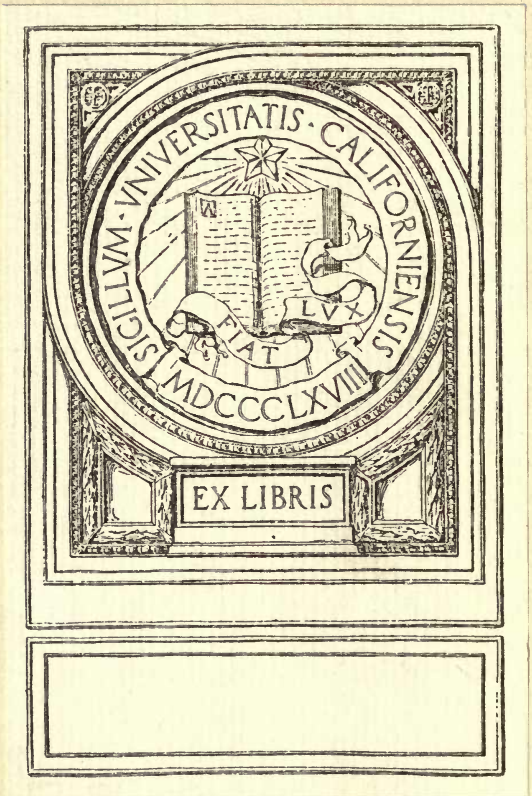

GAS CHEMISTS HANDBOOK

COMPILED BY TECHNICAL COMMITTEE
SUB-COMMITTEE ON CHEMICAL TESTS

1916

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REPORT OF COMMITTEE ON CHEMICAL TESTS.

WRITTEN FOR THE ELEVENTH ANNUAL MEETING OF THE AMERICAN GAS INSTITUTE, OCTOBER, 1916, BY C. C. TUTWILER, CHAIRMAN.

Since the last meeting of the Institute, the Committee on Chemical Tests has directed its activities chiefly toward the revision of the Gas Chemists' Handbook, compiled in 1914 by Mr. W. H. Fulweiler.

Mr. Fulweiler, in presenting his report at the Ninth Annual Meeting of the Institute, stated as follows:

> The magnitude and delicacy of this work is fully realized and this is presented primarily as a progress report. In time, the Institute would be well repaid for the expense incurred in the publication of such a handbook by the uniformity of practice that would result from the adoption of these methods and by the convenience to the gas chemist of having recognized standard methods pertaining to the industry collected in one convenient publication.

While this first issue of the Handbook was a very decided step in the right direction, it was recognized that much was still to be accomplished and the continuance of the work devolved upon the 1915 Committee on Chemical Tests. This Committee was unable to do more than report satisfactory progress at the 1915 meeting of the Institute and the same Committee was re-appointed to continue the revision over 1916.

It was felt from the start that it was of first importance that the work should be carried out by a committee whose activities covered as wide a field as possible, not only in the gas industry but in collateral lines as well, especially in the coke oven and coal tar by-product industries which are becoming yearly more closely identified with the gas business. For this reason, special effort was made to enlist the co-operation of chemists skilled in these various lines and I have felt myself and the Institute most fortunate in having secured the assistance of the gentlemen who served with me on the Committee in 1915 and 1916.

Mr. Fulweiler, in concluding his report, states:

> It is urged that special attention be given to the question of standard methods and to the peculiar conditions under which samples must be taken in the gas industry.

The Committee has felt with Mr. Fulweiler that the standardization of methods of testing and sampling was the chief consideration to which it should devote its attention, and in the Handbook which we now offer for your consideration, we have endeavored to round out as far as possible the work of the first committee and to standardize and bring up-to-date methods which have been developed or improved since the work was inaugurated in 1914. It is hoped that owing to the wide connections of the members of the Committee and the various sources from which these methods have been drawn that progress has been made toward the accomplishment of this much desired result.

The Committee has devoted a considerable amount of time to the consideration of proper methods of sampling, recognizing the fact that unless the sample is properly taken, the analysis might not only be worthless, but absolutely misleading. We have endeavored to have the directions for sampling as well as for testing so clear that little difficulty will be encountered even by chemists of limited experience.

The Committee, recognizing the great progress being made in the application of chemistry to the gas industry and feeling that even companies of moderate size can well afford to have on their staff chemists or men of some chemical training, has kept in mind primarily the assistance of these men rather than the engineer, although it has endeavored to present the subject matter in a manner which may be easily understood by all. It will be noted that no attempts have been made to interpret the results of the analyses, nor have theoretical considerations been touched upon to any great extent, it being felt that this phase of the subject might better be left to succeeding committees, possibly to be covered in a separate publication.

We have included in the Handbook such of the most useful tables of constants and data as are most frequently required. But in view of the fact that there are now so many reference books readily available, matter of this kind has been kept to a minimum.

While the Committee feels that distinct progress has been made in the Handbook, it is not prepared to recommend that all of the methods contained therein be stamped with the official approval of the Institute without further revision by succeeding chemical test committees or by a special committee appointed for the purpose, except possibly the methods covering the analyses of coal and coke, cement, and iron and steel. All of these may safely be adopted, it is thought, since the method for analyses of coal and coke is based on the work of the Bureau of Mines and those for cement, iron and steel are the official methods of the American Society for Testing Materials. The desirability, however, of having the whole work officially approved by the Institute seems apparent and since its value would be so much increased by such action of the Institute, the Committee feels that no unnecessary time should be lost in taking the necessary steps to further standardize and enlarge the work.

In conclusion, I wish to express to the various members of the Committee, my appreciation of their efforts in behalf of the success of the Handbook and especially of the efforts of those gentlemen not directly engaged in the gas business, who have given their assistance. It seems proper in this connection to make special mention of the work of Mr. S. R. Church, Manager, Research Department, The Barrett Company.

I also wish to express my appreciation of the efforts of Mr. A. F. Kunberger, who was appointed editor of the Handbook since the last meeting of the Institute and upon whose shoulders has devolved most of the work in connection with getting into suitable form for publication the data secured by the Committee.

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S. R. Church,
W. H. Fulweiler,
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A. H. White.

GAS CHEMISTS' HANDBOOK.

CHAPTER I.

COAL AND COKE.

The following determinations are covered in the analysis of coal and coke:

Air-Drying Loss.
Moisture.
Volatile Matter.
Fixed Carbon.
Ash.
Sulphur.
Phosphorus.
Calorific Value.
Carbon.
Hydrogen.
Nitrogen.
Oxygen.
Shatter Test for Coke.
Apparent and Real Specific Gravity.

These determinations are based on reports of Committee "E-4" of the American Society for Testing Materials, on Technical Papers No. 8 and No. 76 of the Bureau of Mines.

COAL SAMPLING

The coal should be sampled at the time it is being unloaded from railroad cars or other means of transportation.

To collect samples, a shovel or specially designed tool or mechanical means should be used for taking increments of 10 to 30 pounds of coal. The size of the increments must depend on the size and weight of the largest pieces of coal and impurities.

The increments must be regularly and systematically collected, so that the entire delivery will be represented proportionately in the gross sample. The frequency of collecting the increments should be regulated so that a gross sample of not less than 1,000 pounds will be collected.

If the coal contains an unusual amount of impurities, such as slate, and if the pieces of such impurities are very large, a gross sample of more than 1,000 pounds should be collected.

A gross sample of the above specified quantity should be taken for delivery of 500 tons or less. When deliveries are made in large quantities as in cargoes of from 2,000 to 12,000 tons, the size of the gross sample must be governed by the size and amount of the free impurities. A gross sample of from 2,000 to 4,000 pounds is sufficient for reasonable accuracy unless the size and amount of the free impurities are unusually large.

After the gross sample has been collected it must be systematically crushed, mixed and reduced in quantity to convenient size for transmittal to the laboratory. The crushing should be done by a mechanical crusher or by hand with a tamper or hammer on a smooth and solid floor. In the absence of a smooth, tight floor, the crushing may be done on a heavy canvas, to prevent the accidental admixture of any foreign matter. The mixing and reduction should be done by hand, with a shovel, or mechanically, by means of riffles or sampling machines.

The sizes to which the coal and impurities should be crushed are approximately as here given.

Weight of sample to be divided	Size to which pieces should be broken before each division
1,000 pounds or more	1 inch
500 pounds	¾ inch
250 pounds	½ inch
125 pounds	⅜ inch
60 pounds	¼ inch

If the sample is prepared by hand, the mixing and reducing should be done by the "long pile and alternate shovel" method on amounts of 125 pounds or more, the procedure being as follows:

The crushed coal is shoveled into a conical pile. A long pile is formed by taking a shovelful at a time and spreading it out in a straight line (8 to 10 feet long for a shovel holding about 15 pounds). Each new shovelful is spread over the top of the preceding one, beginning at opposite ends, the pile being occasionally flattened with the flat side of the shovel and so on until all the coal has been formed into one long pile.

By walking around the long pile, advancing a distance equal to the width of the shovel, and systematically taking shovelfuls, and shoveling the coal to one side, alternate shovelfuls being discarded, the sample will be halved in quantity.

Whenever the different increments of sample are collected throughout some considerable period of time, each increment or an accumulation of a number of increments, may be crushed as soon as taken and the pieces of coal and impurities broken sufficiently small to permit two or more reductions of total accumulated sample before further crushing is necessary.

If the sampling should extend over any considerable period, what would otherwise be a gross sample may be worked down in successive stages to samples of a size suitable for transmittal to the laboratory, and these samples which should be approximately equal in quantity and as representing the several equal parts of a delivery may be analyzed and the several analyses averaged.

Preparation of Laboratory Samples.

"The quantity of sample sent to the chemist will be governed by the relative proportion of free impurities and the practical limits of fineness to which these impurities can be crushed at the point of sampling. Ordinarily 5 pounds crushed to pass a 4-mesh screen is a convenient sample to send to the laboratory." In cases where it is not feasible to crush to 4 mesh at the point of sampling, the weight of the sample sent to the laboratory must conform to the following table:

Size of largest impurities In.	Minimum weight of sample Lb.
1/2	75
3/8	30
1/4	9
3/16 or smaller	5

Samples of 125 pounds and less may be reduced to the 5-pound quantity by a riffle sampler or on a canvas as follows: The sample is placed on a canvas about 8 feet square and mixed by raising first one end of the canvas and then the other, thereby rolling the sample back and forth. After thoroughly mixing in this manner, by gathering up the four corners of the canvas, the sample will be formed into a conical pile and is to be reduced in quantity by quartering. The cone is flattened, its apex being pressed down with the flat side of the shovel, or with a board, so that each quarter contains the material originally in it. The flattened mass which should be of uniform thickness and diameter is then marked off into quarters with the board held edgewise or with a piece of sheet iron, along two lines that intersect at right angles directly under the apex of the original cone. The diagonally opposite quarters are shoveled away and discarded and the space which they occupied brushed clean. The coal remaining is successively mixed, coned and quartered on the canvas until two opposite quarters are equal to the quantity required to fill two containers holding about 5 pounds each. The coal should be well packed in the containers so as to exclude air as much as possible.

Special Moisture Sample.

In the reduction of the gross sample to the sample for transmittal to the laboratory, there will be an unavoidable loss of moisture.

To determine the moisture content in the coal, a separate special moisture sample must be taken.

This special moisture sample should contain approximately 100 pounds and should be accumulated by placing in a waterproof receptacle, with a tight fitting and waterproof cover, small parts of the freshly taken increments of the gross sample. These parts should be broken to about ½ inch in size as accumulated.

The accumulated moisture sample must be reduced mechanically or by hand as quickly as possible and immediately placed in a container and sealed air-tight.

Sampling from Loaded Cars.

If it becomes necessary to sample coal from a loaded car, the sample should be accumulated by digging ten or fifteen holes, two or three feet deep, at systematically located points over the car.

Sampling from a Storage Pile.

In sampling from a pile, first estimate the approximate surface of the pile and then determine the relative distance between points for taking increments, sufficient in number to insure the accumulation of the requisite amount of gross sample.

Starting at three or four feet from the bottom of the pile, take shovelfuls at the predetermined distance apart around or along the pile on the same level. Then begin at a certain distance up the pile and circle it again so on to the top.

Systematically alternate the depth of the holes, taking one shovelful at the surface, the next one deeper, the next still deeper, the fourth at the surface again and so on.

Sampling at the Mines.

The sample should be systematically accumulated throughout at least one entire day's loading. The total weight of sample taken should be governed by the size and amount of impurities contained in the coal.

Samples should not be taken from the tops of loaded mine cars as they are likely to be trimmed with lumps and also because pieces of roof or draw slate may have fallen onto the car.

Samples of the coal being shipped should be taken while the railroad cars are being loaded. If any attempt is being made to throw out impurities while loading, shovelfuls should be taken from the slanting surface just before a new mine car is dumped and after the pickers have finished cleaning the one previously dumped. The shovel should be pushed well into the coal to avoid getting only that on the surface from which impurities have been picked, and the shovelfuls should be taken systematically from various parts of the surface.

SAMPLING COKE.

The amount of gross sample of coke that should be accumulated depends on the size of the coal and the size and amount of impurities in the coal from which the coke is made.

In general coke is made from slack or crushed coal and in the crushing and handling of the coal preparatory to charging it into the ovens, it becomes so well mixed that errors due to variations in its quality are minimized.

A 100-pound sample of coke is usually sufficient, to obtain accuracy for a single car, but where larger lots are to be sampled especially when the entire output of a plant is to be sampled, four or five separate samples of 50 pounds or more should be taken and the results averaged.

Physical appearance as regards color and porosity is no indication of the chemical analysis.

In general, the moisture content increases as the size of the pieces of coke diminishes and to some extent this graduation is true in the ash content as well. It is necessary, therefore, especially in sampling run of oven coke that due care should be exercised to obtain the proper proportions of lump and fines. A great many small pieces from many different parts of the lot should be taken by breaking off long slender fingers from the lumps, and there should also be included pieces of all sizes and shapes.

A special moisture sample should be taken as in the case of coal, except that the time should not be spent in crushing finer than 1 inch for the reason that in the crushing and mixing of coke, the moisture loss is much more rapid than with coal.

Preparation of Laboratory Sample.

APPARATUS.

Air-Drying Oven.—The oven is to be used for air-drying wet samples. It is not necessary but is economical where many wet samples are received.[1]

Galvanized Iron Pans 18 x 18 x 1½ *Inches Deep.*—For air-drying wet samples.

Balance on Solution Scale.—For weighing the galvanized pans with samples. It should have a capacity of 5 kilograms and be sensitive to 0.5 kilogram.

Chipmunk Jaw Crusher.—For crushing coarse samples to pass a 4-mesh sieve.

Roll Crusher or Coffee Mill Type of Grinder.—For reducing the 4-mesh product to 20-mesh. The coffee-mill type of grinder should be entirely enclosed and have an enclosed hopper and a receptacle capable of holding 5 pounds of coal. This is to reduce the moisture losses while crushing.

Abbe Ball Mill, Planetary Disk Crusher, Chrome Steel Bucking Board, or any Satisfactory Form of Pulverizer.—For reducing the 20-mesh product to 60-mesh. The porcelain jars for the ball mill should be approximately 9 inches in diameter and 10 inches high. The flint pebbles should be smooth, hard and well rounded. "The reduction in size of coke for the laboratory should not be done by grinding in an apparatus which will give up fine particles of iron to the sample. A

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[1] For details of air-drying oven, see Bownocker, Lord and Somermeier, "Coal" Bulletin No. 9, 4th series, Ohio Geological Survey, P. 312 (1908); or F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," Technical Paper No. 8, Bureau of Mines, P. 4 (1912); or E. E. Somermeier, "Coal, Its Composition, Analysis, Utilization and Valuation," P. 71, McGraw-Hill Book Co., (1912).

jaw crusher which will reduce to 8-mesh and an Abbe Ball Mill for further reduction is recommended."

A Large Riffle Sampler with ½ or ⅝ inch Divisions.—For reducing the 4-mesh sample to 5 pounds.[2]

A Small Riffle Sampler with ¼ or ⅜ inch Divisions.—For dividing down the 20 and 60-mesh material to a laboratory sample.

An 8 inch 60-mesh Sieve with Cover and Receiver.

Containers for Shipment to Laboratory.—A galvanized iron or tin can with a screw top, which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used if packed carefully to avoid breakage in transit.

Upon receipt of the sample at the laboratory, it is to be prepared for analysis by one of two methods, as follows:

(A) WHEN COAL APPEARS DRY.

If the sample is coarser than 4-mesh (0.20 inch) and larger in amount than 10 pounds, quickly crush it with the jaw crusher to pass a 4-mesh sieve and reduce it on the larger riffle sampler to 10 pounds, or to 5 pounds if it is crushed to pass a 6-mesh sieve; then crush it at once to 20-mesh by passing through rolls or an enclosed grinder, and take, without sieving, a 60 gram total moisture sample, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

Thoroughly mix the main portion of the sample, reduce on the small riffle sampler to about 120 grams and pulverize to 60-mesh by any suitable apparatus without regard to loss of moisture.

After all the material has been passed through the 60-mesh sieve, mix and divide it on the small riffle sampler to 60 grams. Transfer the final sample to a 4-ounce rubber-stoppered bottle.

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[2] For details of riffle sampler see Bulletin No. 9, 4th Series, Ohio Geological Survey, P. 313 (1908), or E. E. Somermeier, "Coal, Its Composition, Analysis, Utilization and Valuation," P. 73, McGraw-Hill Book Co., (1912).

Determine moisture in both the 60 and the 20-mesh samples by the method given under moisture.

Computation.—Compute the analysis of the 60-mesh coal, which has become partly air-dried during sampling, to the dry coal basis, by dividing each result by 1 minus its content of moisture. Compute the analysis of coal "as received" from the dry coal analyses by multiplying by 1 minus the total moisture found in the 20-mesh sample.

(B) WHEN COAL APPEARS WET.

Spread the sample on tared pans, weigh, and air-dry at room temperature, or in a special drying oven, at 10 to 15° C. above room temperature, and weigh again. The drying should be continued until the loss in weight is not more than 0.1 per cent. per hour. Complete the sampling as under dry coal.

Computation.—Correct the moisture in the 20-mesh, air-dried sample to total moisture "as received" as follows:

$$\frac{100 - \text{percentage of air-drying loss}}{100} \times \text{percentage of moisture in 20-mesh coal} + \text{percentage of air-drying loss} = \text{total moisture "as received."}$$

Compute the analysis to "dry coal" and "as received" bases as under dry coal, using for the "as received" computation the total moisture as found by the formula in place of the moisture found in the 20-mesh coal.

Notes.—Freshly mined or wet coal loses moisture rapidly on exposure to the air of the laboratory, hence the sampling operations between opening the container and taking the 20-mesh total moisture sample must be conducted with the utmost dispatch and with minimum exposure to air.

The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than the following limits:

No carbonates present	0.4 per cent.
Considerable carbonate and pyrite present...	0.7 per cent.
Coals with more than 12 per cent. ash, containing considerable carbonate and pyrite	1.0 per cent.

Determination of Moisture.[3]

APPARATUS.

Moisture Oven.—This must be so constructed as to have a uniform temperature in all parts and a minimum of air space. It may be of the form shown here. *Technical Paper No. 76*, Bureau of Mines.

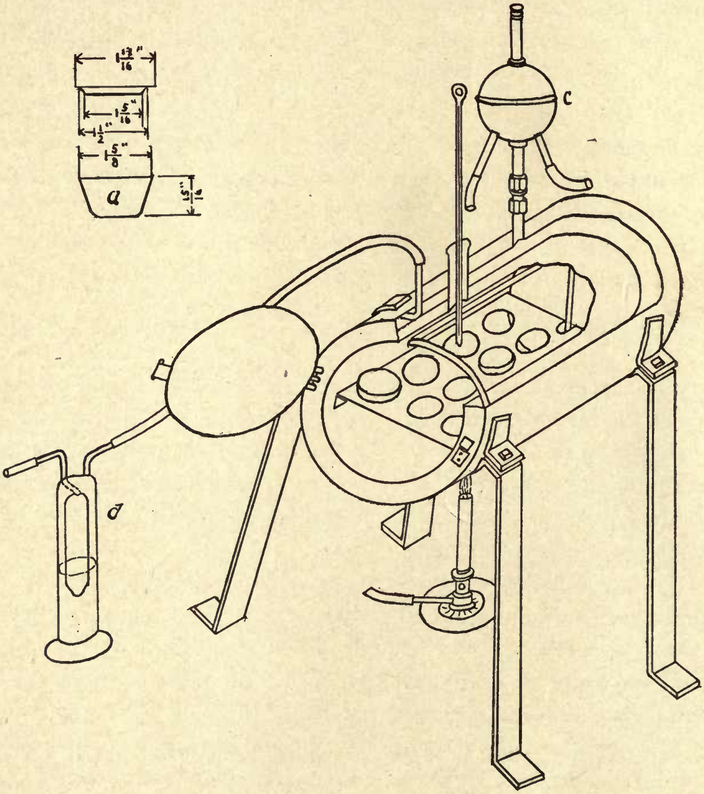

FIG. 1.

Provision must be made for renewing the air in the oven at the rate of two to four times a minute, with the air dried by passing it through concentrated sulphuric acid.

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[3] This method can not be applied to Lignites which have to be dried at a much higher temperature.

Capsules with Covers.—A convenient form, which allows the ash determination to be made on the same sample, is the Royal Meissen Porcelain capsule No. 2, 7/8 inch deep and 1 3/4 inches in diameter; or a fused silica capsule of similar shape. This is to be used with a well-fitting flat aluminum cover. Glass capsules with ground glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

METHOD.

(A) Sixty-Mesh Sample.

Heat the empty capsules under the conditions at which the coal is to be dried. Stopper and cover, cool over concentrated sulphuric acid, specific gravity 184, for 30 minutes and weigh.

Dip out with a spoon or spatula from the sample bottle approximately 1 gram of coal; put this quickly into the capsule, close and weigh at once.

An alternate procedure (more open to error) after transferring an amount slightly in excess of 1 gram is to bring to exactly 1 gram in weight (0.5 milligram) by quickly removing the excess weight of coal with a spatula. The utmost dispatch must be used in order to minimize the exposure of the coal until the weight is found.

After removing the covers, quickly place the capsules in a pre-heated oven (at 104 to 110° C.) through which passes a current of air dried by concentrated sulphuric acid. Close the oven at once and heat for 1 hour. Then open the oven, cover the capsules quickly and place them in a desiccator over concentrated sulphuric acid. When cool, weigh.

(B) Twenty-Mesh Sample.

Use 5 gram samples, weigh with an accuracy of 2 milligrams, and heat for 1 1/2 hours; the procedure is otherwise as with the 60-mesh sample. Methods of greater accuracy may be found in the "Proceedings of the American Society for Testing Materials," Vol. XIV, 1914, p. 421.

The allowable variations are as follows:

	Same analyst per cent.	Different analyst per cent.
Moisture under 5 per cent.......	0.2	0.3
Moisture over 5 per cent.........	0.3	0.5

Determination of Volatile Matter.

APPARATUS.

Platinum Crucible with Tightly Fitting Cover.—The crucible should be of not less than 10 nor more than 20 cubic centimeters capacity: of not less than 25 nor more than 35 millimeters in diameter; of not less than 30 nor more than 35 millimeters in height.

Vertical Electric Tube Furnace; or a Gas or Electrically Heated Muffle Furnace.—The furnace may be of the form as shown here (p. 21, *Technical Paper No. 76,* Bureau of Mines).

It is to be regulated to maintain a temperature of 950° C. (+ 20° C.) in the crucible, as shown by a thermo-couple in the furnace.

METHOD.

Weigh 1 gram of the coal in a weighed 10 to 20 cubic centimeter platinum crucible, close with a capsule cover, and place on platinum or nichrome-wire supports in the furnace chamber, which must be at a temperature of 950° C. (+ 20° C.). After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, tap the cover lightly to more perfectly seal the crucible and thus guard against the admission of air. After heating exactly 7 minutes, remove the crucible from the furnace and, without disturbing the cover, allow to cool. Weigh as soon as cold. The loss of weight minus moisture equals volatile matter.

ALTERNATE METHOD.

One gram of coal is placed in a platinum crucible of 20 cubic centimeters capacity. The crucible should have a tightly fitting cover as above. The crucible is placed in the flame of a Mêker burner, size No. 4, having approximately an outside diameter at the top of 25 millimeters and giving a flame not less than 15 centimeters high. The temperature should be

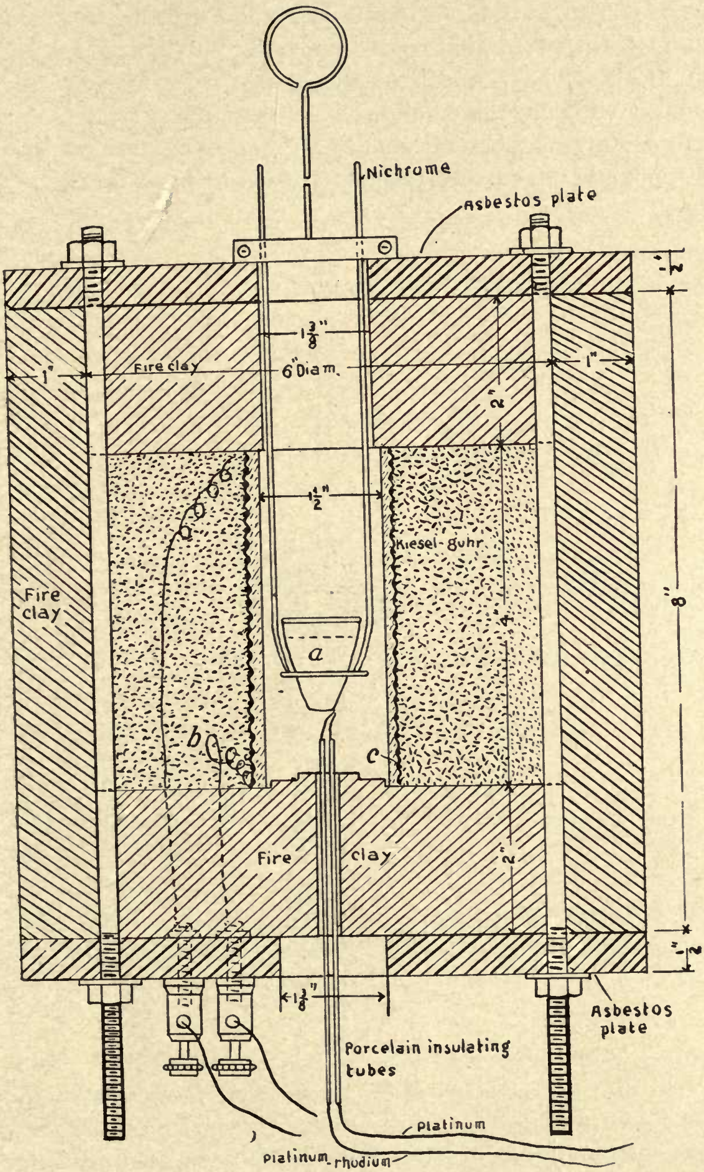
Nichrome
Asbestos plate
$\frac{1}{2}$"
$1\frac{3}{8}$"
Fire clay
6" Diam.
1"
1"
2"
$1\frac{1}{2}$"
Kiesel-guhr
Fire clay
a
4"
8"
b
c
Fire
clay
2"
$\frac{1}{2}$"
$1\frac{3}{8}$"
Asbestos plate
Porcelain insulating tubes
Platinum
Platinum-rhodium

FIG. 2.

from 900 to 950° C., determined by placing a thermo-couple through the perforated cover, which for this purpose may be of nickel. The junction of the couple should be placed in contact with the center of the bottom of the crucible; or the temperature may be indicated by the fusion of pure potassium chromate in the covered crucible (fusion of K_2CrO_4, 940° C.).

