlorine.....Cl	35.45	35.18	Rhodium.....Rh	103.0 102.2
Chromium.....Cr	52.1	51.7	Rubidium....Rb	85.4 84.8
Cobalt.....Co	59.0	58.56	Ruthenium....Ru	101.7 100.9
Columbium			Samarium.....Sm	150 148.9
(Niobium)...Cb	94	93.3	Scandium....Sc	44.1 43.8
Copper.....Cu	63.6	63.1	Selenium.....Se	79.2 78.6
Erbium.....E	166	164.8	Silicon.....Si	28.4 28.2
Fluorine.....F	19	18.9	Silver.....Ag	107.93 107.12
Gadolinium...Gd	156	155	Sodium.....Na	23.05 22.88
Gallium.....Ga	70	69.5	Strontium....Sr	87.6 86.94
Germanium...Ge	72.5	71.9	Sulphur.....S	32.06 31.83
Glucinum.....			Tantalum....Ta	183 181.6
(Beryllium).Gl	9.1	9.03	Tellurium....Te	127.6 126.6
Gold.....Au	197.2	195.7	Terbium.....Tb	160 158.8
Helium.....He	4	4	Thallium.....Tl	204.1 202.6
Hydrogen....H	1.008	1.000	Thorium.....Th	232.5 230.8
Indium.....In	114.	113.1	Thulium.....Tm	171 169.7
Iodine.....I	126.85	125.90	Tin.....Sn	119.0 118.1
Iridium.....Ir	193.0	191.5	Titanium.....Ti	48.1 47.7
Iron.....Fe	55.9	55.5	Tungsten....W	184.0 182.6
Krypton.....K	81.8	81.2	Uranium.....U	238.5 236.7
Lanthanum...La	138.9	137.9	Vanadium....V	51.2 50.8
Lead.....Pb	206.9	205.35	Xenon.....X	128 127
Lithium.....Li	7.03	6.98	Ytterbium....Yb	173.0 171.7
Magnesium...Mg	24.36	24.18	Yttrium.....Yt	89.0 88.3
Manganese...Mn	55.0	54.6	Zinc.....Zn	65.4 64.9
Mercury.....Hg	200.0	198.5	Zirconium....Zr	90.6 89.9



# INDEX

Alumina, in iron ores, determination of . . . . .	34
Alumina, in slags, determination of . . . . .	14, 18
Aluminum, in iron and steel, determination of . . . . .	54
Ammonium molybdate, reagent . . . . .	24
Ammonium molybdate solution, method of standardizing . . . . .	8
Arsenic, in arsenic ores, determination of . . . . .	9
Barium, in slags, determination of . . . . .	12
Calcium, in iron ores, determination of . . . . .	40
Calcium, in slags, determination of	
by Gravimetric method . . . . .	16
by Volumetric method . . . . .	13
Carbonic acid gas, in iron ores, determination of . . . . .	38
Carbon, total, in iron and steel, determination of	
by Chromic acid method . . . . .	40
by combustion in the Shimer crucible . . . . .	43
Carbon, combined, in iron and steel, determination of	
by the Color method . . . . .	45
Carbon, graphitic, in iron and steel, determination of . . . . .	44
Coal and coke, methods for the analysis of . . . . .	19
Chromium, in chrome ore, determination of . . . . .	11
Copper, in copper ores, determination of	
by the Iodide method . . . . .	1
by the Cyanide method . . . . .	3
by the Electrolytic method . . . . .	5
by the Color method . . . . .	5
Copper, in slags, mattes, etc., determination of . . . . .	18
Ferrous oxide, in iron ores, determination of . . . . .	38
Ferrous sulphate solution, method of standardizing . . . . .	12, 30
Iodine solution, method of standardizing . . . . .	50
Iron, in iron ores, determination of	
by Standard solution of $\text{KMnO}_4$ . . . . .	21
by Standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ . . . . .	22
Iron ores, method for complete analysis of . . . . .	38
Jones's reductor, use of, in determining phosphorus . . . . .	26
Lead, in lead ores, determination of, by Alexander's method . . . . .	8
Lead, in slags, mattes, etc., determination of . . . . .	17
Manganese, in iron ores, determination of	
by Volhard's method . . . . .	28
by Ford-Williams' method . . . . .	29
by Julian's method . . . . .	31

Manganese, in iron and steel, determination of	
by Volhard's method . . . . .	47
by Ford-Williams' method . . . . .	48
by Julian's method . . . . .	48
by Color method . . . . .	48
Manganese, in slags, determination of . . . . .	15, 17
Moisture, in iron ores, determination of . . . . .	37
Nitric acid, method of preparing a standard solution . . . . .	27
Phosphorus, in iron ores, determination of	
by Emmerton's method . . . . .	23
by the Acidimetric method . . . . .	26
by Wood's method . . . . .	27
Phosphorus, in iron and steel, determination of . . . . .	47
Phosphorus, in slags, determination of . . . . .	14
Potassium permanganate solution, method of standardizing . . . . .	21
Potassium bichromate solution, method of standardizing . . . . .	22
Potassium ferrocyanide solution, method of standardizing . . . . .	6
Potassium cyanide solution, method of standardizing . . . . .	3
Potassium sulphocyanate solution, method of standardizing . . . . .	10
Potassium hydroxide, method of preparing standard solution . . . . .	26
Silica, in iron ores, determination of . . . . .	32
Silica, in slags, determination of . . . . .	12, 14, 16
Silicon, in iron and steel, determination of . . . . .	53
Slags, methods for the analysis of . . . . .	12, 14, 16
Sodium hydroxide, method of preparing a standard solution . . . . .	26
Sodium thiosulphate, method of preparing and standardizing . . . . .	1, 50
Sulphur, in iron ores, determination of . . . . .	31
Sulphur, in slags, determination of . . . . .	16, 19
Sulphur, in coal and coke, determination of . . . . .	20
Sulphur, in iron and steel, determination of	
by Oxidation and Solution . . . . .	48 51
by Evolution method . . . . .	49
by Wiborgh's color method . . . . .	52
Titanium, in iron ores, determination of . . . . .	34
by Gooch's method . . . . .	35
by Bettel's method . . . . .	36
by Willer's color method . . . . .	37
Zinc, in zinc ores, determination of, by Low's method . . . . .	6
Zinc, in slags, determination of . . . . .	18





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