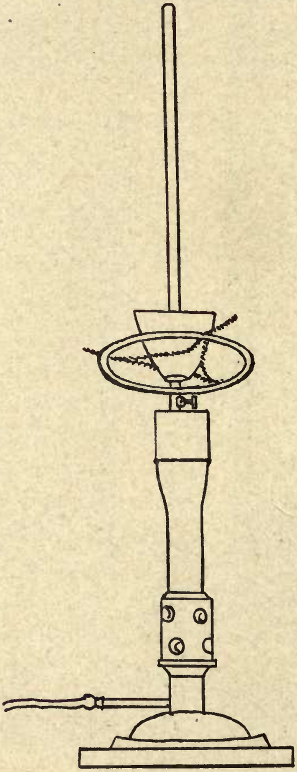

FIG. 3.

The crucible is placed in the flame about 1 centimeter above the top of the burner and the heating is continued for 7 minutes. After the main part of the gases have been discharged the cover should be tapped into place as above described.

When the gas pressure is variable it is well to use a U-tube attachment to the burner to show the pressure.

Mechanical losses are incurred on suddenly heating peat, sub-bituminous coal, and lignite; therefore they must be subjected to a preliminary gradual heating for 5 minutes; this is best done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile matter furnace or place in the full flame of the Mêker burner and heat for 6 minutes at 950° C., as in the regular method.

The allowable variations are as follows:

	Same analyst per cent.	Different analyst per cent.
Bituminous coals	0.5	1.0
Lignites	1.0	2.0

Notes.—The cover should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side.

Regulation of temperature to within prescribed limits is important.

Determination of Fixed Carbon and Ash.

APPARATUS.

Gas or Electric Muffle Furnace.—The muffle should have a good air circulation and be capable of having its temperature regulated between 700° and 750° C.

Porcelain Capsules.—Royal Meissen Porcelain Capsules No. 2, ⅞ inch deep and 1¾ inches in diameter, or similar shallow dishes.

METHOD.

Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace, or on the hearth at a low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter.

Finish the ignition to constant weight (—0.001 gram) at a temperature between 700° and 750° C. Cool in air and weigh as soon as cold. Coals containing carbonate are best cooled in a desiccator.

The results as determined by this method represent the ignited mineral matter in the coal. The actual mineral matters in the original coal are usually very different in weight and composition. The application of corrections for sulphur present in the iron pyrites and for the volatile ash constituent due to hydration of clayey material, may be omitted for technical purposes. For "corrected" ash see *Jour. Ind. and Eng. Chem.*, Vol. 5, June, 1913, p. 523, and *Technical Paper No. 76,* Bureau of Mines.

The allowable variations are as follows:

	Same analyst per cent.	Different analyst per cent.
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12% of ash containing carbonates and pyrite	0.5	1.0

FIXED CARBON.

Compute as follows:

100 = (moisture + ash + volatile matter) = percentage of fixed carbon.

SULPHUR.

ESCHKA METHOD.

Apparatus.

Gas or Electric Muffle Furnace, or Burners.—For igniting coal with Eschka mixture and for igniting the barium sulphate.

Porcelain, Silica, or Platinum Crucibles or Capsules.—For igniting coal with the Eschka mixture.

No. 1.—Royal Meissen porcelain capsule, 1 inch deep and 2 inches in diameter. This capsule because of its shallow form, presents more surface for oxidation and is more convenient to handle than the ordinary form of crucible.

No. 1.—Royal Berlin porcelain crucibles, shallow form, and platinum crucibles of similar size may be used. Somewhat more time is required to burn out the coal owing to the deeper form, than with the shallow capsules described above.

No. 0 or 00 porcelain crucibles, or platinum, alundum or silica crucibles of similar size are to be used for igniting the barium sulphate.

SOLUTIONS AND REAGENTS.

Barium Chloride.—Dissolve 100 grams of barium chloride in 1,000 cubic centimeters of distilled water.

Saturated Bromine Water.—Add an excess of bromine to 1,000 cubic centimeters of distilled water.

Eschka Mixture.—Thoroughly mix two parts (by weight) of light calcined magnesium oxide and one part of anhydrous sodium carbonate. Both materials should be as free as possible from sulphur.

Methyl Orange.—Dissolve 0.02 gram in 100 cubic centimeters of hot distilled water and filter.

Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity 1.20 and 500 cubic centimeters of distilled water.

Normal Hydrochloric Acid.—Dilute 80 cubic centimeters of hydrochloric acid, specific gravity 1.20 to 1 liter with distilled water.

Sodium Carbonate.—A saturated solution, approximately 60 grams of crystallized or 22 grams of anhydrous sodium carbonate in 100 cubic centimeters of distilled water.

Sodium Hydroxide Solution.—Dissolve 100 grams in 1 liter of distilled water. This solution may be used in place of the sodium carbonate solution.

METHOD.

Preparation of Sample and Mixture.—Thoroughly mix on glazed paper 1 gram of coal and 3 grams of Eschka mixture. Transfer to the crucible or capsule and cover with about 1 gram of Eschka mixture.

Ignition.—On account of the amount of sulphur contained in artificial gas, it is preferable to heat the crucible over an alcohol flame or in an electrically heated muffle, as in (*a*) following. The use of artificial gas is permissible only when crucibles are heated in a muffle as in (*b*) following.

(*a*) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulphur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.

(*b*) Place the crucible in a cold gas muffle and gradually raise the temperature to 870°-925° C. (cherry-red heat) in about 1 hour. Maintain the maximum temperature for about 1½ hours and then allow the crucible to cool in the muffle.

Subsequent Treatment.—Remove and empty the contents into a 200 cubic centimeter beaker and digest with 100 cubic centimeters of hot water for ½ to ¾ hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate amounting to about 250 cubic centimeters, with 10 to 20 cubic centimeters of saturated bromine water, make slightly acid with hydrochloric acid and boil to expel liberated bromine. Make just neutral to methyl orange with sodium hydroxide or sodium carbonate solution. Then add 1 cubic centimeter of normal hydrochloric acid. Boil again and add slowly from a pipette, with constant stirring, 10 cubic centimeters of a 10 per cent. solution of barium chloride. Continue boiling for 15 minutes and allow to stand for at least 2 hours, or preferably over night at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulphate in a weighed platinum, porcelain, silica or alundum crucible, allow a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with a flame. After the paper is practically consumed, raise the temperature to approximately 925° C., and heat to constant weight. The residue of magnesia, etc., after bleaching, should be dissolved in hydrochloric acid and tested with great care for sulphur. When an appreciable amount is found it should be determined quantitatively.[4]

Blanks and Corrections.—In all cases a correction must be applied either (1) by running a blank exactly as described above, using the same amount of all reagents that were employed in the regular determination or (2) by determining a known amount of sulphate added to a solution of the reagents after these have been put through the prescribed series of operation. If this latter procedure is adopted and carried out, say, once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulphur content likely to be met with in coals, it is only necessary to add to or subtract from the weight of barium sulphate obtained from a coal. Whatever deficiency or excess may have been found in the appropriate "check" in order to obtain a result, that is more certain to be correct than if a "blank" correction as determined by the former procedure is applied. This is due to the fact that the solubility error for barium sulphate, for the amounts of sulphur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. Barium sulphate is soluble in acids[5] and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, in the event of using reagents of very superior quality or of exercising more than ordinary precautions, there may be no apparent "blank" because the solubility limit of the solution for barium sulphate has not been reached or at any rate not exceeded.

[4] Journal American Chemical Society, Volume 21, page 1125 (1899).

[5] Jour. Am. Chem. Soc. Vol. 32, p. 588 (1910); Vol. 33, p. 829, (1911).

ATKINSON METHOD.

Thoroughly mix on glazed paper 1 gram of the laboratory sample of coal with 7 grams of dry sodium carbonate and spread evenly over the bottom of a shallow platinum or porcelain dish. Place on a triangle slightly elevated above the bottom of a cold muffle. Heat the muffle gradually until a temperature of 650° to 700° C. (dull red heat) has been obtained in half an hour and maintain this temperature for 10 or 15 minutes.

The sodium carbonate should not sinter or fuse. The mixture should not be stirred during the heating process. When the dish has cooled sufficiently to handle, the matter should be examined for black particles of unburned carbon and in case such indications of incompleteness of the process should appear the dish should be replaced and heated for a short time. When all the carbon is burned, remove the dish and digest the contents with 100 to 125 cubic centimeters of warm water and 5 cubic centimeters of concentrated hydrochloric acid. Allow the insoluble matter to settle, decant through a filter and wash several times by decantation. Transfer to the filter adding a few drops of a solution of pure sodium chloride if the insoluble matter tends to pass through the filter. The washings should be continued until the filtrate shows no alkaline reaction. Make the filtrate just acid to methyl orange, add 1 cubic centimeter of normal hydrochloric acid and proceed as described under Eschka method.

THE PEROXIDE FUSION METHOD.

This method is most conveniently carried out in the Parr Calorimeter. The charge consists of 0.5 gram of the air-dry laboratory sample of coal, 1 gram of potassium chlorate pulverized to about 20-mesh, and 10 grams of sodium peroxide of the grade regularly prescribed for calorimetric purposes. The coal and potassium chlorate are first added to the bomb or fusion cup and thoroughly mixed, being careful to break down any lumps that may form. The sodium peroxide is then added, the container closed and the ingredients thoroughly mixed by shaking.

After igniting and cooling the charge, dissolve the fusion in a covered beaker, using 150 cubic centimeters of water. Add concentrated hydrochloric acid just past the neutral point (25 to 30 cubic centimeters). Add 1 cubic centimeter of concentrated hydrochloric acid (specific gravity 1.19) in excess. Filter and wash with hot water, making the final bulk of the solution approximately 250 cubic centimeters. Heat to boiling and precipitate the sulphate by adding 10 cubic centimeters of a 10 per cent. solution of barium chloride. Proceed as described under Eschka method.

Particular care should be taken in washing the precipitate obtained by this method in order to remove all of the soluble salts which are formed in the fusion process.

Determination of Sulphur in the Bomb Washings.

Where the precise content of sulphur is not required it may be approximated from the washings from an oxygen bomb calorimeter as follows:

After the combustion, the bomb is washed out thoroughly with distilled water, and the washings collected in a 250 cubic centimeter beaker. Six to eight cubic centimeters of dilute (1 : 1) hydrochloric acid containing some bromine water are then added and the solution is heated to boiling. The insoluble matter is filtered off and washed free from sulphates with hot water. The filtrate and washings which should have a total volume of 200 cubic centimeters are made just neutral to methyl orange with sodium hydroxide or carbonate solution, 1 cubic centimeter of normal hydrochloric acid is added, and the procedure completed as described under Eschka method.

The allowable variations in sulphur determinations are as follows:

	Same analyst per cent.	Different analyst per cent.
For coal	0.05	0.1
For coke	0.03	0.05

Determination of Phosphorus. (Recommended by Committee E-4.)

To the ash from 5 grams of coal in a platinum capsule is added 10 cubic centimeters of nitric acid and 3 to 5 cubic centimeters of hydrofluoric acid. The liquid is evaporated and the residue fused with 3 grams of sodium carbonate. If unburned carbon is present 0.2 gram of sodium nitrate is mixed with the carbonate. The melt is leached with water and the solution filtered. The residue is ignited, fused with sodium carbonate alone, the melt leached and the solution filtered. The combined filtrates, held in a flask, are just acidified with nitric acid and concentrated to a volume of 100 cubic centimeters.

To the solution, brought to a temperature of 85° C., is added 50 cubic centimeters of molybdate solution and the flask is shaken for 10 minutes. The precipitate is washed, on a filter, six times, or until free from acid, with a 2 per cent. solution of potassium nitrate, then returned to the flask and titrated with standard sodium hydroxide solution. The alkali solution may well be made equal to 0.00025 gram phosphorus per cubic centimeter or 0.005 per cent. for a 5 gram sample of coal, and is 0.995 of one-fifth normal. (1) Or the phosphorus in the precipitate is determined by reduction and titration of the molybdenum with permanganate.

The advantage of the use of hydrofluoric acid lies in the removal of silica. Fusion with alkali carbonate is necessary for the elimination of titanium, which if present and not removed with contaminate the phospho-molybdate and is said to sometimes retard its precipitation.

Ultimate Analysis.

CARBON AND HYDROGEN.

The determination of carbon and of hydrogen is made with a weighed quantity of sample in a 25-burner combustion furnace of the Glaser type. The products of combustion are thoroughly oxidized by being passed over red-hot copper oxide and lead chromate, and are fixed by absorbing the water in a weighed Marchand tube filled with granular calcium chloride ($CaCl_2$) and by absorbing the carbon dioxide in a Liebig bulb containing a 30-per cent. solution of potassium hydroxide (KOH).

The apparatus used consists of a purifying train, in duplicate, a combustion tube in the furnace, and an absorption train. The purifying train consists of the following purifying reagents arranged in order of passage of air and oxygen through them: Sulphuric acid, potassium hydroxide solution, soda lime and granular calcium chloride. One of the trains is for air and one for oxygen. In the sulphuric acid and potassium hydroxide scrubbing bottles the air and the oxygen are made to bubble through about 5 millimeters of the purifying reagent. Both purifying trains are connected to the combustion tube by a Y-tube, the joint being made tight by a rubber stopper.

The combustion tube may be of hard Jena glass, quartz or fused silica. Its external diameter is about 21 millimeters, and its total length is 1 meter. The first 30 centimeters of the tube are empty: following this empty space is an asbestos plug (acid washed and ignited) or in its place a roll of oxidized copper gauze may be used; the next 40 centimeters are filled with copper oxide wire; a second asbestos plug separates the copper oxide from 10 centimeters of fused lead chromate, which is held in place by another asbestos plug 20 centimeters from the end of the tube. The end of the tube is contracted for rubber tubing connection with the absorbing train.

The absorption train consists, first, of a Marchand tube filled with granular calcium chloride ($CaCl_2$) to absorb moisture. The $CaCl_2$ should be saturated with CO_2 before using The Marchand tube is followed by a Liebig bulb containing a 30-per cent. potassium hydroxide solution, in which any possible impurities, as ferrous iron or nitrates, have been oxidized by a little potassium permanganate ($KMnO_4$). A guard tube containing granular calcium chloride and soda lime is attached to the Liebig bulb to absorb any dioxide escaping the potassium hydroxide solution and any water evaporating from that solution.

The train is connected to an aspirator which draws the products of combustion through the entire train. A guard tube of calcium chloride prevents moisture from running back into the absorption train. The suction is maintained constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. The connections are made as tight as possible.

The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there is no more than one bubble per minute in the potash bulb, the apparatus is considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, a blank is run by aspirating about 1 liter of air through the train, which is heated in the same manner as if a determination on coal were being made. If the Liebig bulb and tube containing calcium chloride show a change in weight of less than 0.5 milligram each the apparatus is in proper condition for use.

A porcelain or platinum boat is provided with a glass weighing tube of suitable size, which is fitted with an accurately ground glass stopper. The tube and empty boat are weighed. Approximately 0.2 gram of the air-dry coal (60-mesh or preferably 100-mesh) are quickly placed in the boat. The boat is at once placed in the weighing tube, which is quickly stoppered to prevent moisture change in the coal while weighing, and transferring to the furnace. The absorption tubes are connected and the boat and sample are transferred as quickly as possible from the weighing tube to the combustion tube, which should be cool for the first 30 centimeters. The copper oxide should at this time be red hot and the lead chromate at a dull red heat. As soon as the boat is in place (near the asbestos plug at the beginning of the copper oxide) the stopper connecting with the purifying train is inserted and the aspiration started with pure oxygen gas at the rate of three bubbles per second. One burner is turned on about 10 centimeters back from the boat, and the aspiration is continued carefully until practically all the moisture is expelled from the sample. The heat is then increased very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back into the purifying train.

The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited: after which the temperature may be increased rapidly, but care should be taken not to melt the combustion tube if a glass one is being used. Any moisture collecting in the end of the combustion tube or in the rubber connection joining it to the calcium chloride tube is driven over into the calcium chloride tube by carefully warming with a piece of hot tile. The aspiration with oxygen is continued for two minutes after the sample ceases to glow, the heat is then turned off and about 1,200 cubic centimeters of air are aspirated. The absorption bulbs are then disconnected, wiped with a clean cloth and allowed to cool to the balance room temperature before weighing.

Percentage of hydrogen =

$$\frac{11.19 \times \text{increase in weight of } CaCl_2 \text{ tube}}{\text{Weight of sample.}}$$

Percentage of carbon =

$$\frac{27.27 \times \text{increase in weight of KOH bulb}}{\text{Weight of sample.}}$$

The ash in the boat is weighed and carefully inspected for any unburned carbon.

Method with Electrically Heated Combustion Furnace.

For description of furnace and method see *Technical Paper No. 8,* Bureau of Mines, revised edition 1913, p. 22.

Nitrogen.

The Kjeldahl-Gunning Method.—One gram of the coal sample (coke and anthracite should be ground to an inpalpable powder) is boiled with 30 cubic centimeters of concentrated sulphuric acid (H_2SO_4), 7 to 10 grams of potassium sulphate (K_2SO_4), and 0.6 to 0.8 gram of metallic mercury in a 500 cubic centimeter Kjeldahl flask until all particles of coal are oxidized and the solution nearly colorless. The boiling should be continued for 2 hours after the straw colored stage has been reached. The total time of digestion will be, for coal, from 3 to 4 hours and for coke and anthracite may be from 12 to 16 hours. The addition of a few crystals of potassium permanganate ($KMnO_4$), after the solution has been cooled enough to avoid violent reaction, tends to insure complete oxidation.

After cooling, the solution is diluted to about 200 cubic centimeters with cold water. If the dilution with water has warmed the solution, it should be again cooled and the following reagents added: 25 cubic centimeters potassium sulphide (K_2S) solution (40 grams K_2S per liter) to precipitate the mercury and so prevent the formation of mercurammonium compounds which are not completely decomposed by sodium hydroxide, 1 to 2 grams of granular zinc to prevent bumping, and finally enough strong sodium hydroxide (NaOH) solution (usually 80 to 100 cubic centimeters) to make the solution distinctly alkaline. The danger of loss of ammonia may be minimized by holding the flask in an inclined position while the sodium hydroxide solution is being added. The alkaline solution runs down the side of the flask and forms a layer below the lighter acid solution. After adding the alkaline solution, the flask is at once connected to the condensing apparatus and the solution mixed by gently shaking the flask.

The ammonia (NH_3) is distilled over into a measured amount of standard sulphuric acid solution to which has been added sufficient cochineal indicator for titration. Care should be taken that the glass connecting tube on the end of the condenser dips under the surface of the standard acid. The solution is slowly distilled over until 150 to 200 cubic centimeters of distillate has passed over. To avoid mechanically entrained alkali passing over into the condenser the rate of distillation should not exceed 100 cubic centimeters per hour. The distillate is titrated with standard ammonia solution. Standard NaOH or KOH solution with methyl orange, methyl red or sodium alizarin sulphonate as indicator may be used instead of ammonia and cochineal.

A blank determination should be made in the same manner as described above, except that 1 gram of pure sucrose (cane sugar) is substituted for the coal. The nitrogen found in this blank is deducted from the result obtained with the coal.

Oxygen.

Oxygen is computed by subtracting the sum of the percentages of hydrogen, carbon, nitrogen, sulphur, water and ash from 100. The result so obtained is affected by all the errors incurred in the other determinations and especially by the change in weight of the ash forming constituents on ignition.

A more nearly correct oxygen value may be obtained by making the corrections indicated here.

Corrected oxygen $= 100 - (C - C') + (H - H') + N + H_2O + S' +$ corrected ash.

In which C = total carbon
C' = carbon of carbonates
H = total hydrogen less hydrogen of water
H' = hydrogen from water of composition in clay, shale, etc.
N = nitrogen
H_2O = moisture as found at 105° C.
S = sulphur not present as pyrite or sulphate. This is usually small.

Corrected Ash = Mineral constituents originally present in the coal. For most purposes this can be determined with sufficient accuracy by, adding to the ash, as found, five-eighths of the weight of pyritic sulphur, the CO_2 of carbonates and the water of composition of clay, shale, etc.

Calorimetric Determination.

APPARATUS.

Combustion Bombs.[6]—The Atwater, Davis, Emerson, Mahler, Parr, Peters, Williams, or similar bombs may be used. The bomb shall have an inner surface of platinum, gold, porcelain enamel, or other material which is not attacked by nitric and sulphuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter must be provided with a water-jacket having a cover to protect the calorimeter from air currents. The jacket must be kept filled with water within 2 or 3° C. of the temperature of the room (except in calorimeters which are totally submerged, where the jacket temperature is controlled by a thermostat) and should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water.—The water in the calorimeter must be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. A motor-driven screw or turbine stirrer is recommended and the speed should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for 10 minutes. If the temperature of the calorimeter rises more than about 0.01° C. in this length of time, the rate of stirring

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[6] "The Committee recommends the oxygen bomb. Where no oxygen bomb calorimeter is available, the Parr, when carefully handled (preferably with electric ignition and in conjunction with a Beckman thermometer) will give satisfactory results."

is excessive. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is irregular. The portion of the stirring device immersed in the calorimeter should be separated from the outside by non-conducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers.—Thermometers used shall have been certified by a government testing bureau and shall be used with corrections given on the certificate. This shall also apply to electrical resistance or thermo-electric thermometers. Correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work, either Beckmann or special calorimetric thermometers graduated to 0.01 or 0.02° C. are required. Such thermometers should be tapped lightly just before each reading to avoid errors caused by the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it up with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

Oxygen.—The oxygen used for combustion shall be free from combustible material. If an approximation of the sulphur is to be made from the bomb washings, the latter when filled should contain at least 5 per cent. of nitrogen. The total amount of oxygen contained in the bomb for a combustion shall not be less than 5 grams per gram of coal. But the combustion must be complete as shown by the absence of any sooty deposit on opening the bomb after firing.

Firing Wire.—The coal in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used it should be of about No. 34 B & S gauge and not more than 10 centimeters should be used at a time. A correction of 1,600 calories per gram of wire burned is to be subtracted from the observed number of calories.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of standard combustion samples supplied by the Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same or different standard materials. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same as for coal combustions. In the case of any disagreement between contracting parties a check standardization may consist of two or more combustions of standardizing samples.

MANIPULATION.

1. *Preparation of Sample.*—The ground sample is to be thoroughly mixed in the bottle and an amount, approximately 1 gram, is to be taken out and weighed in the pan or crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. For anthracite and coke the following procedure should be adopted: The inside of the crucible is lined completely with a thin layer of ignited asbestos, pressed well down into the angles. The sample is then sprinkled evenly over the surface of the asbestos. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation in the use of naphthalene for standardization.

2. *Preparation of the Bomb.*—The firing wire, if iron, should be measured and coiled in a small spiral and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean. About 0.5 cubic centimeters of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used

for combustion. When the crucible is put in place in the bomb, the firing wire should touch the sample. For combustion of standardizing materials, or for coke, iron wire is preferable to platinum.

3. *Filling the Bomb with Oxygen.*—Oxygen from the supply tank is to be admitted slowly to avoid blowing the sample from the crucible and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, namely at least 5 grams per gram of coal or other combustible. For coke it will be found better to allow a pressure of 5 atmospheres more than that allowed for coal.

4. *Calorimeter Water.*—The calorimeter is to be filled with the required amount of distilled water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standard flask or by weighing. The amount must be kept the same as that used in standardization of the apparatus.

5. *Temperature Adjustments.*—The initial temperature in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than 1° C., preferably about 0.5° C., above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 2 or 3° C., and the effect of evaporation will also be small.

6. *Firing Current.*—The electric current used for firing the charge should be obtained from storage or dry cells having an electromotive force of not more than 12 volts, since a higher voltage is liable to cause an arc between the firing terminals, introducing additional heat, which cannot be measured with certainty. The circuit should be closed by means of a switch, which should remain closed for not more than 2 seconds. When possible it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out.

7. *Method of Making an Observation.*—The bomb when ready for firing is to be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the thermometer reading has become steady, not less than 2 minutes after the stirrer is started, temperatures are read at 1-minute intervals for 5 minutes and the charge is then fired, the exact time of firing being noted. Observations of temperature are then made at intervals depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings is taken at 1-minute intervals for 5 minutes for determining the final cooling rate.

8. *Titration.*—After the combustion, the bomb is to be opened, after allowing the gas to escape, and the inside examined for traces of unburned material or sooty deposit. If these are found, the observations shall be discarded. If the combustion appears complete, the bomb is to be rinsed out thoroughly and the washings titrated with a standard alkali solution (1 cubic centimeter $=$ 0.02173 gram $HNO_3 = 5$ calories) using methyl orange or methyl red indicator, to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed.

An additional correction of 1,300 calories per gram of sulphur in the coal should be made for the excess of difference in heats of formation of SO_2 and aqueous H_2SO_4 over the heat of formation of aqueous HNO_3. For details of titration see Technical Paper No. 8, Bureau of Mines.

Computation of Results.

The following method of computation is recommended to take the place of the Pfaundler or other similar formulas for computing the cooking correction (radiation correction).

Observe (1) the rate of rise (r) of the calorimeter temperature in degrees per minute for 5 minutes before firing;

(2) the time (a) at which the last temperature reading is made immediately before firing; (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing, 60 per cent. of the expected temperature rise, and noting the time when this point is reached); (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing; (5) the final rate of cooling (r_2) in degrees per minute for 5 minutes.

When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise has reached 60 per cent. of the total. Thus, if the temperature at firing was 2.135°, at 40 seconds, 3.05°, at 50 seconds 3.92°, at 60 seconds 4.16°, and the final temperature was 4.200°, the total rise was 2.07°; 60 per cent. of it was 1.24°. The temperature to be observed was then $2.14° + 1.24° = 3.38°$. Referring to the observations at 40 and 50 seconds the temperatures were respectively 3.05° and 3.92°. The time corresponding to the temperature of 3.38° was therefore

$$40 + \frac{3.38 - 3.05}{3.92 - 3.05} \times 10 = 44 \text{ seconds.}$$

The rate r is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature was falling at the time a) to the thermometer reading taken at the time a. The rate r_2 is to be multiplied by the time $c - b$ and this product added (subtracted if the temperature was rising at the time c and later) to the thermometer reading taken at the time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated.

The result, corrected for the heats of formation of HNO_3 and H_2SO_4 observed and for the heat of combustion of the firing wire, when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the British thermal units per pound.

In practice, the time *b* — *a* will be found so nearly constant for a given calorimeter with the usual amounts of fuel that *b* need be determined only occasionally.

The results should be reduced to calories per gram or British thermal units per pound of dry coal, the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

EXAMPLE.

Observations:

Water equivalent = 2,550 grams. Weight of charge = 1.0535.

Approximate rise of temperature = 3.2°.

60 per cent. of approximate rise = 1.9°.

	Time	Temperature	Corrected temperature
	10.21	15.244°	(Thermometer corrections from the certificate)
	.22	.250	
	.23	.255	
	.24	.261	
	.25	.266	
(a)	.26	.272	15.276°
Charge Fired:			
(b)	27-2	17.200° (d)	
(c)	31	18.500	18.497°
	32	.498	
	33	.497	
	34	.496	
	35	.494	
	36	.493	

Computation:

$^r1 = 0.028° + 5 = 0.0056°$ per minute. $b - a = 1.2$ minutes

The corrected initial temperature is

$$15.276° + 0.0056° \times 1.2 = 15.283°$$

$^r2 = 0.007° + 5 = 0.0014°$ per minute; $c - b = 3.8$ minutes

The corrected final temperature is $18.497° + (0.0014 \times 3.8) = 18.502°$

Total rise $18.502° - 15.283°$ .... $= 3.219°$

Total calories 2.550×3.219 .... = 8.209

Titration, etc. .... = 0.007

Calories from 1.0535 g. coal 8.202

Calories per g. 7,785

or British thermal units per pound 14,013

(d) The initial temperature is 15.27°; 60 per cent. of the expected rise is 1.9°.

The reading to observe is then 17.2°.

The results obtained by the above method of computation and determination is the total heat of combustion at constant volume, with the water in the products of combustion condensed to liquid at the temperature of the calorimeter, that is, about 20° to 35° C.

Net heat of combustion at 20°, shall refer to results corrected for latent heat of vaporization, as follows:

Total heat of combustion in B. t. u. — 1,040 (hydrogen x 9) = net heat of combustion in B. t. u. per pound.

Also total heat of combustion in calories — 580 (hydrogen x 9 = net heat of combustion in calories per gram.

Allowable Variations:

	Per cent.
Same analyst	0.3
Different analysts	0.5

Shatter Test for Coke.

The apparatus consists essentially of a box capable of holding at least 100 pounds of coke, supported with the bottom 6 feet above a cast-iron plate. The doors on the bottom are so hinged and latched that they will swing clearly away when open and will not impede the fall of the coke. Boards are placed around the cast-iron plate to prevent pieces of coke from being lost.

Each sample is approximately 50 pounds and is selected at random using a 2-inch tine fork. The sample is cool when tested but not artificially dry.

The entire sample is placed in the box and dropped on the cast-iron plate. No attempt is made at distributing or arranging the charge in the box before dropping.

The entire material is dropped four times onto the cast-iron plate. The small material including the dust is returned to the box with the large coke each time in order to represent as nearly as possible, the practical conditions to which coke is subjected.

After the fourth drop the coke is screened on a wire screen with square holes, 2 inches in the clear.

The screen is held horizontally and is shaken once after the coke is placed on it, but no attempt is made to force through all the small pieces that might go through if they happened to be placed differently on the screen.

The coke is weighed carefully before being placed in the box the first time and the coke on the screen is weighed on the same scales after the final screening. The coke is weighed accurately to one-eighth of a pound and the result reported in percentage of original coke that does not pass the screen after the fourth drop.

Determination of the True Specific Gravity of Coal and Coke Substance.

To determine the true specific gravity of coal and coke substance, the procedure is as follows: A sample of the 60-mesh coal, weighing approximately 3.5 grams is dried at 105° C., and introduced into a 50 cubic centimeter pycnometer with about 30 cubic centimeters of distilled water. In order to avoid loss of particles of the sample during boiling, a one-bulb 6-inch drying tube (*a*) (Fig. 4) is connected with the pycnometer by means of a small piece of pure gum tubing (*c*). The other end of the drying tube is connected with the aspirator.

Suction is applied and the contents of the flask are gently boiled on the water bath (*d*) under partial vacuum for 3 hours in order to expel all air from the sample. The pycnometer is then detached, almost filled with boiled and cooled water, allowed to cool to the temperature of the balance room, stoppered, and weighed. The temperature of the contents of the

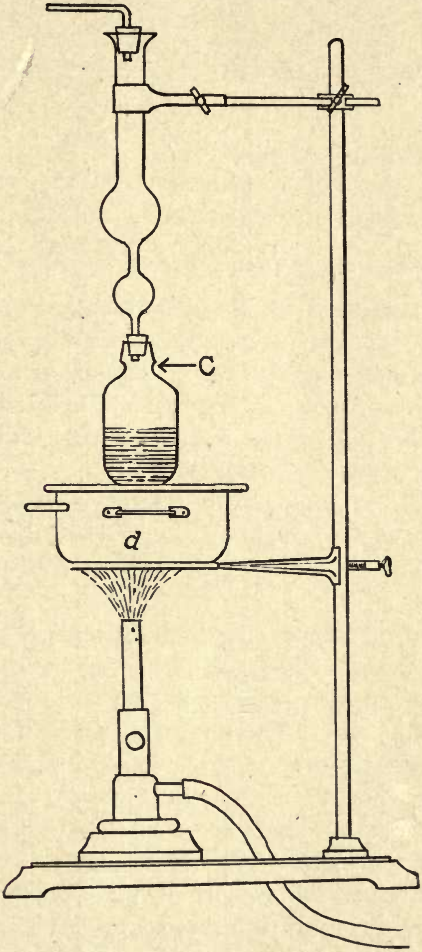

FIG. 4.

pycnometer is taken immediately after weighing. Each pycnometer is accurately calibrated and a table is constructed giving its capacity in grams of water at different temperatures.

True specific gravity is determined by use of the following formula:

$$\text{The specific gravity} = \frac{W}{W - (W^1 - P)}$$

in which

W = weight of coke.
W' = weight of pycnometer + coke + water to fill.
P = weight of pycnometer + water to fill.

Determination of the Apparent Specific Gravity.

The apparatus used for the determination of the apparent specific gravity consists of a galvanized iron cylinder (Fig. 5) which is filled with water to the water line, as indicated in the figure. In the cylinder is immersed a hydrometer made of brass. On the top of the hydrometer are two pans. The upper one is used for weights and the lower one for the sample. Below the air buoy is a brass cage perforated with many holes to allow the air to escape when the instrument is immersed. The cage carries the sample when it is weighed under water.

The method of determining the apparent specific gravity is as follows: Brass weights are placed on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. The total weight required is recorded. The weights are removed, and about 500 grams of the sample in lump form (about 1½- to 2-inch cubes) are placed in the copper dish. Brass weights are then added until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air. The sample is then carefully transferred to the brass cage below the buoy. The weights on the upper pan are now adjusted until the instrument again sinks to the mark on the stem. The weight required to sink the hydrometer to the mark with no sample on the upper pan nor in the brass cage minus the

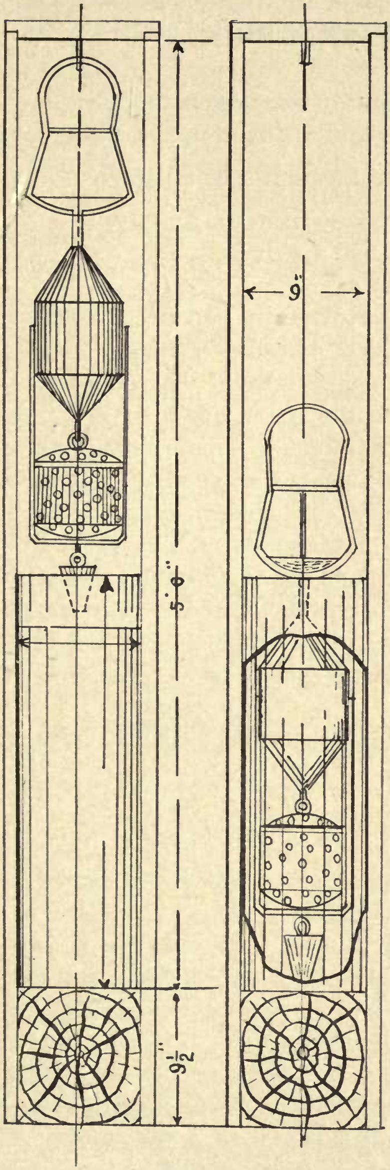

FIG. 5.

weight required to sink it to the mark with the sample immersed in the cage equals the weight of the coke in water. Then

If the weight of the sample in air $= x$
and the weight of the sample in water $= y$

$$\text{The apparent specific gravity} = \frac{x}{x - y}$$

$$\text{And } 100 \times \frac{\text{Apparent specific gravity}}{\text{true specific gravity}} = \text{percentage by volume}$$

of coke substance.

Also 100 percentage by volume of coke substance = percentage by volume of cell space.

In making apparent specific determinations of coke the sample should preferably be in lumps of nearly the same size and shape. When the sample is immersed, the hydrometer should be moved rapidly up and down in the water a number of times in order to remove air bubbles. Since coke samples are porous they take up water rapidly and should not be allowed to remain in contact with water more than 5 minutes during a determination. By observing the above-mentioned precautions satisfactory results can be obtained. All samples should be thoroughly dry before specific gravity determinations are made.

Ash Analysis.

For ash analysis follow the method outlined under refractories.

GAS OIL.

The following determinations are covered in the analysis of gas oil:

Asphalt.
Bromine Number.
Cold Test.
Distillation.
Flash Point.
Fire Point.
Heating Value.
Heat of Vaporization.
Index of Refraction.
Mean Boiling Point.
Mean Molecular Weight.
Paraffin.
Specific Gravity.
Specific Heat.
Sulphur.
Water.

It is not recommended that all are necessary for routine analysis, but special circumstances may require more extended investigation as a means of identifying the source of an unknown sample when such determinations may be of great value.

There are a number of methods in the literature that may be used for the empirical determination of the relative proportion of the various classes or groups of hydrocarbons in gas oils. These methods, however, have not had the extensive use and acceptance that would seem necessary for their incorporation in the Handbook at this time.

Asphalt.

The determination of asphalt is still in an unsatisfactory state as there are a number of precipitants used for the purpose, viz., petroleum ether, alcohol, ether, amyl alcohol, ethyl acetate, butanon. The asphalts thus obtained vary quite widely both as to quantity and hardness and there does not seem to be any well defined relation existing between the results obtained with the different precipitants on different samples of oil.

The more generally recognized precipitant is naphtha, and the method according to Engler, is as follows:

QUANTITATIVE DETERMINATION.

Asphalt Insoluble in Naphtha.—Five grams of oil are shaken in a 500 cubic centimeter bottle with 40 times its volume (220 cubic centimeters, assuming the specific gravity to be 0.9) of normal benzene. If the oil contains only a little asphalt, as much as 20 grams of oil may be taken with the corresponding amount of naphtha. After standing at least 24 hours at a temperature between 15° and 20° and away from direct sunlight, the solution is decanted through two filters folded together (white ribbon S. & S.). The residue is washed with naphtha till the filtrate gives no more oily residue. To prevent the asphalt from becoming insoluble on standing, it is at once dissolved in hot benzol, the main mass evaporated from a flask and the remainder in a tared vessel, the residue dried at

105° and weighed. Foreign substances precipitated by naphtha and insoluble in benzol can be separately determined by using a weighed filter paper. If the suspended asphalt is to be determined, the amount of asphalt is determined in the original oil as well as in the filtered oil; the difference gives the suspended asphalt. In the different crude oils the amount of asphalt runs parallel to the amount of coke obtained on distillation.

The German specifications for the naphtha require a gravity at 15° C. of 0.695-0.705, boiling range 65° C.-95° C. with 100 cubic centimeters using a 3-bulb Le Bel Henninger Column 40 centimeters long. Not over 2 per cent. should dissolve in a mixture of 20 per cent. fuming and 80 per cent. 1.84 H_2SO_4, using equal volumes and shaking for 15 minutes.

Bromine Number.

From 0.3 to 0.5 gram of oil is weighed into a glass stoppered 8-ounce bottle. Ten cubic centimeters of bromine solution is run from the burette, the bottle is then cooled in ice water and 25 cubic centimeters of 10 per cent. potassium iodide solution is added shaking the bottle, but preventing any of the solution from getting on or near the stopper. Add 1 or 2 cubic centimeters of starch solution and titrate against standard sodium thiosulphate solution. The reaction is as follows:

$$Br_2 + 2KI = 2KBr + I_2.$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

Calculation.—Cubic centimeters of bromine used x equivalent to thiosulphate solution = equivalent volume of thiosulphate.

Equivalent volume of thiosulphate — thiosulphate added in titration = cubic centimeters of thiosulphate used.

Cubic centimeters of thiosulphate used x 0.008 = grams of bromine absorbed. $\frac{\text{Grams of bromine absorbed} \times 100}{\text{Grams of oil used}} =$ bromine number.

Solutions.—The thiosulphate solution is made up to contain

24.8 grams of C. P. sodium thiosulphate ($Na_2S_2O_35H_2O$) per liter.

The bromine solution is made up with dry carbon tetrachloride and standardized with the thiosulphate. One cubic centimeter of the bromine solution should equal approximately 1.5 cubic centimeters of thiosulphate solution.

Distillation.

The apparatus shall consist of the following standard parts:

(1) FLASK.

The distillation flask shall be a standard 100 cubic centimeter Engler distilling bulb having the following dimensions (see Stillman's "Engineering Chemistry").

Diameter of bulb	6.5 cm.
Length of neck	15.0 cm.
Diameter of neck	1.6 cm.
Surface of oil to tubulure	9.0 cm.
Length of tubulure	10.0 cm.
Angle of tubulure	75°

A 3 per cent. variation from the above measurements will be allowed.

(2) THERMOMETER.

High temperature nitrogen-filled Fahrenheit thermometer constructed according to the following specifications:

(1) To be made of special German hardened glass.

(2) Diameter of stem not less than 6.75 millimeters nor more than 7.25 millimeters.

(3) Length of thermometer not less than 335 millimeters nor more than 350 millimeters.

(4) Length of thermometer between 0° mark and 1,000° mark not less than 285 millimeters nor more than 300 millimeters.

(5) Length of bulb to capillary not less than 20 millimeters nor more than 22 millimeters.

(6) Diameter of bulb at center of same not less than 5.25 millimeters nor more than 6.25 millimeters.

(7) Mercury column to rise from 60° to 200° in not more than 5 nor less than 3 seconds when plunged into boiling water.

(8) To be correct within 1° at 212° and 750° after 25 successive oil tests.

(3) Condenser.

Liebig glass condenser and tube as follows:

Length of body of jacket	300–350 mm.
Width of body of jacket	25– 40 mm.
Length of inner tube	530 mm.
Width of inner tube	12– 15 mm.
Width of end of inner tube	20– 25 mm.

(4) Stands.

Two iron stands provided respectively with one universal clamp for holding condenser, and one light grip arm asbestos lined clamp for holding the bulb.

(5) Burner and Shield.

Bunsen burner with tin shield 8 inches long by 3 inches in diameter. The shield has a sight hole in the same for observing the flame.

(6) Cylinders.

Ten glass cylinders, 25 cubic centimeters capacity, graduated to 1/10 cubic centimeter.

Setting Up Apparatus.

The apparatus is set up as shown in Fig. 6, the thermometer being so placed that the top of the bulb is opposite the middle of the tubulure. All connections should be tight.

Distillation Test.

One hundred cubic centimeters of the oil to be tested are placed in a weighed bulb, and after adjusting the thermometer, shield, condenser, etc., the distillation is commenced, the rate being so regulated that 1 cubic centimeter passes over every minute. Cold water should be passing through the condenser during the first half of the distillation. When the thermometer reaches 600° F., the cold water should be removed from the condenser and hot water substituted. The receiver is changed as the mercury column just passes the fractionating point. At the end of the distillation, or when no more oil distils over, the flask is disconnected from the condenser, inverted and two burners are used to complete the coking.

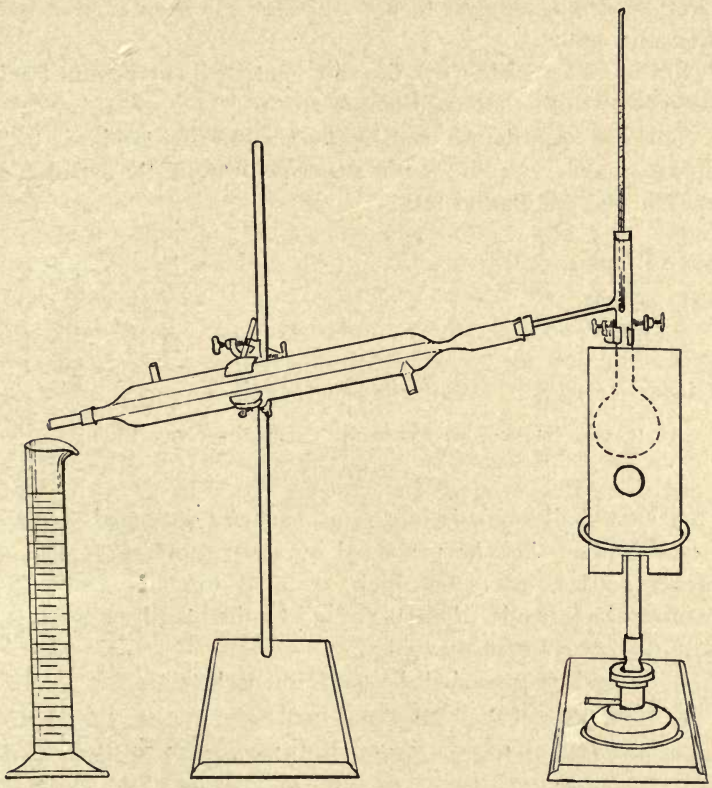

FIG. 6.

The fractionating points in the distillation are at every 50° F., *i. e.*, at 300°, 350°, 400° F., etc. The number of cubic centimeters obtained between each cutting point will give the per cent. by volume distilling between these temperatures.

The per cent. by weight is obtained as follows: Multiply the per cent. by volume of each fraction by its specific gravity and divide by the specific gravity of the original oil.

In case the oil contains more than 2 per cent. of water, it should be dried by the following method before carrying out the distillation: A definite volume of oil is placed in a copper still and heat gradually applied until all water has distilled over, returning any oil to the still that has been carried over with the water.

For more accurate work the emergent stem correction should be applied to the observed temperature.

This has been determined by the Bureau of Standards to be approximately as follows for a thermometer in the position as used in the distillation test:

200° C.	4.50° C.
250° C.	6.0° C.
300° C.	10.5° C.
350° C.	15.5° C.

Flash and Fire Tests.

DIRECTIONS FOR OPERATING TAGLIABUE OPEN CUP.

General Directions.

1. Test shall be made in a room partially darkened.
2. The cup shall be protected by a surrounding screen, 16 inches square, 30 inches high, open at top and front, and painted black inside. Drafts caused by the breath of the operator shall be carefully avoided.
3. A fresh sample shall be used for each test.
4. The instrument must stand level.

Preparation of Water Bath.—Fill the metal bath with water at a temperature of 25° C. (77° F.) so that when the glass cup is in place, the water in bath will come to the rim of the metal cup.

Preparation of Sample.—Suspend a calibrated thermometer (see specifications) in the center of the cup with the top of the bulb of same ½ inch below the upper level edge of the glass cup. Bring sample to be tested to a temperature of 15.5° C. (60° F.). Fill the glass cup with 59 cubic centimeters of the sample. See that there is no oil on the outside of the cup or its upper edge, using a filter paper to clean the cup. Remove air bubbles, if any, from the surface of the oil.

NOTE.—*The horizontal flashing-taper guide wire* (as specified by direction of the manufacturer) *is not to be used in these tests.*

Application of Heat to Oil Cup.—Heat the bath with an alcohol, gas or other flame, so adjusted that the temperature will not be raised faster or much slower than 1° C. (1.8° F.) per minute, without removing the flame.

Description of Test Flame.—The test flame shall be spherical in form, and shall have a diameter equal in size to the bead furnished herewith, which may be attached to the cover of the water bath. This flame is best produced by passing gas through a straight thin metal blow-pipe tube. (See Eimer and Amend Catalogue C (1913, p. 54, Item 784) or Scientific Materials Co. (1912, p. 69, Item 618) or C. J. Tagliabue special tube.

Initial Test.—When the sample under test reaches a temperature of 30° C. (86° F.) the first test shall be made, and tests shall be made thereafter at each rise of 1° C. (1.8° F.) until the flash point is reached.

Method of Applying Test Flame.

(Two Methods, both to be used and reported.)

(A) Sweep Method.—Holding the burner tube in a truly horizontal position the flame is passed in a straight line continuously across the center of the cup, with the tube touching the edge of the cup. The time for one sweep from edge to edge of the cup to be gauged to 1 second. The temperature at which a flame first appears anywhere on the surface of the oil shall be considered the flash point.

(B) Dip Method.—Holding the burner tube in a vertical position with the flame 3 inches above the surface of the sample, the flame is quickly lowered to ⅛ inch from the sur-

face of the sample near the outer edge of the cup, and withdrawn; entire operation consuming one second. This operation is quickly repeated at three equidistant points around the circumference of the cup. The temperature at which a blue flame jumps from the taper to the surface of the oil is the flash point.

DIRECTION FOR OPERATING THE ELLIOTT OR N. Y. STATE TESTER.

General Directions.

1. Test shall be made in a room partially darkened.
2. The cup shall be protected by a surrounding screen, 16 inches square, 30 inches high, open at top and front, and painted black inside. Drafts caused by the breath of the operator shall be carefully avoided.
3. A fresh sample shall be used for each test.
4. The instrument must stand level.

Preparation of Water Bath.—Fill the metal bath with water at a temperature of 25° C. (77° F.) so that when the metal cup is in place, the water in bath will come to the rim of the metal bath.

Preparation of Sample.—Bring the sample to be tested to a temperature of 15.5° C. (60° F.). Fill the metal cup with the sample to such a point that the surface of the oil will be ⅛ inch below the lower inner flange. Remove air bubbles, if any, from the surface of the sample. Place the glass cover in position and insert the calibrated thermometer (see specifications) through the cork in the central opening so that the top of the bulb will be ¼ inch below the surface of the sample.

Application of Heat to Oil Cup.—Heat the bath with an alcohol, gas or other flame, so that the temperature will not be raised faster or much slower than 1° C. (1.8° F.) per minute, without removing the flame.

Description of Test Flame.—The test flame shall be spherical in form, and shall have a diameter equal in size to the bead furnished herewith, which may be attached to the cover of the water bath. This flame is best produced by passing gas through a straight thin metal blow-pipe tube. (See Eimer and Amend Catalogue C (1913, p. 54, Item 704) or Scientific Materials Co. (1912, p. 69, Item 618) or C. J. Tagliabue special tube.

Initial Test.—When the sample under test reaches a temperature of 25° C. (77° F.) the first test shall be made. Tests shall be made thereafter at each rise of 1° C. (1.8° F.) until the flash point is reached.

Method of Applying Test Flame.—Holding the burner tube at an angle of 45°, the flame is passed through the side opening in the cover to a point half way between the surface of the sample and the cover. The time consumed in entering and withdrawing the flame is to be 1 second. The temperature at which a blue flame is seen through the glass is the flash point.

Specification for Thermometer for Flash Point Tests.

To be used with Tagliabue and Elliott or N. Y. State Testers.

The thermometer shall be graduated from —10° to +110° C. in 1° intervals. There shall be a small reservoir above the 110° mark. The thermometer shall be finished at the top with a small glass ring.

The stem shall be made of enamel backed thermometer tubing, but not of Jena 16^{111} glass. The bulb shall be made of Jena 16^{111}, Corning normal, or Jena or Corning borosilicate glass.

Every fifth graduation shall be longer than the intermediate ones and the marks shall be numbered at every 10° interval. The graduation marks shall be clear cut and fine, and the numbering clear and distinct.

Each thermometer shall be provided with a suitable case. A serial number for identification shall be engraved on the stem.

All material and workmanship shall be of the best grade.

Accuracy.—The maximum error at any point shall not exceed three-tenths (0.3) degree Centigrade.

Dimensions:

Total length, not over 300 millimeters.
Diameter stem, from 5.5 to 7 millimeters.
Diameter bulb, same as stem.
Diameter capillary, not less than 0.1 millimeter.
Length of bulb, from 8 to 12 millimeters.
Distance—10° to bottom of bulb, from 40 to 60 millimeters.
Distance—10° to 110° on scale, from 180 to 220 millimeters.

Heating Value.

Refer to Heating Value of coal analysis on page 30.

Heat of Vaporization.

The heat of vaporization may be calculated with sufficient accuracy for purpose of design from the mean molecular weight and the mean boiling point and specific heat from Trouton's rule.

$$(\text{Heat of vaporization}) = 20.\ \frac{\text{Mean boiling point}}{\text{Mean Molecular Weight}}$$

The total heat of vaporization = sensible heat from room temperature to boiling point + latent heat of vaporization so there must be added (mean boiling point — room temperature) (specific heat).

Refractive Index.

The Zeiss refractometer is recommended for the refractive index at a temperature of 25° C., at which point all fractions of the usual gas oils are sufficiently liquid for observation. As detailed instructions are furnished with the instrument they are not repeated here.

The use of the refractive index instead of the specific gravities for the fractions of gas oils is recommended as giving really more information and requiring but a fraction of the time to determine.

Mean Boiling Point.

This figure is the arithmetical mean of the temperature at which equal volumes of the oil distil off.

The oil is distilled in the usual form of apparatus and the temperatures noted when the first drop, 10 per cent., 20 per cent., 30 per cent., etc. have distilled over. The sum is divided by the number of fractions. The mean boiling point is expressed in absolute temperature for use in calculating the heat of vaporization.

Mean Molecular Weight.

This figure is frequently quite useful for identification purposes and for use in calculating the heat of vaporization. The determination is made in a Beckman freezing point apparatus. Commercial stearic acid previously standardized with a substance of known molecular weight or benzol may be used as solvents. The operation is as follows:

The freezing tube *A*, with the stirrer and garnets, is carefully washed and dried, and from 15 to 20 grams of the solvent accurately weighed into it. It is stoppered both at the top and side tube and placed in the jacket tube *B*. The jar *C* is then filled with a freezing mixture (for benzol, water with a small piece of ice is suitable).

The Beckman thermometer is adjusted so that the mercury at the freezing point of the solvent (benzol = 5° C.) is somewhat above the middle point of the scale. The thermometer is inserted in the perforated stopper holding the platinum stirrer and after dropping in a few small garnets the thermometer and stirrer are rapidly inserted in place of the stopper in the freezing tube. By this time the solvent should be from 1° to 2° below the freezing point. The stirrer is worked up and down to cause the formation of crystals—as these begin to form the thermometer rises and as it reaches the freezing point remains practically stationary (vibrating a few thousandths under the magnifying glass however) the mean point is observed. The freezing mixture should be stirred constantly and the solvent should be stirred at a uniform rate of from 30 to 35 strokes per minute.

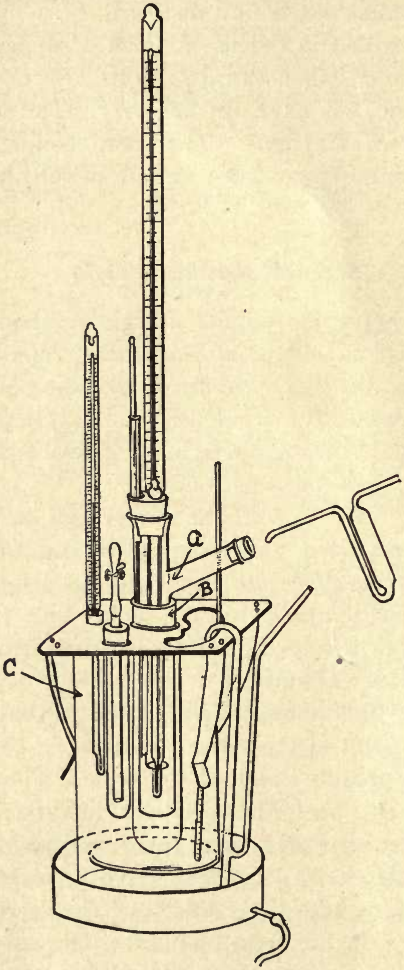

FIG. 7.

The freezing tube is removed and from 0.5 to 0.7 gram of the substance is brought into the solvent through the side tube. For oils a weighing pipette is useful, as the quantity must be accurately weighed out. Care must be taken to allow the temperature to rise until all crystals have disappeared but not far enough to destroy the setting of the thermometer. The freezing tube is replaced and when the substance has gone into solution the freezing point is observed as before. The difference is the depression (t). Repeated additions of the solvent may be made and the depressions noted. The depression (t) should not be less than 0.5° and not over 3.0°.

If M = molecular weight of substance.
C = constant of solvent.
P = grams of substance per 100 grams of solvent.
t = depression of freezing point.

$$M = \frac{C\,P}{t}$$

The solvent should be standardized with a pure substance of known molecular weight (naphthalene may be used with benzol). If 20 grams of benzol were used and 0.5 gram naphthalene added, producing a depression of 0.986° we would have

$$\text{Constant} = \frac{M\,t}{P} = \frac{128 \times 0.986}{\frac{0.5 \times 100}{20}} = 50.48$$

Then assuming 19 grams of benzol used, 0.7 gram of oil added and $t = 1.195$ we would have

$$M = \frac{C\,P}{t} = 50.48 \times \frac{\frac{(0.7 \times 100)}{19}}{1.195} = 155$$

REFERENCES.—Z. phys. Ch., 1, pp. 577, 631; 2, pp. 307, 491, 638, 964; 5, p. 94; B., 21, pp. 711, 860; 22, pp. 1430, 2501; 23, R 1; 24, pp. 1431; 27, R 542, R 845, R 974.

Paraffine.—One hundred grams of crude oil are distilled rapidly from a tubulated retort till the temperature of 300° is reached. A weighed receiver is then put into position (without a condenser) and all oil driven over until the residue cokes completely (without thermometer); the amount of heavy oil distilled is determined.

Five-tenths gram of the substance is dissolved at room temperature in a mixture of ether and absolute alcohol (1 : 1) to a clear solution, then cooling to —20°, just enough alcohol-ether mixture added till all oily drops are dissolved and paraffine flakes are visible. With much paraffine, it is advisable to warm with ether to complete solution and then add the same volume of alcohol. The precipitated paraffine is then filtered on a funnel surrounded with a rock-salt and ice-freezing mixture, all traces of the alcohol-ether solution being removed, and then washed free from oil by means of cooled alcohol-ether. The residue is then washed into a weighed glass dish with hot benzol, or naphtha and the solvent evaporated on a water bath.

The paraffine is carefully washed with cooled alcohol-ether until 5 cubic centimeters of the filtrate on evaporation will give no residue, or only a trace of material solid at room temperature, is obtained; too prolonged washing is to be avoided because of the still quite noticeable solubility of paraffine in alcohol-ether. If on cooling, the paraffine is seen to be hard, it is heated at 105° for 15 minutes and weighed after drying in a desiccator; if the paraffine is soft (with melting point under 45°), it should be dried several hours in a vacuum desiccator at 50° before weighing.

Determination of Specific Gravity.

For control tests on the original sample, the specific gravity may be taken with sufficient accuracy with a hydrometer.

The oil should either be brought to the normal temperature 15.5° C. or 25° C., or else the temperature observed and the gravity corrected back to normal temperature.

Specific gravity at T = observed gravity at temperature

$$t^\circ + (T - t \times 0.009).$$

In determining the specific gravity of the fractions the Sprengel tube type of pycnometer is recommended. The tube is completely filled and is immersed in water at the normal temperature for 15 minutes. The tube is tilted and the excess material removed from the capillary with filter paper until the liquid reaches the calibrated mark. The tube is then dried and weighed.

Platinum or nickel wire should be used in suspending the tube on the balance.

For a calibration of the tube made by weighing empty and filled with water at the normal temperature the specific gravity is given by the formula:

$$\text{Specific gravity}\quad \frac{\text{Weight filled with oil} = \text{weight empty}}{\text{Weight filled with water} = \text{weight empty}}$$

While the former practice has been to determine specific gravity at 15.5° C., the later standards of the American Society for Testing Materials have very generally used 25° C. as the normal temperature, and the use of this temperature is recommended.

Specific Heat.

This determination is made with a Parr or bomb calorimeter, using the oil instead of water as a calorimeter liquid, and burning a definite quantity of a pure substance such as sugar or benzoic acid. Owing to the low specific heat of the oil, the quantity to be burned should be roughly calculated, using 0.45 as an assumed specific heat of the oil to secure a temperate rise of not over 2.5°.

The operation is carried on exactly as described for determining the heating value:

$$\frac{(\text{Grams substance} \times \text{heating value}) = (\text{Water equivalent} \times \text{corrected rise})}{(\text{Weight of oil taken}) \times (\text{Corrected rise})}$$

Sulphur.

This determination is most conveniently carried out together with the determination of the heating value in the bomb calorimeter. After the combustion the gases are allowed to escape slowly through a 10 per cent. solution of sodium carbonate using about 20-25 cubic centimeters in a small beaker or test tube.

The bomb is then washed out thoroughly with water, the soda solution is added to the washing and the solution boiled until the aluminum and iron are precipitated, filtered and washed. The solution should have a volume of 70-100 cubic centimeters—is accelerated with HCl and precipitated in a boiling solution with $BaCl_2$.

$$BaSO_4 \times 0.1373 = S.$$

A METHOD BY ROTHE.

Three-fourths gram of oil with 1.5 grams of MgO and 30-40 cubic centimeters of nitric acid (specific gravity 1.48) are placed in a 250 cubic centimeter round bottom Jena flask. Hood. After the first violent reaction, the flask is heated gently for 1½-2 hours in a sand bath, the liquid being kept boiling gently. The excess nitric acid is then evaporated over a free flame and the residue heated till the nitrates begin to decompose. After cooling, 10 cubic centimeters concentrated acid are again added. After 15 minutes heating, the mass is evaporated to dryness, keeping the flask in constant motion, then heated with a triple burner until the nitrates are completely decomposed. The residue is generally white; by adding 10 cubic centimeters of hydrochloric acid (specific gravity 11.24) and heating, it is dissolved and then filtered after diluting with 20-30 cubic centimeters of water. In the filtrate, the sulphuric acid is determined by precipitation with barium chloride in the customary manner.

Water.

Small quantities of water may be determined in the course of the distillation test. Should the water exceed 2 per cent. it should be determined separately.

Water is quantitatively determined as follows:

About 100 grams of oil (less if much water is present) are distilled from an oil bath with toluol; this toluol should have been previously saturated with water. Pumice is added to avoid bumping. Eighty to ninety cubic centimeters are caught in a cylinder constricted to a narrow graduated tube at the bottom (Hoffman-Marcusson). After washing the inside of the condenser with toluol and loosening any water drops on the side of the cylinder with a stirring rod, the amount of water can be directly read on the graduations.

TESTING OF PURIFICATION MATERIAL.

New Material.

The following determinations are covered in the analysis of new oxide:

Weight per Bushel.
Sampling.
Moisture.
Metallic Iron.
Iron Sesquioxide.
Fouling Test.

Used Purification Material.

The following determinations are covered in the analysis of used oxide:

Sampling.
Moisture and Light Oils.
Total Sulphur.
Soluble Sulphur and Tarry Matter.

New Purification Material.

WEIGHT PER BUSHEL AND SAMPLING.

These two determinations can conveniently be done in one operation. The necessary apparatus are:

Bushel box, made of wood, the capacity to be 2,150.4 cubic inches, approximate dimensions inside 12 x 12 x 15 inches.

Sampling tool made of brass tubing, 2 inches in diameter, 18 inches long, upper surface cut away to a length of about 15 inches, and rounded. A wooden handle is attached to the other end. Fig. 8.

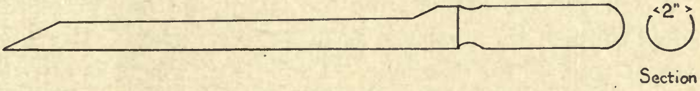

FIG. 8.

Ordinary garden trowel.

The operations are as follows:

Samples are taken from a number of bags by thrusting the sampling tool into each bag in turn. The number of bags sampled depends on the size of the lot of oxide received. It should be at least 10 per cent. of the total number of bags. For instance, if the lot contains 500 bags, a sample should be taken from every tenth bag, or from 50 of the bags.

These samples are then thrown together on a clean surface, mixed, and spread out to a depth of about 3 inches. Portions are then taken over the surface at equal distances with the garden trowel, digging down to the bottom when taking each portion. These portions are thrown into the bushel box and well mixed. Sufficient material is taken in this manner to fill the box level with the upper edge. The box and contents are then weighed. The weight of the empty box deducted from this weight gives the pounds of oxide per bushel. The contents of the box are quartered down and the sample finally obtained put into a quart glass Mason jar, or a tin can with air-tight cover.

CAUTION.—If the oxide contains metallic iron, it must be mixed as little as possible consistent with obtaining a representative sample, because the greater density of the iron will cause it to pass to the bottom, thus interfering with the uniformity of the sample.

If the oxide is not shipped in bags, the operator must use his judgment when sampling, bearing in mind that the portions should be taken throughout the shipment in a uniform manner, so that the final sample will be representative of the entire shipment.

MOISTURE.

Weigh out 100 grams from the jar or can into a counterpoised tin dish, on a balance accurate to 0.1 gram. Dry in an oven at 100° C. for one hour. The loss of weight is reported as moisture.

The dried sample is then ground in a coffee mill until it is about 30-mesh size, and quartered down until about 30 grams are finally obtained. This final sample is kept in a tightly stoppered, wide mouth bottle, and used in subsequent determinations.

Note.—The grinding is best done by first having the mill set to grind coarsely, then repeating as many times as necessary, adjusting the mill to grind finer each time. By this method, usually, no difficulty will be found in breaking down any iron borings that may be in the oxide.

METALLIC IRON.

Weigh one gram of the dried oxide from the bottle above into a 100 cubic centimeter beaker and treat with 50 cubic centimeters neutral, saturated solution of cupric ammonium chloride, allow to stand with frequent stirring for at least an hour in a warm place, when all particles of metallic iron should be dissolved. Filter off the residue and wash free of chlorides, and to the hot filtrate add ammonia in excess. The iron will be precipitated as hydroxide, while the blue cupric hydrate dissolves in excess. Filter off the precipitate, wash with water containing a little ammonia until practically free from copper salts.

Dissolve the precipitate on the filter with hot, dilute hydrochloric acid, 1 in 10, and wash free from HCl. To the hot filtrate, ammonia is again added in excess to precipitate. The precipitate is then filtered, washed, and ignited. Weigh as Fe_2O_3. This weight multiplied by 69.94 gives the percentage of metallic iron found.

Note.—This method must be regarded as only approximate. It is, however, the best method the Committee has been able to find. It gives low results, due to the oxidation of the iron when the residue is being filtered from the cupric ammonium chloride. The error varies with the percentage of metallic iron present, being greatest when this percentage is low.

If large pieces of iron borings are present it is advisable to remove them with a magnet, brush off the adhering oxide of iron, etc., returning the latter to the sample to be analyzed. The clean pieces are weighed and the percentage calculated and added to the metallic iron found by the method described above.

IRON SESQUIOXIDE.

Iron is usually present in an oxide in some form of hydrated ferric oxide. It is not practicable to determine accurately the state of hydration; hence, it has been thought best to determine and report the oxidized iron present as sesquioxide.

Dissolve 0.5 gram of the dried sample in 20 cubic centimeters (1 : 1) hydrochloric acid in a 100 cubic centimeter beaker, evaporate to dryness, adding a few drops of nitric acid from time to time. Take up with 5 cubic centimeters concentrated hydrochloric acid, add 50 cubic centimeters hot water, boil and filter. Wash filter well with hot water. To the filtrate, add 25 cubic centimeters bromine, water and heat to boiling. When the excess of bromine has been driven off, remove beaker from heat and precipitate the iron as hydroxide with ammonia. Boil for five minutes; allow the precipitate to settle. Filter, wash well with hot water, dry, ignite, and weigh as Fe_2O_3. This gives the total iron in terms of Fe_2O_3. If metallic iron is present, it must be determined by the previous method, and its amount also in terms of Fe_2O_3 deducted from the total iron as Fe_2O_3. The difference will be iron sesquioxide. This weight multiplied by 200 gives the per cent. of iron sesquioxide.

Alternate Method.—The residue obtained from the cupric ammonium chloride solution in the method for metallic iron is ignited in a platinum crucible until all carbonaceous matter is destroyed and there remains only a mass of red ferric oxide.

Transfer as much as possible of this to a 100 cubic centimeter beaker, dissolve in 15 cubic centimeters to 30 cubic centimeters concentrated hydrochloric acid, at the same time dissolving from the crucible any adhering particles of ferric oxide. When solution is complete, filter into a 250 cubic centimeter graduated flask. Wash and ignite the residue in a platinum crucible, and fuse with two grams of dry sodium carbonate. Dissolve the fusion in hydrochloric acid, add this to the contents of the 250 cubic centimeter flask, fill to the mark with distilled water, and mix well. With a pipette, transfer 50 cubic centimeters to a 150 cubic centimeter beaker, add ammonia to precipitate the ferric hydroxide, boil for five minutes, allow to settle, and filter. Wash with hot water, dry, ignite, and weigh as Fe_2O_3. The weight multiplied by 500 gives the per cent. of iron sesquioxide.

FOULING TEST.

The fouling test of an oxide offers the best means for determining its value for purification purposes.

A glass tube with a bulb at one end is most suitable to hold the oxide to be tested, but a U-tube or almost any other tube compact enough so that it can be weighed on analytical balance will answer. (See *C* in Fig. 9.)

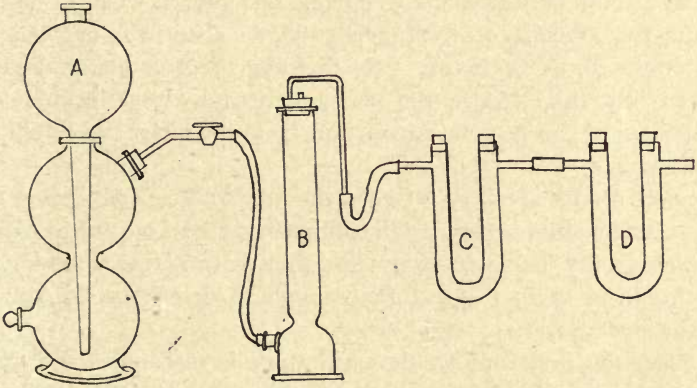

FIG. 9.

Five grams of the oxide to be tested are next mixed with about 2 grams of coarse sifted sawdust and placed in the tube, and covered with a layer of cotton to prevent any of the contents from falling out at the stopper end of the tube. The stopper is then inserted. The entire tube is accurately weighed and the total weight noted. For sponge ore oxide already mixed with shavings the sawdust is omitted. This tube is followed by a U-tube containing calcium chloride and weighed together with the tube holding the oxide. Another large U-tube or a tower filled with calcium chloride to dry the hydrogen sulphide issuing from the generator is connected with the test tube by means of a piece of rubber tubing and the whole connected with the generator. A small piece of glass tubing closed at one end so as to leave only a hole the size of a small pinhole and placed between the U-tube and the generator regulates the flow of gas.

The hydrogen sulphide gas generated in the Kipp generator *A,* and dried by passing it through the calcium chloride in the U-tube or tower *B,* is decomposed by the iron oxide in the test-tube *C,* forming iron sulphide and water. The water formed is absorbed by the calcium chloride in the second test-tube *D.*

The test is carried on for one hour, after which time the test-tubes are disconnected and weighed. The gain in weight represents the amount of hydrogen sulphide absorbed, or rather decomposed, by the oxide. By dividing the amount of oxide taken into this weight, the percentage of hydrogen sulphide decomposed can be determined, and from the latter the sulphur calculated.

Some oxides are very active at the first fouling (when new), but revivification is slow and incomplete, and on second fouling they give far lower results. For this reason it is sometimes desirable to carry the test far enough to determine the total absorbing capacity of an oxide.

After the first fouling, the oxide tube is disconnected from the $CaCl_2$ tube, and air passed over it until completely revivified. To prevent an oxide which has the tendency to revivify very rapidly from getting too hot and consequently burning, thus becoming more or less inert, it is advisable to pass the air used for revivification over water so as to saturate it with water vapor. For this reason it is not advisable to remove the oxide from the tube for revivification, for it being very dry, on direct exposure to air, any very active oxide is found to take fire.

After complete revivification, the tubes of oxide and $CaCl_2$

are again weighed and connected with the Kipp apparatus, and fouled a second time. This second fouling as a rule is sufficient to show how active the material is, for if the results of the second fouling are very close to those of the first, the material is very active, but the test can be repeated the same number of times as the oxide is revivified in practice. Thus the entire capacity of the oxide can be determined before it is placed in service.

Used Purification Material.

SAMPLING.

Used purification material may be required to be sampled under two conditions.

I. When removed from the box for revivification.
II. When revivified in the box.

When the oxide has been removed from the box and spread out, portions may be taken to the entire depth of the bed with the trowel at points situated at equal distances over the surface. When about a bushel has been obtained, this is thoroughly mixed, quartered down, and a quart jar or can filled and tightly closed.

When the oxide is revivified *in situ,* samples should be taken in different parts of the box, the operator using his judgment and endeavoring to obtain a sample which represents the entire contents of the box.

MOISTURE AND LIGHT OILS.

Weigh 100 grams of the sample from the jar or can into a counterpoised tin dish. Place the dish in a drying oven, the temperature of which is not allowed to exceed 95° C. For coal gas oxide it is advisable to air-dry the sample for 5 to 10 hours in a warm place or drying oven kept at 55° C. Examine occasionally by removing from the oven and allowing to cool. It will be found that some oxides containing much tarry matter require several days to dry.

When the oxide appears hard on cooling, the dish and contents are weighed and a loss reported as moisture and light oils.

The sample is then ground in a coffee mill to 30-mesh fineness, and quartered down until about 30 grams are obtained which are kept in a well corked bottle for subsequent determinations.

TOTAL SULPHUR.

Laboratory routine method, gravimetric or volumetric as desired: Oxidation of Sulphur:—Mix 0.5 gram of the sample in a 100 cubic centimeter nickel crucible with 5 to 10 grams of sodium peroxide, depending on the sulphur content of the oxide. Place the crucible in a water bath containing cold water, attach a fuse by passing it through a slip in the edge of the crucible, put on the cover, which must be weighted to prevent it blowing off, and light the fuse. The fuse is prepared by soaking a cotton string in a strong solution of potassium nitrate and drying. Transfer the fused mass to a 500 cubic centimeter beaker and dissolve it in cold water. Next, add dilute HCl (1 : 3), while stirring, until the iron precipitate coagulates in a flocculent form, but keep the solution distinctly alkaline to avoid the solution of iron hydroxide. Heat to boiling, filter off the precipitate and wash well with hot water.

Gravimetric determination of sulphur.—Acidify the filtrate with dilute HCl, heat to boiling and precipitate with barium chloride. Filter, wash and ignite as usual after two hours standing.

Volumetric determination of sulphur.—Solutions required: Barium chromate, 40 grams dissolved in dilute HCl, (80 cubic centimeters HCl specific gravity 1.2, 920 cubic centimeters H_2O,) approximate value of 1 cubic centimeter 0.04 gram $BaCrO_4$. Sodium thiosulphate, N/10, 1 cubic centimeter equals 0.001066 gram of sulphur.

Method.—Catch the filtrate and washings in a 500 cubic centimeter volumetric flask, cool, and dilute to the mark. Transfer 100 cubic centimeters of the solution to a 200 cubic centimeter volumetric flask, add 25 cubic centimeters of barium chromate solution, shake for a minute and then add dilute ammonia, a few drops at a time, until the color changes to a pure yellow, indicating the complete precipitation of the excess of $BaCrO_4$. Dilute to 1 cubic centimeter above the 200 cubic centimeter mark, filter through a *dry* filter paper into a 100 cubic centimeter flask. Throw away the first part of the filtrate. Transfer the 100 cubic centimeters of the filtered solution to a glass stoppered bottle, acidify with 10 cubic centimeters HCl, add 1 gram of solid potassium iodide, shake, and titrate the liberated iodine with N/10 sodium thiosulphate.

Multiply the number of cubic centimeters of sodium thiosulphate by 2.132; this gives the per cent. of sulphur in the oxide.

Alternate method.—Weigh 0.5 gram of the oxide into a 300 cubic centimeter Erlenmeyer flask and treat it with 30 cubic centimeters of a mixture of 3 parts HNO_3 and 2 parts HCl. Heat gently and when the action ceases add a few crystals of potassium chlorate, and boil. Add 20 cubic centimeters HCl and evaporate to dryness on a water bath. Heat in an air oven to 110° C. for one hour to dehydrate silica. Next, cool the flask, moisten the mass with 5 cubic centimeters HCl, take up with 100 cubic centimeters of hot water, boil, filter, and wash well with hot water. Dilute the solution to about 600 cubic centimeters and precipitate with barium chloride. Filter after two hours standing, ignite, and weigh the barium sulphate in the usual manner.

SOLUBLE SULPHUR AND TARRY MATTER.

Extraction with Carbon Tetrachloride.

Weigh one gram of the dried oxide, wrap it in a 9 centimeter filter paper. Place the paper and contents in a 10 cubic centimeter porcelain Gooch crucible, which is equipped with an aluminum wire bail. Weigh the crucible and contents and suspend from the hook of a Wiley-Soxhlet extraction apparatus, as shown in Fig. 10. Fifty cubic centimeters of carbon tetrachloride are placed in the extraction flask, and the whole apparatus is assembled and heated in a water bath. Boil the water and continue the extraction until the droppings from the Gooch crucible remain colorless for at least a half-hour. The extraction will probably be complete in three hours. Remove the crucible and contents to a drying oven and dry for one hour or until no odor of carbon tetrachloride is apparent. Weigh the crucible and contents. The loss in weight will be soluble sulphur and tarry matter.

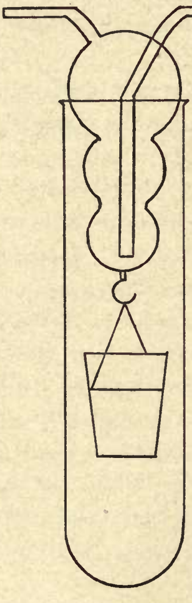

FIG. 10.

Pour the contents of the extraction flask into a 100 cubic centimeter Erlenmeyer flask, and with a little fresh carbon tetrachloride, wash out the former flask into the latter. By means of a cork and bent tube, connect the Erlenmeyer flask with a Liebig condenser and distil on a water bath. When the carbon tetrachloride has been distilled off, add 30 cubic centimeters concentrated nitric acid, warm gently on a sand bath, and add cautiously, at short intervals, potassium chlorate crys-

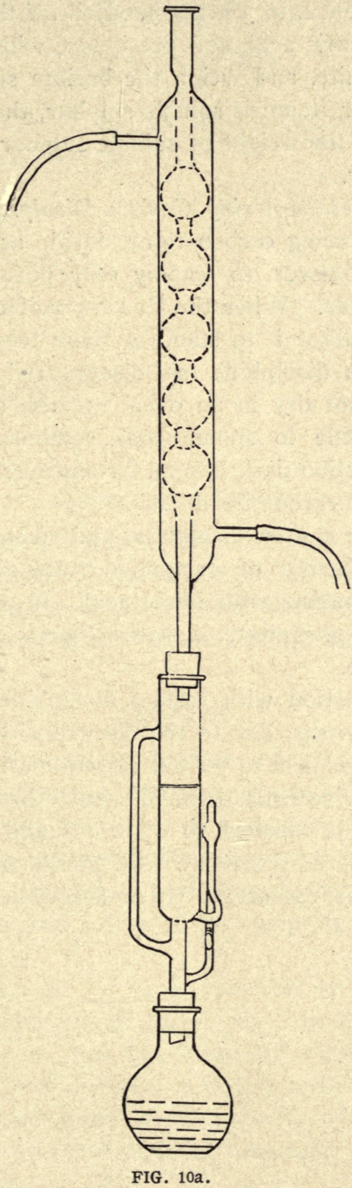

FIG. 10a.

tals, (in all about 2 to 3 grams). Boil off the nitric acid, add dilute hydrochloric acid, and precipitate with barium chloride. Filter, dry, ignite, and weigh the barium sulphate. The per cent. of sulphur found is soluble sulphur, the weight of which deducted from the weight of soluble sulphur and tarry matter gives the latter.

Alternate Method Using Carbon Disulphide.—Proceed exactly as when using carbon tetrachloride as described above, taking care, however, to employ only pure, freshly distilled carbon disulphide. When the Gooch crucible is removed from the extractor, allow it to stand at room temperature until all odor of carbon disulphide has disappeared before weighing. Caution—Do not dry in an oven, because of the liability of carbon disulphide to spontaneous combustion. Empty and wash the extraction flask into an Erlenmeyer flask, using pure, freshly-distilled carbon disulphide.

Distil off the carbon disulphide and remove the last traces by means of a current of air applied to the gently heated flask. Oxidize the contents with nitric acid and potassium chlorate as above, and precipitate in hydrochloric acid solution with barium chloride.

Note.—Extraction with carbon disulphide is liable to give high sulphur results, due to the decomposition of the solvent during and subsequent to the extraction. It is therefore necessary to use only recently distilled carbon disulphide, and when the extraction is finished to distil off and remove the last traces as rapidly as possible. The Gooch crucible is used instead of the usual extraction cup on account of the convenience in weighing.

CHAPTER II.

GAS ANALYSIS.

The following determinations are covered in the analysis of illuminating and furnace gas:

Benzol.
Illuminants.
Carbon Monoxide.
Hydrogen.
Methane.
Ethane.
Carbon Dioxide.
Oxygen.
Nitrogen.

Source of Method.

The method of determining benzol is that due to Pfeiffer, published in *Chemiker-Zeitschrift,* 1904-28-76.

The other methods are those due to the paper by Mr. E. H. Earnshaw, published in the JOURNAL of the Franklin Institute, September, 1898.

Sampling.

The method of sampling depends upon whether it is purified or unpurified under pressure or vacuum. In some instances, it is possible to draw the samples directly into the analyzing burette, but more often they must be transferred to the laboratory in containers specially provided for the purpose. The figures show two forms of gas sampling tubes in general use.

The one shown in Fig 11 is provided with cocks, and is, therefore, somewhat more convenient than the one shown in the Fig. 12, which must be closed by sealing off the ends. These tubes are very useful in taking a sample sufficient for a single analysis, and in the great majority of cases, a tube of this kind will be all the equipment necessary, provided the gas is under pressure.

In taking a sample with the tube as shown in Fig. 11, it is first filled with water and connected to the gas supply by a short piece of hose which, together with the connections, has been thoroughly purged of air and dead gas. The water is then permitted to run out ahead of the gas, after which the outlet cock is closed; then the inlet, which places the gas under a slight pressure and lessens the liability of air being subsequently drawn in by a leakage at the cock.

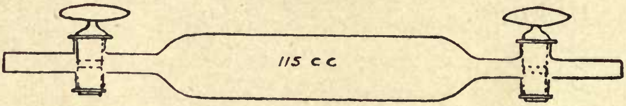

FIG. 11.—Gas sampling tube—with stop cock

This may be further guarded against by dipping the ends of the tubes in melted sealing wax, and, as an extra precaution by placing sealing wax around the exposed portion of the barrel of the cock. This serves the double purpose of preventing the cock from leaking and also from being accidentally turned.

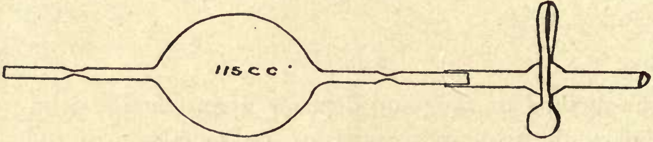

FIG. 12.—Gas sampling tube for sealing.

In using the tube described in Fig. 12 the procedure is the same, except that the end is temporarily closed by means of a short piece of rubber tubing and a pinch cock, as shown in the sketch, after the water has run out. The outlet to the tube is then sealed off at the construction by means of a flame such as that furnished by a gasoline torch or a Bunsen burner. A candle flame may sometimes be used, but it is rare that the glass is soft enough to make the operation easy. Having sealed off the outlet, the inlet is closed in the same way without disconnecting from the gas supply.

When a sample is to be transported long distances or is to be preserved for any great length of time before analysis, it is far better to use sealing tubes, as there is no possibility of leakage unless the end of the tube is broken, and this may be largely guarded against by fusing the end to a blunt point or turning it back upon itself. The tubes may be used repeatedly and when the end gets too short, a short piece of glass tubing may be sealed on.

It is sometimes desirable to collect a sample out of contact with water. In this event, if there is an abundant supply of gas, it should be allowed to flow through the dry tube for 4 or 5 minutes in order to displace the air, and then sealed as described above. When the gas supply is small, mercury should be used to displace the air.

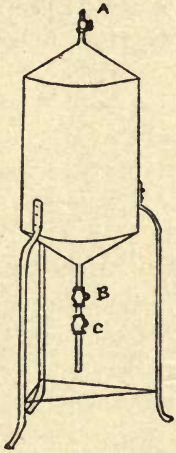

Fig. 13.—Aspirator for large gas supplies.

If a large sample is required, the aspirator shown in Fig. 13 may be employed. This consists of a galvanized iron cylinder with conical base and top having a capacity of about ½ cubic foot. The top is provided with a cock (*A*) and the bottom with two cocks (*B*) and (*C*) as shown. The whole apparatus is mounted on a suitable tripod or stand. It is used ordinarily precisely as the tubes described above. When, as is sometimes necessary, an average sample (of a run) for a definite period is described, the cock *B* is set so that the water will just run out in the stated time. The apparatus is then filled with water and the cock *C* closed. When the apparatus is connected and *C* is opened an average sample of the whole run will be obtained.

Aspirating Tubes.

In sampling gas from services and moderate size mains and connections, a fair average can usually be obtained direct without the use of the aspirating tube. If, however, the gas chamber or passage is large, as for example in a generator or large sized main, such a tube must be inserted as currents are always set up, and a sample taken simply through the shell will not give a correct average. Even when a tube is inserted to the middle of the chamber, it is difficult to get a true average of the gas passing.

Glass aspirating tubes should be used when possible, as they are easily cleaned and they do not act upon, nor are they affected by, the gas passing through them. They may be used in temperatures up to 600° C. (1,112° F.). Lead tubes may be used up to temperatures of 300° C. (527° F.) and are very convenient as they are easily handled and may be bent into any required position. For temperatures higher than 600° C. (1,112° F.) porcelain tubes, platinum tubes, fused silica pipes may be used, or water-cooled iron tubes. Fig. 14 shows a tube which may be made from the ordinary fittings procurable around a gas works.

The tube shown in Fig. 14 is made as follows:

A ¼-inch by ⅛-inch reducing socket is threaded through from the inside to receive the end of a ⅛-inch pipe. Into this socket is screwed a 1¼-inch pipe threaded at both ends of a length depending upon the desired length of the complete apparatus. On the end of the 1¼-inch tube is placed a 1½-inch by 1¼-inch bushing threaded from the inside and through which the 1¼-inch pipe extends about 2 inches. A 1¼-inch cross is screwed on the top of the pipe. One side of the cross contains a 1½- by a ⅛-inch bushing which carries a ⅛-inch nipple 3 inches long, the other side of the cross contains a 1½-inch by ⅛-inch bushing which carries a ⅛-inch nipple 3 inches long, a ⅛-inch *L*, on the inside of the cross and a piece of ⅛-inch pipe of such a length that it extends to within 1 inch of the bottom of the 1¼-inch pipe as shown in sketch.

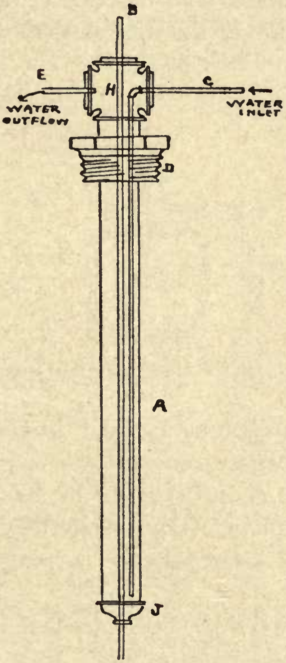

Fig. 14.—Water cooled sampling tube.

The pipe *B*, which consists of a piece of ⅛-inch pipe threaded at one end, is passed through the top of the *T* and threaded through the reducing socket. The top of the pipe is made tight with the top of the cross by means of a lock nut or stuffing box. When in use, the water supply is connected to pipe *C* and the water overflows through the nipple *E*. The complete apparatus, when in use, is held in place by means of the bushing *D*. The sample of gas is obtained from the outlet of the pipe *B*.

It is of very little use to provide branches to, or a slit in, the aspirating tubes, as the currents are of less velocity near the shell due to friction, and besides, with a slit pipe or one drilled with holes, more gas will be drawn in near the sides as the suction here is strongest. The best method is to set up a strong primary current and take the sample from a secondary current at the side of the tube as shown in Fig. 15.

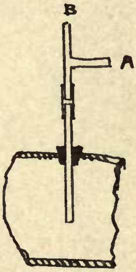

FIG. 15.—Method of supplying from large main.

Fig. 15 shows a glass tube inserted through a rubber stopper into a 16-inch condenser connection. A glass or metal *T* is fastened close to the end of the tube by means of heavy rubber hose, and the sample is taken from the secondary current flowing from *A*, the large primary current all the while flowing from *B*.

The foregoing directions presuppose that the gas is under pressure. If such is not the case, an aspirating apparatus must be employed. For small samples the aspirating bulb shown in Fig. 16 is recommended by analysts.

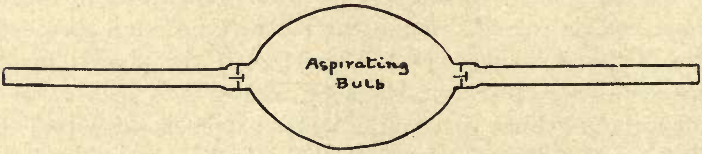

FIG. 16.—Aspirating bulb.

This consists of a small rubber bulb with valves working opposite to each other, thus enabling it to work as a suction, and as a pressure pump. In use, one end of the empty gas sampling tube is connected to the gas supply, and the bulb is connected to the other end, with the valves in such a position that the pressure and relief on the bulb will suck the air out and admit the gas. This should be continued for some time to insure thorough displacement of the air. If there is no objection to water coming into contact with the gas or if mercury be conveniently used, a more satisfactory method is to connect up as shown in Fig. 17 in which *A* is a glass or metal aspirating tube, *B* a rubber tube, *C* the sampling tube. The whole apparatus, including the hose and tube *A*, is filled with water or mercury, and the tube introduced into the stack or flue. Upon opening the cock on the sampling tube, the water or mercury will flow out and the tube will materially increase the pull.

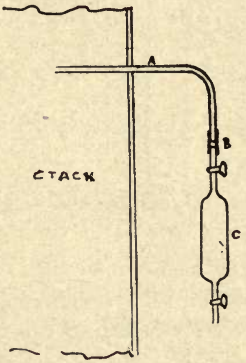

FIG. 17.—Method of sampling from stack and breeching of boiler

Where running water is at hand, a water suction pump may be used to advantage. There are many forms of these pumps in use, but for durability and general adaptability for the purpose, the "Chapman" pump shown in Fig. 18 is probably the most satisfactory. By its use a strong primary sample may be drawn off, and a secondary sample, taken from a side connection as previously explained. A steam jet aspirator may also be employed in the same way where high pressure steam is available. It is shown in Fig. 19 and may be constructed as follows:

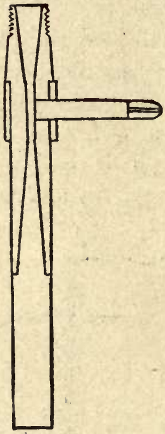

FIG. 18.—Chapman filter pump.

The steam jet aspirator shown in Fig. 19 is made as follows: Two ¾-inch nipples *E* and *J* are threaded into a ¾-inch by ¼-inch reducing tee *A*. *E* is left open for steam exhaust, while on *J* is threaded a ¾-inch union *D*, a ¼-inch pipe is then threaded through a ¾-inch by ¼-inch bushing *H*, one end of which has been hammered down to a point leaving a 1/16-inch opening. The ¾-inch bushing *H* is then threaded into the union *B* and end of piece *C* connected to steam supply. A ¼-inch nipple is then threaded into the ¼-inch connection on tee *A* and connected to place where sample is to be taken from.

Where it is necessary to take samples of crude gas, particularly crude coal gas for the determination of tar, or naphthalene, it is essential that the temperature of the gas be not changed after the sample is withdrawn from the main. It is, therefore, necessary that the sample tube be surrounded with a water bath maintained at the same temperature as the gas in the main. Tubes similar to Fig. 14 should be used for this purpose, water at the proper temperature being supplied with a water-jacket.

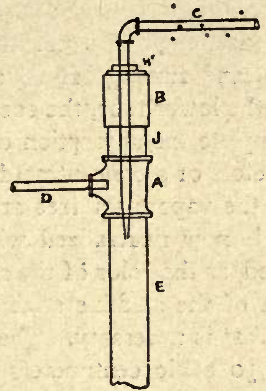

FIG. 19.—Steam or compressed air respirator.

Where crude gas is being sampled for its ammonia content, a certain amount of ammonia liquor exists as a mist in the gas, and at the same time, the walls of the main are also coated with ammonia liquor. It is, therefore, necessary to arrange the inlet of the sampling tube so that liquor collected on it from the gas will flow into the sample. This is best secured by placing an iron tube in the main approximately 83 per cent. of the diameter from one side and inserting in this a slightly smaller glass tube which will be inclined to the sample bottle so that the ammoniacal liquor condensed in the glass tube will be collected in the sample.

Volumetric Determination of Benzols.

The determination depends on the reaction

$$NO_2 + 3SnCl_{12} + 6HCl = NH_2 + 3SnCl_4 + 2H_2O.$$

The gas is treated in a glass stoppered separatory funnel of a known content, the stopper and cork of which have been lubricated with a drop of H_2SO_4, the gas is allowed to blow through the apparatus for 2 minutes, the stopper put in place and the cock closed. The apparatus is disconnected from the source of supply and the cock opened for a moment to insure atmospheric pressure, the barometer and the thermometer are read. Two cubic centimeters of a mixture of equal parts of concentrated H_2SO_4 and fuming HNO_2 allowed to enter the funnel by means of the lower tube, the cock closed, and a half-hour allowed to complete the absorption of the benzol vapors. Thirty cubic centimeters of a concentrated NaOH solution are now added, and all the vapors set free are absorbed by shaking. The solution is now neutralized with very weak HCl; no indicator is needed, as the color of the solution as it changes from an orange red of the alkaline state to a wine yellow of an acid state, is all that is necessary. The solution is now extracted twice with 50 cubic centimeters of ether shaking 5 minutes each time; it is then separated from the other nitro products and put into a flask containing 1 gram of potash and ½ gram of finely powdered animal charcoal, which on shaking and standing, takes out the strong yellow red coloration.

The solution is now filtered into a 200 cubic centimeter graduated flask, and washed with absolute ether, which is evaporated off on a water bath. As soon as this has taken place, 10 cubic centimeters of absolute alcohol and about 10 cubic centimeters of a stannous chloride solution (150 grams of tin dissolved in 50 cubic centimeters of HCl and made up to 1 liter) are added, and the flask warmed for 10 minutes on the water bath. The flask is filled to the mark with water and 20 cubic centimeters are titrated with 1/10 N. iodine solution and starch paste. A blank is run with 10 cubic centimeters of $SnCl_2$ solution, 10 cubic centimeters of alcohol, diluted to 200 cubic centimeters and 20 cubic centimeters titrated. The difference between the two titrations gives the value of the dinitro benzol and is calculated $(b - a)$ 10 x 0.0014 gram. The percentage is calculated 1 gram dinitro benzol = 0.4643 gram C_6H_6, 1 gram of benzol = 279.2 cubic centimeters of vapor of 0° and 760 millimeters. The combined formulae would appear as follows: J = volume of gas

$$\text{Vol. per cent. } C_6H_6 = 0.4643 \times 279.2 \times \frac{(273 = \mathrm{t})\ 760}{273}$$

$$\frac{100}{\mathrm{J}} = \frac{36{,}090}{\mathrm{J}} \times g \times \frac{273 + \mathrm{t}}{b} \times \text{weight}$$

of dinitro benzol or this can be simplified to read where b = barometer, t = temperature, g = dinitro benzol and j = flask content.

Volume per cent. of benzol = $(36{,}090 + j) \text{ x } g \text{ x } (273 + t + b)$.

It is now generally admitted that the accuracy of a gas analysis made by direct absorption in a gas burette is not very great, and that the applicability of the method is also limited by the fact that only those absorbents which do not rapidly attack rubber can be used. On the other hand it is claimed that the time lost in connecting up absorption pipettes and in passing the gas backward and forward is not compensated for by the increased accuracy resulting.

The following apparatus was designed for the purpose of meeting the above objection while retaining the essential features of Hempel's method.

The burette as seen in Figs. 20-21 is similar to that described in Hempel's Gas Analysis on page 28, except that a four-way cock *C* replaces the three-way cock used by Hempel and the burette is bulbed, thereby shortening the same and allowing a finer graduation.

The capacity of the burette is about 105 cubic centimeters, graduated in 1/20 cubic centimeter from 40 to 102 cubic centimeters. It is connected through the capillary tube *D* coming out from the back of the cock *C* with manometer tube *M*. The manometer is connected with the Petterson correction tube *R*. A water jacket *J* surrounds the Petterson tube and burette. A potash absorption pipette *K* which rests on the adjustable stand *S* is connected permanently with the capillary tube *B*.

This modification of Hempel's apparatus has the following advantages:

1. It permits of the potash absorption pipette being permanently attached and so does away with at least five attachments and disengagements of a piece of apparatus disagreeable to handle, saving thereby considerable time and annoyance; for after both the explosion and combustion the gas can be passed directly into the potash without stopping to connect up any other pipettes. This is also true after the absorption of illuminants by bromine and carbonic oxide by cuprous chloride when it becomes necessary to remove the fumes of bromine and hydrochloric acid.

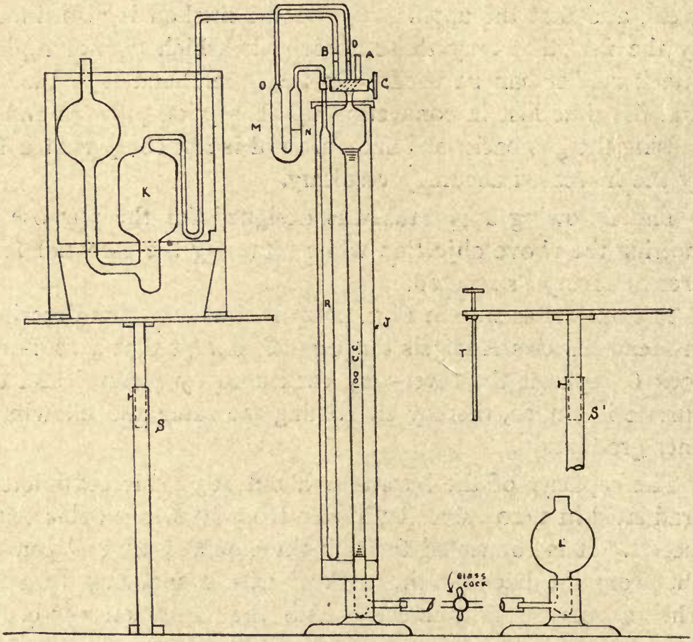

FIG. 20.

2. With the apparatus constructed in the modified form the two limbs of the manometer tube and the perpendicular portion of the capillary tube coming out from the back of cock *C* are in the same plane, so that you connect up the trouble-

some "sagging" of the manometer tube common to Hempel's apparatus is overcome.

3. The bulbing of the burette make the apparatus much less top-heavy and cumbersome and also permits of a much closer reading, as the narrowed portion may be graduated to read to 1/20 cubic centimeter without trouble.

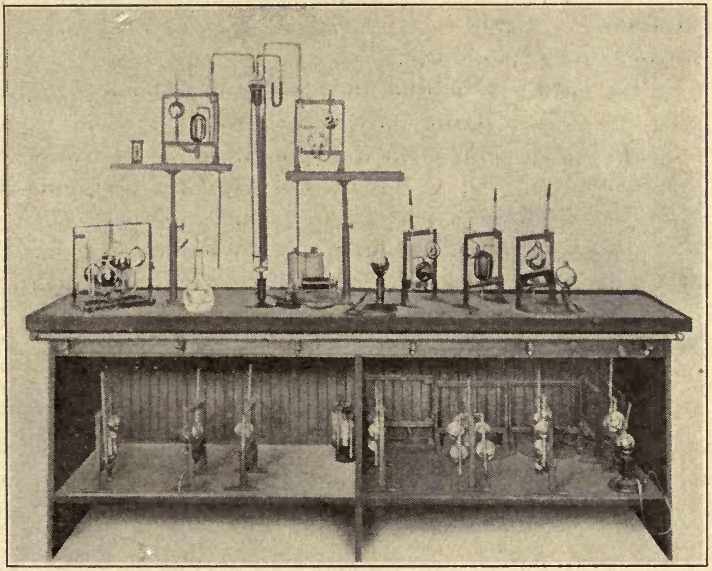

FIG. 21.

Besides the above important modifications, several minor changes have been introduced which greatly reduce the time necessary for an analysis, while not jeopardizing the accuracy of the results.

The following pipettes and reagents are required for the analysis:

A potash absorption pipette which is permanently attached to the burette, as shown in sketch. (For reagent see page 125.)

A pipette filled with strong bromine water. In order that this solution remain concentrated an excess of free bromine is kept in the pipette.

A pipette for solids filled with stick phosphorus covered with water.

A double U. G. I. absorption pipette. This combines in one piece of apparatus the two solutions of cuprous chloride which are necessary to remove the carbon monoxide.

A simple pipette filled with gas-saturated water for storage purposes.

A mercury explosion pipette.

A U-shaped combustion tube containing about ½ gram palladium black is also required.

The following is the method of procedure for an analysis of a gas containing CO_2, C_nH_{2n}, O_2, CO, H_2, CH_4, C_2H_6, and N_2.

Completely fill water jacket with distilled water.

Turn cock *C* so that the interior of the burette *Y* communicates with *A*, open cock *C*, raise levelling bulb *L*, which has been filled with gas-saturated water, until water flows out *A*. Turn *C* so that interior of burette communicates with *K*, and draw over potash solution to just above cock *C*.

Turn cock *C* so that *Y* communicates with *D*, and by raising and lowering *L* and allowing air to escape through *A*, fill *M* with water to *N*. Open *C* to *A* and by lowering *L*, draw in air. Close *C*, raise *L*, open *C* to *D*, and admit air in *M* to *C*, and close *C*.

Disconnect *M* momentarily at *P* and reconnect. The air in *R* is now at atmospheric pressure.

Connect the tube containing gas sample with *A*, using glass connector similar to one used on potash pipette, being careful to displace with water all air that may be in connection. Open *C* to *A*, lower *L* and draw in 100 cubic centimeters of gas. Close *C*, raise *L*, open *C* to *D*, and allow gas to flow into *M* until the water level is at *O*, and close *Z*. Take the reading on burette after allowing a minute for water to run down off the sides of the burette, add 1 cubic centimeter to observed reading for the 1 cubic centimeter gas occupying space between *O* and cock *C*. Disconnect from sample tube or gas supply as the case may be. Open *C* to *B*, raise *L* and allow gas to flow into *K*, until the water from burette reaches the bulbed portion of *K*, being careful to draw the 1 cubic centimeter from manometer and to force that into the potash likewise. Turn *C* to *D* and adjust water-level at *N* in *M*. Turn *C* to *B*, lower *L*, and draw back gas until the potash solution just reaches its previous position above *C* and close *C*. Raise *L* and turn *C* quickly through arc of 180° so as to allow no gas to flow back to *B* while turning cock so that the interior of the burette communicates with manometer *M*. Raise *L* until water in *M* is level with *O*, close *Z* and read burette, adding 1 cubic centimeter to observed reading as before. The difference between this reading and the preceding gives directly the percentage of CO_2 in the gas.

Connect absorption pipette containing bromine to *A* resting it on stand *S*, being careful as before to exclude all air from connections. Open *C* to *A*, raise *L*, and force gas from the burette into the pipette until water reaches the bulbed portion of the pipette, drawing the gas from the manometer tube as before, and close *C*. Shake the bromine pipette slightly until gas is colored by bromine fumes, open *C*, lower *L*, and draw gas back into burette. Close *C*, raise *L*, *C* to *B*, and force all gas immediately into potash. Close *C* to *B*, and open *D*, and adjust water-level. Open *C* to *B*, lower *L*, and draw back gas until potash assumes former position.

Close *C*, raise *L*, adjust water-level and read as before; the difference between this reading and the preceding gives the percentage of C_nH_{2n}. Disconnect the bromine pipette from *A* and connect the phosphorus pipette.

Force the gas over the phosphorus as was done with the bromine pipette, turn *C* to *D*, raise *L* and adjust water-level, close *C*. If no white fumes are given off by the gas when in the pipette it is a sure indication that all of the C_nH_{2n}, compounds in the gas have not been completely removed. In this event it is necessary to again pass the gas into the bromine pipette. If fumes are given off, wait a minute or two to allow them to partially condense, then open *C* to *A*, lower *L*, and draw gas back into burette. Close *C*, raise *L*, open *C* to *B*, adjust water-level at *O*, and take reading. The difference between this reading and the preceding gives per cent. oxygen present. Disconnect phosphorus pipette and connect double absorption pipette containing cuprous chloride, being careful to have all capillaries filled with the solution. Open *C* to *A*, raise *L*, and force all gas over one solution of cuprous chloride. Shake for two or three minutes and then draw gas back into burette until solution just passes cock on cuprous chloride, pipette, turn this cock so as to connect with other solution of cuprous chloride, raise *L*, and force gas over second solution to remove last of carbon monoxide, and close *C*. Shake for a few minutes, draw gas back into burette, and then immediately force it into the potash pipette. Adjust water-level, draw gas back from potash pipette and take reading.

The difference between this reading and the preceding gives percentage of carbon monoxide.

It is important to notice that even with the precaution of using two pipettes with freshly prepared cuprous chloride the absorption of the carbonic oxide is seldom complete, usually a trace remaining unabsorbed. However, this fact introduces no error in the analysis, as this residue of carbonic oxide can be determined by the combustion made to determine hydrogen.

The residue of the gas mixture remaining after the absorptions may consist of the following:

$$H_2 + CO + N_2 + CH_4 + C_2H_6, C_3H_8, \text{etc.}$$

For all ordinary purposes it is sufficient to assume that the highest paraffine present is C_2H_6, as all others higher than this exist only in traces.

There being no satisfactory known absorbent for any of these gases, recourse is had to the method of combustion.

The analysis is accordingly continued as follows:

The double absorption pipette is replaced by the storage pipette containing gas-saturated water. Pass approximately 15 cubic centimeters of the residue back into the potash by opening *Z*, raising *L* and opening *C* to *B*. Turn *C* to *A*, and pass remainder of residue into storage pipette. Close pipette with a pinch-cock and disconnect. Adjust water-level in *M* at *N*. Turn *C* to *A* and by lowering *L* draw into the burette about 85 cubic centimeters of air. Close *C* raise *L* and open *C* to *D* draw the gas stored over the potash into the burette, close *C* raise *L*, turn *C* quickly through arc of 180° to connect with *D* adjust water-level at *O*, close *Z* and take reading. The increase over the previous reading is the amount of gas taken for the explosion.

Connect mercury explosion pipette at *A* and pass mixture of gas and air into pipette and explode, first partly withdrawing glass connecting tube from rubber connection and placing clip on same.

Adjust water-level in *M* at *N*, draw back gas from explosive, pipette and measure contraction resulting from the explosion. Pass the gas into potash, and the resulting contraction gives the amount of carbonic acid formed during the explosion. Disconnect explosion pipette and connect phosphorus pipette. Pass gas residue over phosphorus to remove all oxygen in excess of that which was required for explosion and measure the amount of nitrogen left. This gives nitrogen introduced with gas. By subtracting amount of air used for explosion X 79.2 from this reading, one obtains nitrogen introduced with gas for explosion. This multiplied by factor obtained by dividing the amount of gas residue taken for the explosion into the whole amount of gas left after absorbing carbon monoxide, gives the total nitrogen in the original sample of gas taken for analysis. The percentage of nitrogen thus obtained should check that obtained by subtracting the sum of the other constituents in the gas from 100.

The equations obtained from the explosion are as follows:

(1) Contraction in volume $= 3/2H_2 + \frac{1}{2}CO + 2CH_4 + 2\frac{1}{2}C_2H_6$.

(2) CO_2 formed $= CO + CH_4 + 2C_2H_6$.

(3) Residual nitrogen $= N_2 + N_1$.

Where N_1 is the nitrogen introduced with the air.

An examination shows that the equations 1 and 2 contain 4 unknown quantities and therefore two more equations are needed for the solution. Fortunately, the method of fractional combustion over palladium affords the needed information. As is well known, when a mixture of hydrogen and CH_4 with oxygen or air is passed over heated palladium black, the hydrogen burns to H_2O, but the CH_4 remains unaltered. If CO and any of the higher paraffines are also present, the CO burns, but the paraffines do not.

Returning to the analysis, proceed as follows: Fill burette to *A* by raising *L*, adjust water-level at *N* in *M*. Draw in about 70 cubic centimeters air and measure it.

Connect storage pipette and draw in about 30 cubic centimeters gas residue, and measure, the increase in volume giving the amount of gas taken for combustion.

Place explosion pipette with mercury level about one-half up to capillary, on stand *S*, connect combustion tube to *A* and explosion pipette, equalize pressure in combustion tube and gas burette and re-measure gas in burette. Place combustion tube in hot water by resting beaker containing water on *T* and pass gas mixture backward and forward over palladium until there is no further contraction, measure gas and decrease in volume gives contraction due to combustion of hydrogen and carbon monoxide. The equations are:

(4) Contraction in volume $= 3/2H_2 + \frac{1}{2}CO$.

(5) CO_2 formed $= CO$.

From these two equations, the value of hydrogen and CO may be readily determined.

For the sake of simplicity, let us now assume that the same quantity of gas residue was used in both the explosion and the combustion.

We may then subtract equation (4) from (1) and (5) from (2), whence, designation the difference between the contraction due to combustion by the letter (*a*) and the difference in the CO_2 formed by the letter (*b*) we find

(6) $2\ CH4 + 2 - \frac{1}{2}\ C_2H_6 = a$.

$$(7)\quad CH_4 + 2\,C_2H_6 = b.$$

whence
$$(8)\quad C_2H_6 = \frac{4b - 2a}{3}$$

and
$$(9)\quad CH4 = \frac{4a - 5b}{3}$$

A very useful check on the accuracy of this determination is obtained from the following:

Volume of gas taken for explosion $= H_2 + N_2 + CO + CH_4 + C_2H_6$. $H_2 + CO$ are found by (4) and (5), and N is given by (3).
Therefore, we have

$$(10)\quad \text{Volume taken} = (H_2 + N_2 + CO) = CH_4 + C_2H_6$$

and this value should be the same as the algebraic sum of (8) and (9) or

$$(11)\quad \text{Volume taken} + (H_2 + N_2 + CO) = \frac{2a - b}{3}.$$

This method if carefully pursued will give results that are extremely accurate, and what is much to be desired, the method is very rapid. Analyses have repeatedly been made in from 30 to 35 minutes.

The Modified Elliott Gas Analysis Apparatus.

This apparatus is shown in Fig. 22. It consists of three glass tubes marked *A, B,* and *C,* mounted on an iron stand.

Tube *A,* called the absorption or laboratory tube, has a one-way stop-cock, 1, at the top, and three-way stop-cock at the bottom, 2. The funnel, 3, is ground to fit the top of *A,* and has two marks 10 cubic centimeters and 20 cubic centimeters etched on the glass. The lower outlet of cock 2, drains to the sink through a piece of rubber tubing. The side outlet is connected with level bottle, 4, by another piece of rubber tubing which is long enough to allow bottle 4 to be placed on the shelf above the apparatus. There is a 100 cubic centimeter mark near the lower end of *A*.

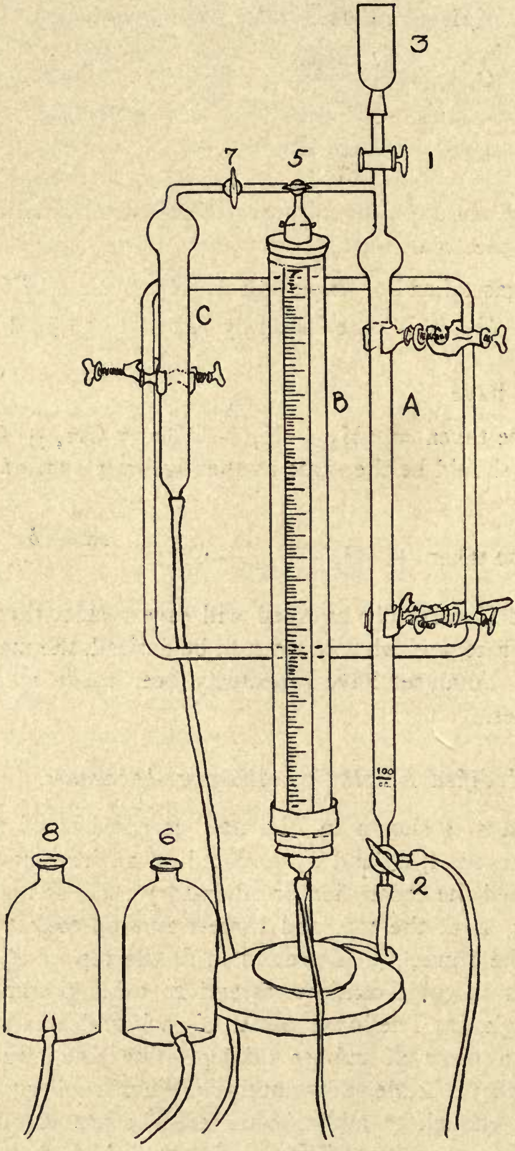

FIG. 22.

Tube, *B,* is called the explosion tube. It is graduated to 100 cubic centimeters in 1/10 of a cubic centimeter. It has a three-way stop-cock, 5, the arms of which are connected to tubes *A* and *C* by means of short pieces of rubber tubing, the connections being made by bringing the glass side pieces close together and fastening the rubber with fine wire. The level bottle, 6, is connected with the lower end of *B* by a rubber tube long enough to allow the bottle to be placed on the shelf above. The upper end of *B* has two platinum wires fused into the glass. The electrodes are attached to these wires when the gas is to be exploded. *B* is enclosed in a water-jacket which extends from the platinum wires to below the 100 cubic centimeter mark.

Tube *C,* called the residual tube, is a plain glass tube having a one-way stop-cock, 7, and a level bottle 8. Connection is made with *B* as described above.

REAGENTS.

Sodium hydroxide 10 per cent. solution.

Pyrogallic acid 10 per cent. solution, used by mixing in the funnel with equal volume of 10 per cent. sodium hydroxide.

Acid cuprous chloride, made as follows:

Four hundred grams chloride dissolved in 1,800 cubic centimeters hydrochloric acid, (specific gravity 1.2) to this solution add 400 cubic centimeters water. This solution is to be kept in a bottle containing pieces of copper wire.

Fill bottles 4, 6, and 8 with water and place them on the shelf above the apparatus. Open stop-cock 1, turn 5 so that *C* is connected with *A*. Then open 7, allowing water from bottle 8 to fill tube *C* and pass into *A*. Close 7 and turn 5 so that *B* is connected with *A,* allowing water from 6 to fill *B* and pass into *A,* then shut off 5. Turn 2 so that water from 4 fills *A* and flows out at 1, then close 1. The apparatus is now filled with water and the next step is to transfer the gas into it from the collection tube. Before doing this, examine the apparatus to see if there are any air bubbles imprisoned in it, paying particular attention to the capillary tubes in the upper part. If any bubbles are seen, drive them out with water from the level bottles.

The sample of gas is transferred to the apparatus by removing funnel 3, replacing it with a piece of soft rubber tubing which is filled with water, and attaching the collection tube and passing the gas into *A* in the usual manner. When the gas fills *A* to below the 100 cubic centimeter mark, cock 1 is closed and the collection tube detached.

METHOD OF ANALYSIS.

Place the funnel 3 on the tube *A*. Set bottle 4 on the shelf and bottle 6 on the table. Turn cock 5 to connect *B* with *A* and turn cock 2 so that the gas in *A* passes *slowly* into *B*. While the gas is passing into *B*, raise bottle 6 and hold it so that its water-level coincides with the 100 cubic centimeter mark on *B*, and at the same time regulate the speed of the gas by manipulating cock 2. When the meniscus in *B* reaches the 100 cubic centimeter mark, close cock 2, and without changing the position of bottle 6, reach up and close cock 5. Place bottle 6 on the table and wait one minute to allow the water adhering to the inside of *B* to run down, then raise bottle 6 bringing its water-level to that in *B* and verify the volume in *B*.

Note.—If the transfer of gas from *A* to *B* is done very slowly, it will be found that the water adhering to the inside of *B* will all have run down at the same time that the meniscus in *B* reaches the 100 cubic centimeter mark.

After making sure that there is a volume of 100 cubic centimeters of gas in *B*, place bottle 4 on the shelf, open cock 1 and turn cock 2 so that the water in 4 will drive out the gas left in *A*. Open cock 7 and allow the water from *C* to pass into *A* driving out the gas left in the capillary tubes between *B* and *A*. Close cocks 7 and 1.

It will be noticed that there is a little gas above the zero mark in tube *B*. This is less than 1/10th of a cubic centimeter and may be ignored, or it may be compensated for during the analysis by allowing the water from *A* to come only to the cock 5 when gas is being transferred from *A* to *B*.

Place bottle 4 on the table and bottle 6 on the shelf, turn cock 5 to allow the gas in *B* to pass into *A*. When the water from *B* has reached the capillary above the bulb of *A*, close 5. Do not allow any unnecessary water to flow from *B* into *A*. Now pour 10 cubic centimeters of the sodium hydroxide reagent into the funnel 3, and slightly open 1, allowing the reagent to pass into *A*. At the same time, manipulate 1, and give the whole apparatus a rotary motion on its base to spread the reagent over the inner surface of *A*. Let the reagent enter slowly and spread evenly. Use only 10 cubic centimeters of this reagent; it is unnecessary and dangerous to use more, because 10 cubic centimeters will absorb about 50 cubic centimeters of CO_2 and any excess is liable to absorb a few tenths of a cubic centimeter of illuminants for every 10 cubic centimeters of the reagent. Close cock 1 when the reagent is near the bottom of the funnel, and be careful not to allow any air to enter tube *A*.

Open cock 5 slightly, allowing water from *B* to wash out any reagent that may have crept into the capillary tubes between *A* and *B*. Place bottle 4 on the shelf and bottle 6 on the table and drive the gas from *A* into *B*, shutting cock 5 when the water from *A* reaches it. When the gas is back in *B* and cock 5 closed, open cock 1 and turn cock 2 so that the water in *A* will pass through its lower outlet into the sink.

When *A* is empty, fill funnel 3 with water and allow this water to flow down and spread on the inside of *A* in the same manner that the reagent was applied. This washes tube *A* clean. While doing this, open cock 7 to allow water from *C* to wash out the capillary tubes. Close cock 7. When *A* is thoroughly washed, turn cock 2 to connect its lower outlet with bottle 4 thus washing out the rubber tube connecting *A* and 4. Turn cock 2 so that its lower outlet connects with *A*, fill the funnel with water and again wash out *A*. Turn cock 2 so that water from 4 may enter *A* and when the water reaches the 10 cubic centimeter mark on the funnel, close cock 1.

Now take bottle 6 from the shelf and bring its water-level to the meniscus in *B*, and carefully note the graduation on *B* where the two levels coincide. Note the reading. This reading subtracted from 100 will be the percentage of carbon dioxide, CO_2 in the gas.

The above method of applying reagents, manipulating the apparatus, excluding air and washing out and preparing for the next absorption refers to all subsequent operations except the following:

Illuminants are absorbed by adding 3 drops of bromine to the water in the funnel and causing the bromine to enter *A* very slowly and spread evenly, sodium hydroxide is then used to absorb the bromine vapors.

Caution.—The bottle from which the bromine is taken should never be lifted to the funnel 3, as serious accidents may occur. This bottle should be on the table and the small quantity needed removed by a pipette dropper to the funnel.

Oxygen is absorbed by a mixture of 5 cubic centimeters each of the pyrogallic acid and sodium hydroxide solutions. These are poured into the funnel from their respective bottles, and well mixed.

Carbon monoxide is absorbed by 20 cubic centimeters of acid cuprous chloride solution. This reagent must be added a little at a time, waiting half a minute between each addition as its action is slow. After absorption of CO place about 10 cubic centimeters of water in the funnel and allow it to enter *A*, spreading evenly and washing down the white salt. The object of adding water is to absorb the acid vapors.

The residual gas consisting of hydrogen, methane and nitrogen is passed into tube *C* retaining 12 cubic centimeters in tube *B*. Tube *A* is filled with air to the 100 cubic centimeter mark and air is passed from *A* into *B* mixing with the 12 cubic centimeters of gas until the volume in *B* is about 72 cubic centimeters. This proportion is not absolute and must be found by experiment as it varies for different gases. The above volume is usually correct for carbureted water-gas. The excess air in *A* is expelled, and the contents of *B* passed to and fro between *B* and *A* to thoroughly mix. When finally mixed the volume in *B* is read, bottle 6 is placed on the floor and the gas exploded by an electric spark. After waiting three minutes the volume in *B* is read. The CO_2 formed by the explosion is absorbed by the sodium hydroxide, the gas is then passed back to *B* and the volume again read. The oxygen remaining in the gas is then absorbed by alkaline pyrogallol and the final volume read.

The hydrogen, methane and nitrogen are calculated as follows: Let R be the residual gas, T the gas taken for explosion (12 cubic centimeters), C the contraction after explosion. D the CO_2 absorbed. Then,

$$\text{Hydrogen in T} = \frac{2\,C - 4\,D}{3}\ (H\,T);\ \text{Hydrogen in R} = \frac{H\,T \times R}{T}$$

$$\text{Methane is T} = D; \qquad \text{Methane in R} = \frac{D \times R}{T}$$

The sum of all the constituents subtracted from 100 will give the nitrogen. There are two methods of varifying the above results:

1. Subtract the sum of the hydrogen and methane in T from T, multiply this result by R and divide by T. This gives the per cent. of nitrogen which should come within 1/10 of one per cent. of the nitrogen found by difference. Expressed in formulas this would be,

$$T - (HT + D) = \text{Nitrogen in T.} \quad \frac{NT \times R}{T} = \text{Nitrogen in gas.}$$

2. Multiply the air added by 0.791; this gives the nitrogen in this air volume. Subtract this from the final reading; this gives the nitrogen in T, (NT). Multiply this result by R and divide by T. This gives the nitrogen in the gas. Expressed in formulas this would be:

Volume 1 — T = air taken for explosion, (A)
A × 0.791 = nitrogen in A, (NA)
Final reading — NA = nitrogen in T, (NT)

$$\frac{NT \times R}{T} = \text{nitrogen in gas.}$$

This result should agree within one per cent. of the nitrogen found by difference. If all the calculations have been found correct and a difference exists then this is due to the presence of ethane. In this case the per cent. of nitrogen found by method 2 is added to the sum of all the other constituents, except methane, and the difference between this sum and 100 considered as methane.

The Morehead Apparatus.

This type of apparatus has been used for the past fifteen years in the laboratories of The Peoples Gas Light and Coke Company of Chicago, and by other large companies.

The gas analyzing apparatus as shown in Fig. 23 consists of a graduated burette (4) fitted with platinum electrodes (13) and a storage bulb (6). The three aspirator bottles (7, 8 and 9) with rubber tubing (14, 15, 16 and 17), and an electric sparking outfit are also required. Both glass pieces are fitted with three-way cocks (1, 2 and 3). The measuring, explosion, washing, and the entire analysis is made in the graduated burette; the bulb (6) is used only for storage of the reserve supply of gas after the CO absorption in case the explosion is unsatisfactory. The burette (4) is usually provided with a water-jacket (11) consisting of a large glass tube confining by large rubber stoppers at the ends clear distilled water. A bottle or beaker (10) is placed under cock (2) to form a seal and catch waste reagents and wash water. A removable funnel or cup (5) is attached to burette capillary tube at the top by a ground joint. A secondary funnel (12) beneath (5) serves to drain away excess reagent or wash water by means of drain tube (18).

In preparing the apparatus for an analysis, first fill the aspirator and seal bottles (8, 9 and 10) and the levelling bottle (7) with distilled water previously saturated at the temperature of the water-jacketed buretted with the gas to be analyzed, and place aspirator bottles (7, 8 and 9) on shelf (21). By manipulating cock (3) displace all air from rubber tubing (15, 16 and 17) until water entirely free of bubbles flows upward through ground joint into cup (5). Then open cock (2) to seal bottle (10) and purge all air out of tube (14) through

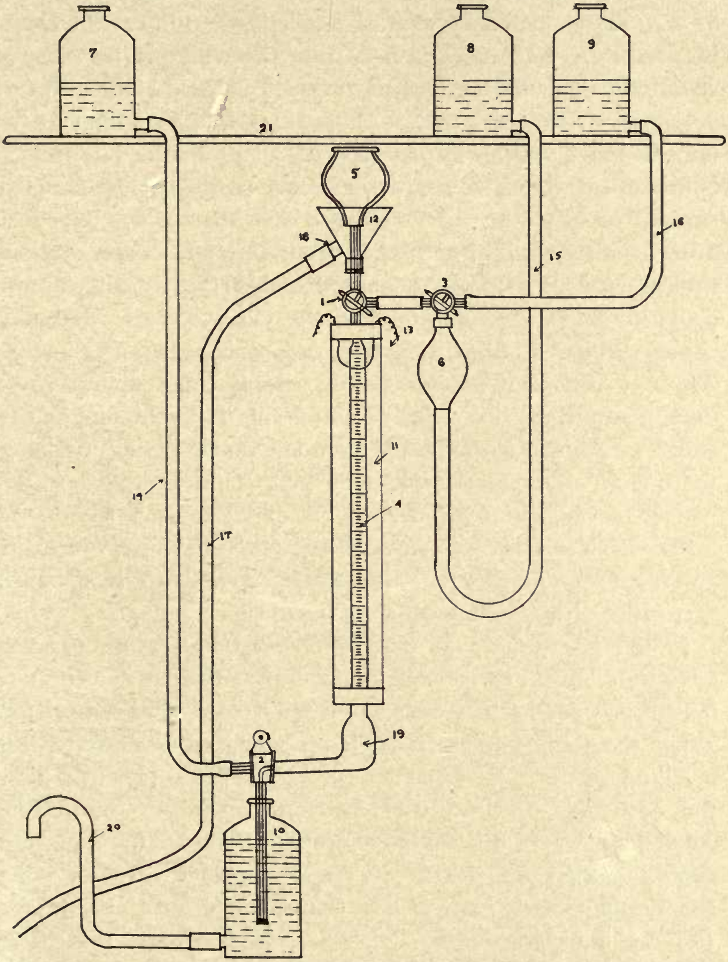

FIG. 23.

cock (2) into seal bottle (10). Similarly open cock (2) to burette (4) and fill same with water up to funnel. When the apparatus is quite full of water, as described, remove cup (5) open cock on sampling can or pipe from which the sample is to be taken, allow gas to blow through the hose for a few seconds to insure the explosion of all air, and then attach hose to the ground joint end of the capillary tube at the top of the burette. Turn cock (2) so that the water in burette (4) communicates with the levelling bottle (7), held level with funnel (5). Now open cock (1) so that the gas sample enters burette only, and as the surface of water in the burette (4) is depressed, slowly lower the levelling bottle (7), keeping the surface of water in same slightly above that in the burette in order to insure no inward leaks of air through loosely attached tubing, etc. When the gas has displaced nearly all water to about a point (19) in the burette, close cock (1), remove rubber tubing at top of burette and replace cup (5). Open cock (3) for a few seconds and expel gas from capillary tubes until water flows into cup (5) and fills it about one-quarter full. If the sample is taken from the house piping, or where there is an abundant sample, it is well to allow the gas to flow entirely through the burette and out at the lower stop-cock for a few seconds, care, of course, being taken to purge out excess gas from stem of cock (2) into bottle (10) before securing the 100 cubic centimeter sample for analysis.

If the gas sample be at a different temperature than the burette, allow it to remain in the burette for a few minutes before proceeding to secure the desired 100 cubic centimeters. When the gas has assumed the temperature of the burette, raise levelling bottle (7) so that the water-level is sufficiently above the 100 cubic centimeter graduation of the burette to force small bubbles of the confined sample through the water into cup (5), when the cock (1) is slightly opened. Bubble excess gas sample slowly outward in this manner until closing cock (1) and lowering bottle (7), its water-level and that in the burette are at the 100 cubic centimeter mark. If the zero mark of the burette be at the cock (1), then the 100 cubic centimeter mark is taken for a levelling point as just described, but if the zero graduation be at the point of capillary retention, where the capillary tube immediately below cock (1) widens into the burette proper, then excess gas is bubbled outward, until the water-levels in the bottle (7) and burette (4) are at a mark equal to 100 cubic centimeters, minus the previously determined volume (usually 0.3 or 0.4 cubic centimeter) of the capillary tube between cock (1) and the zero graduation at the point capillary retention. In the latter case, after adjusting the burette water-level a 99.7 or 99.6, as the case may be, bottle (7) is placed on a level with (10) and the cock (1) is slightly opened until the water in cup (5) slowly enters the burette capillary tube at the top to the point of capillary retention, when it will be found upon raising bottle (7) that the water-level corresponds with the one in the burette, which will be at the 100 cubic centimeter graduation.

When there is just 100 cubic centimeters in the burette the analysis may be started.

Turn the cock (2) so as to connect the burette with the bottle (10) raise the funnel (5) until it is just off its ground joint and drain, leaving about ¼ inch of water in the bottom. Lower the funnel onto its seat and put into it about 20 cubic centimeters of potassium hydrate solution. Be sure that cock (2) is set so that the burette is connected with (10). Now open cock (1) and let the potassium hydrate solution *drain* very slowly into the burette. When it has nearly all gone into the burette close cock (1) and open cock (3) and let water from bottle (8) or (9) through into the funnel (5) for about ten seconds. Rinse the funnel and fill it with about 50 cubic centimeters of distilled water previously saturated with the gas being analyzed. Pass this wash water *slowly* through the burette. Then turn cock (2) so that burette is connected with bottle (7), and read the contraction of the gas, at the same time holding the bottle (7) with the surface of the water in the bottle, level with the surface of the water to the burette; also note the reading on the burette graduations coinciding with the bottom of the meniscus of the water-level in the burette. The amount absorbed as indicated by the contraction in cubic centimeters, or difference in cubic centimeters, between the 100 and the burette reading, equals the per cent. of carbon dioxide.

Turn cock (2) to connect the burette with the bottle (10), and with a 1 cubic centimeter pipette put about two drops of bromine into the funnel (5) which should contain about 20 cubic centimeters of distilled water. Drain this *slowly* into the burette, as in the previous operation, until the entire gas space in the burette is filled with reddish brown bromine fumes, then admit the rest of the bromine and most of the water in the funnel. Next pour into the funnel about 30 cubic centimeters of potassium hydrate solution and drain part of this solution in slowly until the water ceases to rise and the burette and the surface of the water are quite free from bromine fumes. Wash with about 75 cubic centimeters of aerated distilled water. Wait two minutes and measure as explained above. The amount absorbed in cubic centimeters equals the per cent. of illuminants.

Now place in cup (5) about 20 cubic centimeters of pyrogallic acid solution, and add 20 cubic centimeters of KOH solution and allow mixing to take place naturally for about ten seconds, then drain this through, wash out the burette with about 75 cubic centimeters of distilled water and measure in the way previously explained, after waiting at least two minutes for gas to resume temperature of burette jacket. The resulting contraction in cubic centimeters equals the per cent. of oxygen.

Next place about 40 cc. of copper monochloride solution in the funnel and drain through very slowly until no further contraction is observed. Then if no reagent remains in cup (5) add 10 cubic centimeters of same reagent and pass it through the burette. Pass in about 50 cubic centimeters of distilled water and after this 10 cubic centimeters KOH solution, drain through and wash out with about 100 cubic centimeters of distilled water. The amount absorbed in cubic centimeters equals the per cent. of carbon monoxide. This reagent should be added rather slowly and several minutes allowed for its action on the CO.

The carbon monoxide is the last constituent to be determined by absorption. Of the remaining three, two must be determined by an explosion and the third by difference.

Make a careful note of the reading of the burette after the CO absorption, as this figure has to be used in the H_2 and CH_4 calculation.

Turn cock (2) so as to give connection between bottle (7) and burette, cock (3) so as to connect (7) through burette (4) and bulb (6) with (8). Place (8) on the table level with (10) and hold (7) so that its water-level is opposite the graduation indicating 10 cubic centimeters. Now open cock (1) carefully and allow gas to pass very slowly through cocks (1) and (3) into the storage bulb (6). When all but exactly 10 cubic centimeters has passed into the bulb (6) close cocks (1) and (3) and place bottle (7) on a level with (10). Pass a little water from (9) directly into the cup (5) so as to get all of the gas out of the passages between the bulb (6) and the cup (5). Also open cock (1) slightly and allow water to pass from cup (5) into burette to zero mark. By manipulating (7) have the amount of gas in the burette exactly 10 cubic centimeters. A small excess may be gotten rid of through cock (1) and the funnel (5). Turn cock (2) so as to connect burette (4) and bottle (10); remove funnel (5) and connect oxygen hose to top capillary tube. Then open cock (1) and let about 20 cubic centimeters of oxygen enter. Remove oxygen tubing and allow about 10 cubic centimeters of air to enter burette; exact proportion of oxygen and of air admitted to burette are not essential. Close cock (1), allow water to pass from (9) through (3) and (1) into cup (5), and with bottle (7) lowered, open cock (1) until water passes into burette to zero mark. Then read contents of the burette accurately. The quantity of the mixture in the burette should be in the neighborhood of 40 cubic centimeters. Attach wires to the electrodes on the sides of the burette, turn cock (2) so that the burette is connected to the bottle (7), see that tubing is straight and cause a spark to pass between the electrodes. After the explosion allow the gases to stand at least three minutes before reading the burette. Measure the contraction. This contraction is known as the "1st contraction." Make a note of this, then place about 20 cubic centimeters of potassium hydrate solution in the funnel (5) and drain the burette. Wash with about 100 cubic centimeters of air saturated distilled water and measure. The contraction due to absorption by the KOH solution is known as the "2nd contraction." The amount of gas left after the absorption for CO, divided by the amount taken for the explosion is called the "constant."

The amount of hydrogen in the original mixture is equal to the first contraction multiplied by two, minus four times the second contraction divided by three and multiplied by the constant.

FORMULA FOR H_2

Per cent. by vol. of H_2 =

$$\frac{2 \times (\text{1st contraction}) - 4 \times (\text{2nd contraction})}{3} \times \text{constant.}$$

Per cent. by vol. of CH_4 = 2nd contraction × constant.

The constituent which we call "methane"—CH_4—often contains in addition ethane—C_2H_6—especially in rich gases and in natural gas from wells which are approaching exhaustion.

The ethane present is burned to the explosion and is reported as methane increasing the per cent. of methane slightly, and lowering to the same extent the percentage of hydrogen and of nitrogen.

It may, however, be readily determined separately if it is desired. The hydrogen must first be separately absorbed by means of a palladium tube. This is done by adding to 10 cubic centimeters of the residual gases oxygen and air just as directed above for explosion.

The palladium tube is installed between the burette and the storage bulb. A beaker containing water, which is kept at the boiling-point by a Bunsen lamp, is so placed as to have the loop of the tube immersed in the hot water. An accurate reading of the amount of mixture is then taken and the mixture passed very slowly through the tube into the storage bulb and then back. Care must be taken not to pass the gas through the tube too rapidly, or the heat generated is apt to break up some of the methane. The palladium does not really absorb the hydrogen from the mixture, but by a catalytic action causes it to combine with the oxygen present and form water, and hence two-thirds of the contraction due to passage of the mixture over the palladium is the percentage of hydrogen. The known volume of mixture after the hydrogen absorption is then exploded and the contraction noted.

A second contraction due to the absorption of the carbon dioxide by KOH formed is also noted.

The volume of the methane and ethane may then be calculated from the following formulae;

First contraction, due to condensation of water formed, and

Second contraction, due to the absorption of carbon dioxide formed,

$$\text{Per cent. by vol. of } CH_4 =$$

$$\frac{4 \times (\text{1st contraction}) - 5 \times (\text{2nd contraction})}{3} \times \text{constant.}$$

$$\text{Per cent. by vol. of } C_2H_6 =$$

$$\frac{4 \times (\text{2nd contraction}) - 2 \times (\text{1st contraction})}{3} \times \text{constant.}$$

The difference between the sum of all the percentages found by the above determinations and 100 is the percentage of nitrogen.

GENERAL NOTES FOR ANY TYPES OF APPARATUS.

SOLUTIONS.

1. The potassium hydrate, or hydroxide solution, is made by dissolving 5 parts by weight of chemically pure potassium hydroxide (purified sticks) in 100 parts by weight of distilled water. This solution should be kept in well stoppered bottles using rubber stoppers to prevent sticking and deterioration of solution due to absorption of carbon dioxide from the air. The same hydrate solution is used for the absorption of CO_2, of bromine fumes and with the pyrogallic acid for oxygen, and

of CO_2 after methane. The hydroxide which comes marked "Pure by Lime" is better for this use than that marked "Pure by Alcohol."

2. The pyrogallic acid solution is made by dissolving 10 parts by weight of chemically pure pyrogallic acid in 100 parts by weight of the above hydrate solution. To every 1,000 parts by weight of this solution add 5 parts by weight of oxalic acid as a preservative.

Do not mix the pyrogallic acid solution with the potassium hydrate solution except in the funnel and until quite ready for use, as the potassium pyrogallate thus formed will absorb oxygen from the air and lose its strength. At least two minutes should be given the oxygen absorption with potassium pyrogallate when flue gases or engine exhaust is being analyzed.

3. The copper monochloride solution is made by dissolving 75 parts by weight of chemically pure copper monochloride in 720 parts by weight of concentrated hydrochloric acid, to which has been added 400 parts by weight of distilled water. Ten or twenty grains or more of clean bare copper wire or foil should be added and kept constantly in the bottle with the mixture to prevent deterioration. When a small quantity of the solution is added to a large amount of water a cloudy white precipitate of copper monochloride appears. When no cloudiness is thus produced, and the mixture shows a blue tint, the preparation has become oxidized and is unreliable.

4. Gas-saturated distilled water may be prepared by passing gas through the water at a temperature not less than, and preferably a few degrees above, that at which it is to be used so as to avoid evolution of the dissolved gases in the burette.

5. Distilled water may be sufficiently aerated by shaking it vigorously for two or three minutes in a large bottle three-quarters full of distilled water.

Apparatus.

6. The apparatus may be cleaned from time to time by running through it a solution of potassium bichromate in sulphuric acid. This is useful, when the platinum points become

coated with carbon. This cleaning solution should be used with care, as sudden mixing of the sulphuric acid solution with the water in the burette generates considerable heat which may break the burette.

7. For constant use it is well to install the water-jacketed burette by means of clamps attached to a permanent pipe stand supporting shelf over a sheet lead drain. The electrodes leading from burette are insulated from the water-jacket by rubber tubing, containing copper wires fused to the platinum leads and leading to the terminals of a ¼-inch spark coil, operated by at least two ordinary dry batteries. A drain funnel connected by rubber tubing to a glass tube of ¼-inch bore extending to sink or drain pipe, will be found of great convenience in a permanent installation for getting rid of waste from funnel or cup. A drain tube leading from bottom of the seal bottle upward and curved in a semi-circle at the top so that the outlet is level with the desired water-level in the bottle will be found advantageous in securing cleanliness.

8. Rubber tubing should be of the heavy-wall, pure gum variety, and of such internal diameter as to give tight joints over the glass tubing, etc. The joints should be wired to insure freedom from leaks incident to loosely attached tubing.

9. By keeping the apparatus and all of the bottles filled with water, especially when not in use, and the reagent bottles in immediate proximity, the entire outfit acquires about the temperature of the room, and the error arising from the source of temperature in the sample is eliminated.

10. The explosions take place in the explosion burette. A coil which will give a ¼-inch spark is ample. Too strong a spark is apt to crack the glass as is a continuous play of sparks between the points, or a play of sparks when the burette is dry. If the explosion does not occur simultaneously with the first spark, the spark need not be continued. Something else is wrong. The usual trouble is that the confined mixture is not an explosive one and the proportion of air or oxygen to gas residual must be changed.

11. The reagent funnel and top ground joint of burette

should be washed well after the completion of each analysis to prevent sticking at the ground joint, due to any potassium hydrate solution which may be present. This rule is applicable also to other movable parts such as cocks which are likely to stick.

12. The bulb which is not graduated, or an extra pipette is used to hold the excess of gas when the explosion is being made. The analyst occasionally loses an explosion, and were it not for the gas thus held, the entire analysis would have to be made over. By putting into the bulb all of the gas that is left after the CO absorption, except the 10 cubic centimeters which is used for the explosion, several explosions may be made as checks on one another, or in case the first one is lost.

13. If the cocks stick, they can usually be loosened by a little hot water on the outside. They should be kept well lubricated with a mixture of equal parts of vaseline, tallow and paraffine.

14. For getting samples, it is best to get four sample cans. The sketch above will show what these are. In getting the sample the can is placed in an upright position and filled quite full of water, perfectly saturated with the gas to be sampled in order to expel all of the air. A tube connected with the upper stop-cock is then introduced into the space from which the gas sample is to be drawn, and the lower stop-cock is opened, allowing the water to run out and thus the sample is aspirated into the can.

In drawing samples from places which have a suction instead of a pressure, such as the inlet of an exhauster, or at the base of a stack, or in the breeching of a boiler, the water should be allowed to flow through a U-shaped glass tube attached by a piece of rubber hose to the lower stop-cock. If this is not done, after the water is all out, air will enter and spoil the sample. It is essential to draw out all of the water, even if only a small sample is required, as a number of the constituents, illuminants and CO_2, for example, are soluble in water. If the gas to be sampled is under pressure it is well enough to allow it to flow through the can for a few seconds after all of the water has run out.

To get the sample out of the can, the lower stop-cock is connected by a hose with a source of water under pressure such as an aspirator bottle filled with water and placed at a level above that of the sampling can, and as the water runs into the can the gas will be displaced and may be led by means of a hose to the burette.

15. The principal precaution necessary in gas analysis is to see that the temperature of the apparatus and of the water used, and of any additional water which may be used as well as the temperature of the sample undergoing examination, does not change during the analysis. A change of 5.2° F. will cause a change of about 1 per cent. in the volume of any gas at an ordinary temperature of 60° F. The temperature at which an analysis is made is immaterial but that temperature MUST remain constant.

16. In reading the burette, hold levelling bottle front and just to one side of the burette, so that the eye of the analyst can sight along the under surface of the water-level and bring it in the same horizontal plane with the bottom of the meniscus in the burette.

Analysis.—The quantities of reagents and wash water described in the foregoing method of analysis are intended mainly for the analysis of carbureted water-gas, hence in the analysis of any other gas the quantities specified should be changed if it is found to be necessary in order to insure complete absorption of the various constituents. This is also true of the oxygen and air required for explosion.

18. Introduce potassium hydrate solution slowly for first absorption as the tendency otherwise is to secure too high a percentage for the carbon dioxide.

19. Care should be taken in handling bromine. Keep it always under water, and do not allow it to come in contact with the skin. Bromine is an exceedingly energetic reagent and will cause painful chemical burns. If bromine fumes are breathed, relief from the irritation caused to the throat can be

obtained by inhaling alcohol or steam. The slick feeling caused by getting potassium hydrate on the hands may be removed by a little dilute hydrochloric acid.

20. The absorption of illuminants by bromine is a heat producing reaction, and the increased temperature is apt to cause the sample to expand unduly and may cause the loss of a part of the sample by forcing it out through the cock and thus vitiate the analysis. If it is seen that the expansion is becoming excessive a little water may be added. The bulb at the lower end of the Morehead burette is provided for this contingency. In the analysis of acetylene, which contains over 90 per cent. of illuminants, this is especially apt to occur. If the percentage of illuminants is high, it is well to admit a little water during the absorption with bromine to restore the normal temperature of the gas.

21. Twenty cubic centimeters of potassium pyrogallate solution when mixed with 20 cubic centimeters of potassium hydrate solution produce a rise in the temperature of the mixture of about 5° F. over that of the original solutions. The heat gained by the gas in the burette due to this cause should be taken into consideration and sufficient time allowed the burette gases to resume initial temperature before reading. This solution should be passed into the burette very slowly, as the absorption of oxygen is rather sluggish. The absorption may be considered complete when no further discoloration to purple or brown occurs upon introduction of the clear reagent.

22. The absorption of the last traces of CO is attended with difficulty, and hence the analyst should be careful to add sufficient copper monochloride solution and allow plenty of time for the complete absorption. The reagent being strongly acid, about 10 cubic centimeters of potassium hydrate solution should always be added, after passing in about 50 cubic centimeters of wash water to insure removal of all fumes of hydrochloric acid and followed with the customary wash water.

23. When carbureted water-gas is being analyzed, double quantities of residual gases, oxygen and air may be taken for the explosion in order to secure higher accuracy.

24. Prior to all explosions, sufficient time (at least two minutes) should be allowed for the gases to thoroughly diffuse through the oxygen and air added so as to give a homogeneous explosive mixture and insure the combustion of all the oxidizable gases.

25. No special care need be taken in measuring the amount of air, or of oxygen added for the explosion, though the amounts taken should not be less than those stated in the "Method." Care must be taken, however, to measure accurately the amount of gas taken for the explosion, and the total amount of the gas, air and oxygen just before the explosion.

26. Air is added to the mixture to be exploded merely to lessen the jar.

If the gas is very poor, or contains large quantities of nitrogen, no air need be added, and on the other hand if the gas is quite rich, no oxygen need be added, air being sufficient, although if oxygen is available it is best added to insure combustion. With extremely poor gas such as blast-furnace gas and the like, no explosion will take place even when oxygen is used and no air added. Oxyhydrogen gas may be necessary, in such cases. This is made by the electrolysis of water slightly acidulated with sulphuric acid. Five to ten cubic centimeters of the oxygen and hydrogen mixture added in addition to the oxygen will always insure an explosion. As it recombines to water, no special reading or note of the volume added need be made.

27. Use only C. P. chemicals.

28. Never allow the funnel to become entirely empty; always keep about ¼-inch of water or other liquid in the bottom to prevent the suction of air into the burette.

29. In acetylene, flue gas, engine exhaust, air and gasoline gas, there is no hydrogen or methane, and hence the analysis need not be carried beyond the absorption with copper monochloride for CO, and the oxygen tank or apparatus, the electric coil, batteries, etc., need not be provided. In analyses of these gases the sum of the first found contractions subtracted from 100 gives the percentage of nitrogen.

30. Where analyses are to be made, or where dispatch is an important element, it will be more satisfactory to obtain a cylinder of compressed oxygen for use in the hydrogen and methane determinations, but where the apparatus is to be moved from place to place, or is to be used only occasionally, or where the analyses are confined for the most part to gases which do not contain hydrogen or methane, such as flue gases, acetylene, air, engine exhaust, etc., a cheaper and quite satisfactory substitute can be had in a small retort by means of which oxygen can be generated on the spot as needed.

To generate oxygen this retort is filled not more than half full with a pulverized thoroughly mixed charge of potassium chlorate and manganese dioxide in the proportions of 20 of the first to 1 of the latter by weight. This is heated gently over a Bunsen lamp. The evolution of oxygen begins at once and it may be led to the burette by means of a rubber tube. As 100 grams of potassium chlorate will produce 27,000 cubic centimeters of oxygen and only about 20 cubic centimeters of oxygen are used for one analysis, a very small spoonful of the mixture will suffice for a great many explosions.

31. The method of analysis is so laid out that each determination must be made in its turn. With the exception of the absorption of CO_2 with KOH, and possibly that of CO with cuprous chloride, no isolated determination of any one constituent can be made with anything approaching accuracy without starting at the beginning and making all of the absorptions down to that constituent.

Careful readings of the burette should be taken before and after each determination, and especial care should be taken in making the analysis to thoroughly absorb each constituent in its turn. Partial absorption, or errors in the readings, will not only introduce an error in the percentages of the constituents in question, but the remaining portions of this constituent will effect the latter determinations in the analysis and thus have a doubly vitiating effect upon the accuracy.

Any CO_2 left after the first absorption will be absorbed by the KOH following the bromine and will be reported as illuminant or if by chance it is not absorbed by the KOH following the bromine, it will be absorbed by the alkaline pyrogallate solution used for oxygen absorption and will appear as O_2.

Any illuminant not absorbed will remain and burn to approximately 3½ times its volume of CO_2 when the explosion is made and will appear as CH_4. A very small proportion of illuminant left and burned and calculated to CH_4 will be sufficient to run the total of the analysis to more than 100 per cent. Any bromine vapors left after the absorption with bromine will be absorbed by the pyrogallate solution and will be reported as O_2.

Any unabsorbed CO will be burned to CO_2 in the explosion, H_2 and CH_4, and increase the percentage of N_2 to the same extent.

Any unabsorbed O_2 left would decrease the percentage of H_2 and CH_4, and increase the percentage of N_2 to the same extent.

Any unabsorbed CO_2 after the explosion will decrease the percentage of CH_4 and increase that of the H_2 and N_2.

The N_2 being determined by difference will necessarily show the net effect of any and all errors in either readings of the burette, or in the performance of the analysis.

Specific Gravity of Gas.

Schilling's apparatus for ascertaining the specific gravity, or density, of gases, is both simple and convenient.

It consists of a glass jar with a metal top into which fits a brass column having suspended from its base a long graduated glass tube and at its top a cock and a ground joint socket, into which sets a socket holding a small glass tip closed in at the top with a very thin piece of platinum. In this platinum is a very small hole to permit the passage of gas or air at a very slow rate. All metal parts are nickeled.

The mode of operation is as follows: The glass jar is filled with water to or a little above the top graduation of the tube. The tube is then withdrawn so as to fill it with air. The cock on the standard is then closed and the tube replaced in the jar. The cock is then opened and with a stop watch the time is taken that elapses while the water passes from the lowest graduation to the top or the next to the top graduation.

FIG. 24.

The tube is then withdrawn and filled with gas and the procedure repeated the same as with air.

The specific gravity, air being one, is obtained by dividing the gas time squared by the air time squared.

Heating Value of Gas.

(*From Report of American Gas Institute.*)

Set up the apparatus as shown in cuts of the different sets.

Screw on the inlet water pipe and see that the air vent tube is in its place in this pipe.

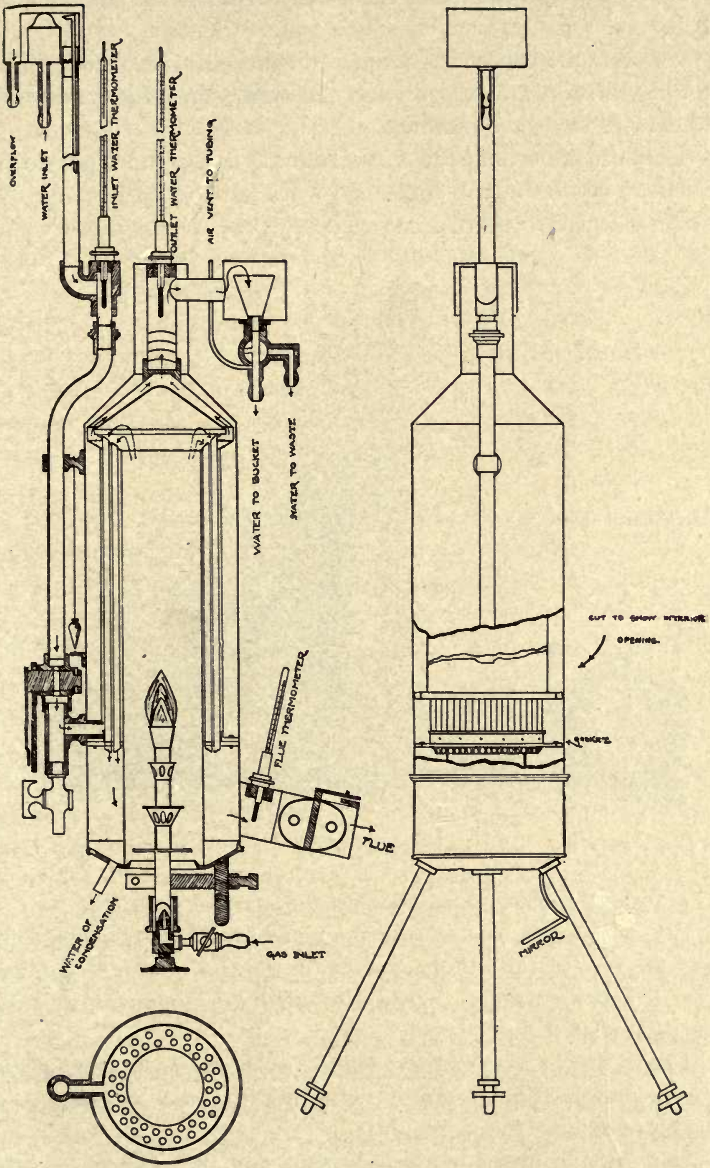
OVERFLOW
WATER INLET
INLET WATER THERMOMETER
OUTLET WATER THERMOMETER
AIR VENT TO TUBING
WATER TO BUCKET
WATER TO WASTE
FLUE THERMOMETER
FLUE
WATER OF CONDENSATION
GAS INLET
CUT TO SHOW INTERIOR
OPENING.
MIRROR

FIG. 25.

Level the calorimeter by means of the screw feet and plumb-bob.

Connect the center hose nipple on the inlet weir with rubber tubing to the water supply and the side connection to the sink to carry away the overflow.

Connect the tubing for water running to weighing pail to the vertical nipple on the three-way cock on the outlet weir and for the waste to the side nipple.

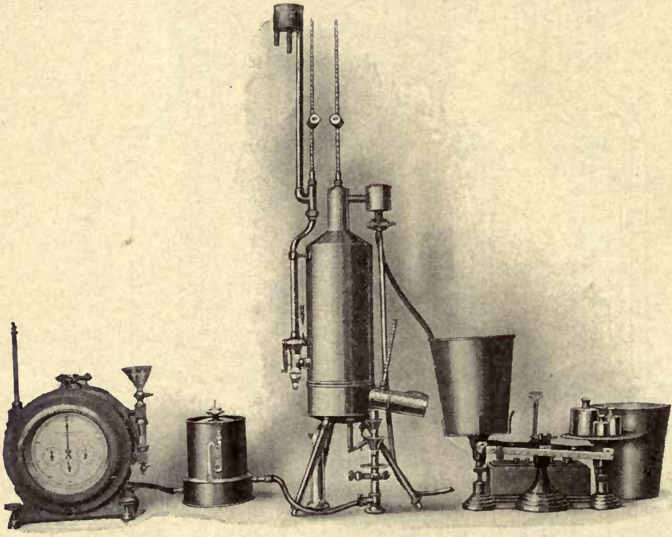

FIG. 26.

Handle the thermometers with the greatest of care.

Screw the 32° to 100° thermometer on the inlet water pipe and the 60° to 110° thermometer on the top of the instrument for the outlet water. Screw the small thermometer in place on the exhaust flue.

Place the two telescopic sights in position on the water thermometers, being very careful not to break them off by pressure against the sights.

Connect the meter to the governor and the governor to the burner with short pieces of rubber tubing, or with flexible metal tubing having coupled ends.

The calorimeter should be set up in a quiet, light and well ventilated room or cabinet, which is free from draughts and in which the temperature can be maintained constantly at not less than 60°F. The room should be provided with a sink and with a good supply of running water. It is advisable to have a large shallow overhead covered tank, from which the water supply can be taken. Should the tank capacity be small and not hold enough water for a prolonged series of readings, a small gas water heater may be employed as already noted to bring the water to approximately the room temperature. It is desirable to use water that is clear and free from suspended matter in the calorimeter, therefore, a filter should be installed in the water supply line before it enters the overhead tank.

If only a single test is desired, gas may be taken from the house piping, but if an average value is required, a small gas holder, or averaging tank, should be used, and the gas flowing into the holder adjusted to a rate of flow to just fill it in the time during which the sample is to be taken. Care should be taken to have a short service to this holder in order that an average sample of gas may be obtained, and if the sample be taken from a line on which there is no considerable consumption, see that this line is thoroughly purged before sampling. It is recommended that the gas be metered at a pressure not to exceed two inches of water; if this is not obtainable, it is advisable to insert a holder or diaphragm governor in the supply line to reduce the pressure to within this limit.

Set up the calorimeter so that the overflow and outlet water can be easily led to the sink. Make water connections with rubber tubing, being careful not to cramp the tubing. To avoid air currents caused by the movement of the observer's body, set up the calorimeter so that the water supply and waste may be easily adjusted and that all temperatures may be readily observed. Lead the outlet water to a waste funnel supported a little above the top of the copper or glass container used in collecting the water, so that the water can be shifted from the funnel to the container and back without spilling.

Set up the gas meter facing the observer and level it carefully. Then adjust the water-level of the meter, both inlet and outlet being open to the air. To do this, remove the plug from the dry well, open the funnel cock and disconnect the tubing on the outlet of the meter. Add or remove water (through the funnel or by the cock under the gauge glass) until the lowest edge of the meniscus just touches the scratch on the gauge glass, or is even with the fixed pointer. If the meter has been filled with fresh water the gas must be allowed to burn at least two hours before making a test. When the water in the meter is saturated with gas, 20 minutes should be sufficient.

Fill pressure regulator with water, about ¾ full, then connect it to the calorimeter burner. Metallic tubing is preferable, but when rubber tubing is used to connect meter, pressure regulator and burner, connections should be as short as possible, and should be saturated with the gas.

Turn on gas and allow it to burn for 5 to 10 minutes with the burner on the table. Shut off gas at burner and watch hand on meter for leakage. Be sure that all leaks are stopped before attempting to make a test. Start water running through the calorimeter at a rate of about 3 pounds per minute. Then regulate the gas to flow at the rate of 4 to 7 feet an hour, as may be found by experiment to give the highest result with the gas to be tested, admitting enough air through the burner so that the flame shows a faint luminous tip, then insert the burner as far up into the combustion chamber as the bracket permits, and observe again the condition of the flame to see that it is all right, using a mirror.

The excess of air passing through the calorimeter is controlled somewhat by the position of the damper in the exhaust port, and the best results are obtained by having the excess air as low as possible and still maintaining complete combustion of the gas. To determine this position of the damper, some experimentation may be necessary. Operate the calorimeter until a thermal balance is established on the inlet and outlet water thermometers. Start with the damper closed, then open slightly, observing carefully the outlet thermometer. When this thermometer reads at a maximum—or in other words, when the greatest rise in temperature is given to the water, which is presumably passing through the calorimeter uniformly—the damper is in approximately the correct position for the amount of gas being burned, and the excess air necessary for perfect combustion is at a minimum.

Water should be regulated so that there is a difference between the inlet and outlet temperatures of about 15° F. The temperature of the inlet water should vary but little when an overhead tank is used and the water maintained at room temperature. Be sure that both overflows are running.

Before making the test, the barometer, temperature of the gas at the meter, temperature of room and temperature of exhaust products should be recorded. It is desirable to have the temperature of the inlet water and temperature of exhaust products as nearly as possible at room temperature, in order to establish more nearly a thermal balance—the difference in these temperatures should never exceed 5°.

Next allow the gas to burn in the calorimeter until a thermal balance is established, or until there is the least change in the inlet and outlet waters.

The test may now be started by shifting the outlet water from the funnel to the container just as the large hand on the meter passes the zero point. Readings are then made of inlet and outlet thermometers, making the readings as rapidly as the observer is able to record them during the consumption, preferably of two-tenths of a cubic foot of gas. At least ten readings should be made of both inlet and outlet water temperatures. Water is again shifted from the container to the waste funnel as the hand passes the zero point the second time. Water is then weighed or measured. The uncorrected heating value per cubic foot is obtained by multiplying the difference of the averages of inlet and outlet temperatures, by the number of pounds of water and by dividing by two-tenths. This quantity is divided by the correction factor for barometer and temperature, obtainable from tables, to give the heating value at 30 inches pressure and 60° F. The weight or contents of container should be obtained while the inside is wet. This may be done by filling it with water, emptying and shaking for about five seconds in an inverted position. This will do away with any correction where several consecutive tests are required with same container.

A second, and perhaps a third test is advisable, and these should be made without disturbing the existing conditions, provided all readings are within the above prescribed limits. In practice the operator should get consecutive results on the same holder of gas within ten (10) B. t. u.'s. Under such conditions an average of the results may safely be taken.

RESULTS AS OBTAINED BY CALCULATION.

The method of calculating the calorific value of the gas from the observations indicated is very simple when all readings are made in English units, as recommended, and entered in some form conveniently arranged. A simple record sheet is shown herewith, a convenient size for which is 5 by 8 inches.

The averages of the inlet and outlet water temperatures are determined and necessary corrections for thermometer errors are made. The difference in these averages should give the rise in temperature of the water. This rise in temperature of the water is then multiplied by the number of pounds of water passed through the calorimeter during the test.

The product of these two is then divided by the quantity of gas burned—0.2 of a cubic foot. This quotient will give the heating value of one cubic foot of gas in B. t. u.'s at the indicated temperature and barometric pressure. To correct this to 60° F. and 30 inches pressure, divide by the "Correction Factor" for the indicated temperature, and pressure as obtained from some standard table. [Printed on card sent with apparatus.] The final result will be the corrected heating value of the gas tested, in B. t. u.'s.

Expressing the above in a formula we have:

$$\text{B. t. u.'s per cubic foot} = \frac{W \times T}{G}.$$

W = weight, in pounds, of water passed.
T = the average difference in temperature, in degrees Fahrenheit, between inlet and outlet water.
G = corrected volume of gas burned, in cubic feet.

The correction for atmospheric humidity is made finally, if so desired.

USE OF COMPUTER.

The labor of making the calculations for determining the heating value from observations of a calorimeter may be lessened by the use of a heating value computer. The computer consists of a circular slide rule, with divisions corresponding to the readings made on the calorimeter. This computer gives the corrected heating value of a cubic foot of gas in B. t. u.'s, having the barometric pressure and temperature of the metered gas, and the difference in temperature between the inlet and outlet water, and the pounds of water passed. This computer is designed to operate within the limits of from 300 to 800 B. t. u.'s. Should a gas of a lower or higher heating value be measured, the computer can still be used by dividing or multiplying one or the other of the factors in its computation. A cut of this computer can be found on page 373, Vol. III, *Proceedings of the American Gas Institute.*

Corrections for Atmospheric Humidity.

(From Report of American Gas Institute.)

This correction is found to be the greatest when the percentage of humidity of the atmosphere is the lowest. The reason being that the relatively dry air entering the calorimeter causes to be carried out in the exhaust products a larger amount of the water in the form of a gas or vapor, that is formed by the combustion of the gas, and which does not condense. and, therefore does not give up its latent heat to the calorimeter.

The humidity correction should correct for any discrepancy in water vapor carried in by the air and gas, compared with that carried out by the products of combustion.

Owing to the contraction in volume, during the combustion of ordinary illuminating gas and air, this discrepancy is practically nothing when the percentage of atmospheric humidity is about 80 per cent., at normal temperatures, and the excess of air introduced for combustion is about 30 per cent.

In correcting for atmospheric humidity it is assumed that the gas is saturated with water vapors—having passed through a wet meter. This assumption might not be absolutely true, but the percentage of saturation has been found always to be high, and as the volume of gas is only about one-eighth of the mixture, the error involved may be neglected.

TABLE I.—CORRECTIONS TO OBSERVED HEAT TO GET TOTAL HEAT VALUE. AIR, GAS AND EXHAUST MUST BE AT THE SAME TEMPERATURE.

If 7 volumes of air per volume of gas are used.

Humidity	Room temperatures					
Per cent.	65°	70°	75°	80°	85°	90°
10	+4.8	+5.7	+6.7	+7.9	+9.2	+10.5
20	+4.1	+4.9	+5.7	+6.8	+7.8	+ 9.0
30	+3.4	+4.1	+4.7	+5.6	+6.5	+ 7.4
40	+2.7	+3.2	+3.7	+4.5	+5.2	+ 5.9
50	+2.0	+2.4	+2.8	+3.4	+3.8	+ 4.3
60	+1.3	+1.6	+1.8	+2.2	+2.5	+ 2.8
70	+0.6	+0.8	+0.8	+1.0	+1.2	+ 1.2
80	—0.1	+0.0	—0.1	—0.1	—0.1	— 0.3
90	—0.8	—0.9	—1.1	—1.3	—1.5	— 1.9
100	—1.6	—1.8	—2.0	—2.4	—2.8	— 3.4

Note—These corrections are expressed in B. t. u.

Directions for Using Orsat Apparatus.

The gas burette *A* (in Fig. 27) is attached to the levelling flask *B*, which is filled with water. By raising *B, A* is filled with water to the uppermost mark. In order thus to fill *A* with water, the air must have opportunity to escape from the uppermost portion of *A*.

The absorption pipette *D* is used to absorb carbonic acid gas.

It contains such a quantity of caustic potash solution that when the solution is drawn entirely into the front part of the pipette (the proper position for the solution when the pipette is ready for use), the front part of the pipette is filled with the solution, and the rear part is empty. The solution is drawn up into the front part of the pipette *D*, as follows: Communication is established with the outside air by means of the stop-cock *a*. Stop-cock *d*, *e* and *f* are closed. *A* is filled with water by rais-

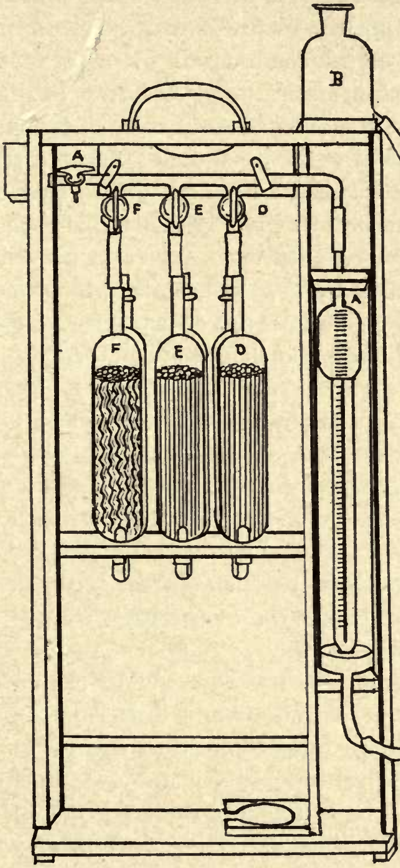

FIG. 27.

ing *B*. Stop-cock *a* is closed, stop-cock *d* is opened, and the solution in pipette *D* is drawn into the front part of the pipette, by lowering *B*. When the solution has filled the front part of *D*, close stop-cock *d*.

Rubber bags are usually attached to the capillary opening at the rear of the pipettes to prevent free access of air and to allow the escape of the confined air when the solution is permitted to flow back again in the pipette after having been used.

Pipette *E* is for the absorption of oxygen gas, and pipette *F* for the absorption of carbon monoxide gas. Pipette *E* is filled similar to *D*, with a solution of pyrogallic acid or with thin sticks of phosphorus in water. In case the phosphorus is used, the pipette is covered with black paper to prevent the action of light on the phosphorus. Just as in the case of *D*, before using *E* and *F*, the solutions are drawn into the front parts of the respective pipettes, and held there by closing their respective cocks. Pipette *F* contains a solution of cuprous chloride. The front part of each of the pipettes contains a bundle of glass tubes, in order to increase the absorption power of the pipettes. The glass tubes for pipette *F* contain curved copper wires to maintain the cuprous chloride solution at a constant strength.

The pipettes being in readiness with stop-cocks *d, e* and *f* closed, and *A* open, burette (*A*) is filled with water by raising (*B*). The other end of the capillary tube or beam is now connected with the gas to be tested. A bent tube is provided for purifying the gas before allowing it to pass into the apparatus. This tube is fastened outside the case on the upper left side, and is connected with the capillary stop-cock tube by means of rubber tubing. Before attaching the bent tube it is filled with a sufficient quantity of calcium chloride, or glass wool. When everything is ready, with a connection made for the gas to enter the apparatus through the bent tube, (*B*) is lowered, by which means the gas is drawn into *A* to the *O* mark. Particular care must be taken that there is exactly 100 cubic centimeters of the gas. Stop-cock *A* is now closed, stop-cock *D* opened, vessel (*B*) raised, burette (*A*) filled with water, and the 100 cubic centimeters of gas forced into the pipette *D*. Here it is allowed to stay for some minutes, the pipette being shaken slightly, if practicable, in order to bring the gas fully into contact with the solution.

When the absorption is complete, the flask (*B*) is again lowered, thus drawing the gas back again into *A*. One hundred cubic centimeters minus the amount of gas remaining shows the amount of carbonic acid gas absorbed by the caustic potash solution. Stop-cock *d* is now closed, stop-cock *e* opened, and (*B*) again raised thus forcing the gas into *E*. Here the gas is treated as it was in D, (*B*) is then lowered, the gas forced back into (*A*) and the amount read. The gas unabsorbed by the caustic potash minus the present remainder shows the amount of oxygen which has been absorbed by the pyrogallic acid, or by the phosphorus, as the case may be.

Stop-cock *e* is now closed, stop-cock *f* opened, and (*B*) again raised. The gas is now forced into *F*. Here especial care must be taken to be sure that complete absorption takes place. When the absorption is finished, (*B*) is again lowered and the gas drawn back into (*A*). The previous remainder minus the present remainder shows the amount of carbon monoxide which has been absorbed by the cuprous chloride solution. The last remainder is usually reckoned as nitrogen, though it contains also small quantities of other gases. In case there is reason to suspect the presence of considerable quantities of hydrogen, a four-pipette apparatus, Fig. 28, is used.

The gas left over from the last operation is increased by the admission of air from the outside until it is again as nearly as possible 100 cubic centimeters. The air added will allow of the burning of a quantity of hydrogen corresponding to two-fifths of its volume; that is, twice the volume of the oxygen contained in the air. This suffices for ordinary producers' gas; but when analyzing "Water Gas" or similar mixtures containing a rather considerable quantity of hydrogen, a smaller quantity of gas must be employed for analysis, or also oxygen is used instead of air. After reading off the total volume, the spirit lamp (*h*) is lighted and turned so that it heats the capillary (*i*) very gently. Then (*B*) is raised, *g* being open and all other stop-cocks closed.

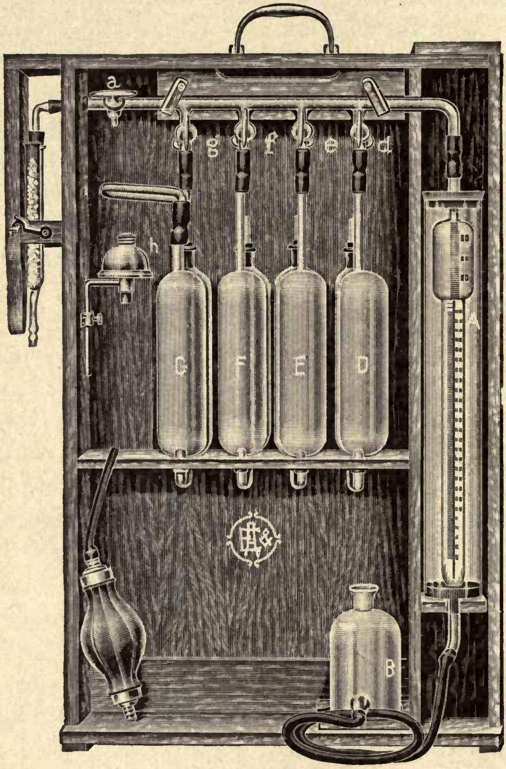

FIG. 28.

The gas passes through the capillary *i*, into the pipette *G*, and then on lowering (*B*) the gas passes back again into the burette (*A*). One end of the palladium asbestos should become hot in this operation. The volume of gas is read off and the passage through *i* is repeated. If, which is usually not the case, a further contraction is now observed, the passage through *i* must be repeated once more. The residual gas is now finally measured, and two-thirds of the diminution is read as hydrogen, the other one-third being, of course, oxygen.

REAGENT.

SOLUTIONS FOR ABSORPTION PIPETTES.

(Method in use December 7, 1914.)

Potassium Hydrate.—Five hundred grams of potassium hydrate (not purified by alcohol) are dissolved in 1,000 cubic centimeters of water. Capacity: 1 cubic centimeter absorbs 40 cubic centimeters of CO_2. Sodium hydrate, at present, has replaced KOH, in many works. This reagent, although not quite as active, may be used; but solutions should be changed oftener to avoid clogging of capularies by sodium bicarbonate formed.

Potassium Pyrogallate.—Fifty grams of pyrogallic acid are dissolved in 1,000 cubic centimeters of the solution as made above.

Cuprous Chloride.—Mix 35 grams cuprous chloride (CuCl) and 200 cubic centimeters HCl (specific gravity 1.19) and to this arrange a bunch of copper wire to reach the entire length of the bottle.

LIFE OF REAGENTS.

If the solutions are protected from the air, their life is about as follows: One cubic centimeter of caustic potash solution will absorb 40 cubic centimeters or more of CO_2. The absorption of O by pyrogallic solution should be at temperatures not less than 15° C.; 1 cubic centimeter of pyrogallol solution will absorb about 13 cubic centimeters of O. Phosphorus will last a long time, inasmuch as the oxidation products are dissolved off by the water leaving the phosphorus free to combine with more O. One cubic centimeter of the cuprous chloride solution is equal to about 16 cubic centimeters of CO. The palladium renews itself constantly by contact with the air, so that its activity is almost inexhaustible.

There is also largely used, the modification of the Orsat apparatus known as Franklyn Flue Gas Analyzer for the determination of CO_2, O and CO, which is explained by the following illustrations. Its chief advantages are, its compactness, that is, its parts are more compact and not as easily broken as those of the Orsat Muencke apparatus.

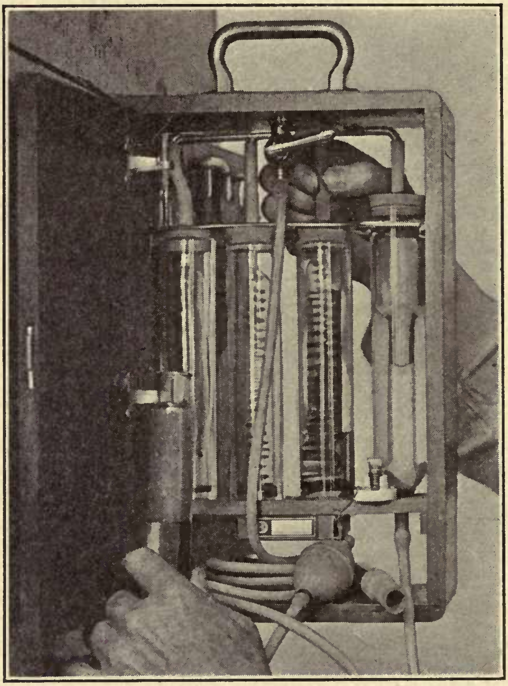

FIG. 29.

Construction and Operation of Hygrometer for Determining the Minimum Temperature of Saturation of Gas in Distribution Mains.

The instrument is employed to determine the minimum temperature to which illuminating gas has been cooled on its way to the burner, its action being dependent upon the fact that the gas will be saturated with vapor at the minimum temperature to which it has been cooled. The instrument reduces a small quantity of the gas back to the minimum temperature, and upon further slightly cooling, it gives evidence, in the deposition of dew, that the point has been reached. The temperature is then noted on a delicate thermometer placed inside the instrument.

The function of the instrument is therefore to duplicate, on a small scale, what has previously taken place in the main.

Construction of the Apparatus.

The apparatus consists of an interior glass vessel *A* (Fig. 30) known as the condensing tube, the glass jacket *D* surrounding the condensing tube, the thermometer support *O*, and the thermometer *T* which is suspended in the condensing tube. The cap *K* covers the top of the instrument and carries the burner-head *E*. The whole is mounted on a base provided with a cock, which is so constructed that the gas may be made to pass straightway into the instrument or first through either one of the scrubbers (*G* — *H*). The needle valve *L* is provided in order to permit of the gas being passed directly to the burner instead of through the vaporizing tube. The instrument may be taken apart at *C* for the purpose of cleaning the jacket; the cap also unscrews, giving access to the condensing tube. The two scrubbers may be unscrewed at the bottom for filling and cleaning.

Setting up the Apparatus.

The support for the apparatus *M* is screwed on to a convenient gas bracket (no rubber connections should be used), the outside jacket *D* is screwed on the base of the apparatus at *N*, and the instrument then placed upright on the support with the handle of the cock toward the observer. The cap *K* is removed and the thermometer support *C* pulled out and the thermometer placed in position, as shown. The cap *K* is then replaced and surmounted by burner-head *E*. The right-hand scrubber cover *H* should then be unscrewed from the base,

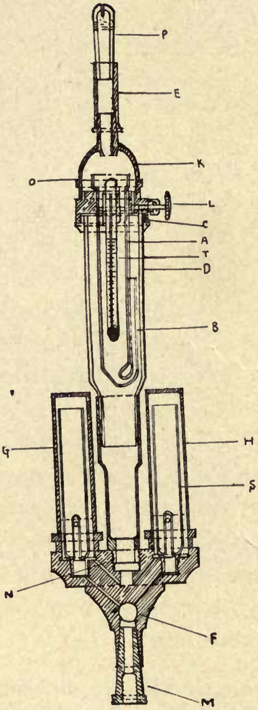

FIG. 30.—Hygrometer.

uncovering the calcium chloride scrubber. This tube should be filled with small pieces of calcium chloride. Replace the scrubber cover, screwing firmly into place with the fingers. Likewise unscrew the left-hand scrubber cover *C* and see that the glass tube is filled with rubber bands; then replace cover. The gas should now be turned on and lighted, the cock at the base of the instrument being turned so that the gas passes straight into the jacket. By turning the cock to the right or the left, the gas can be made to pass through the scrubbers (*G* — *H*) at will, or cut off entirely. A good flow of gas (from 2 to 3 feet per hour) should be obtained either straightway or through the scrubbers. The instrument is now ready for observation.

Making the Test.

Shut off the gas at the cock on the base of the instrument and lift off the burner-head. Place the stem of the small funnel sent with the instrument through the cap and pour pentane or ether into the condensing tube until it contains about 1 inch of the liquid. Replace the burner-head and open needle valve *L*. The gas is now turned on with the cock set so that it passes straight into the jacket and out through the burner-head, the condensing tube being by-passed. By throttling the needle-valve *L*, a portion or all of the gas may be made to bubble through the pentane, the rate of its passage through the pentane being regulated entirely by the needle-valve. The vaporization of the pentane causes a reduction in temperature of the tube and finally dew will be deposited on its outer surface.

The temperature at which the dew commences to deposit opposite the bulb of the thermometer is noted *and recorded* as the "dew point" or minimum temperature of the gas. When this point is reached the needle-valve should be opened, by-passing the condenser tube. Soon the thermometer will rise and the dew will disappear. The observance of the point of disappearance furnishes a check upon the first reading. The gas before passing into the instrument may be first passed through the scrubbers (G — H) to remove a portion of the unfixed hydrocarbon vapors or water vapor. The functions of these scrubbers are described in a paper by C. C. Tutwiler, published in the *Journal of the American Chemical Society,* April, 1908, and republished in the *American Gas Light Journal,* of April 20, 1908.

TAR.

For tar shipments it is, as a rule, sufficient to determine the specific gravity and the water in the tar. The following two methods are recommended for these determinations. For a more complete analysis, refer to chapter on Tar Products.

SAMPLING.

Tar is best sampled while being unloaded from or loaded in the tank car or barge. A pet cock with a nipple projecting about one-third of the diameter, should be placed in the pipe line and a continuous stream of tar drawn off into a barrel during the time of unloading. The pet cock should be so regulated that the sample will represent approximately 0.1 per cent. of the shipment. The tar may then be stirred up and a sample taken from the barrel. Samples of tar should be placed in heavy clear bottles or screw top tin cans. When necessary to sample from storage tanks, or wells, it should be done by means of a "thief." This is particularly necessary when different shipments of tar of widely different gravities have been run into the same tank. A simple and efficient apparatus may be made from a piece of 2-inch pipe provided with a lever handle cock. This may be closed by means of a small iron rod as shown in Fig. 31.

By cutting away part of the cock and one-half of the plug, an opening nearly as large as the interior of the pipe is produced. In taking the sample, the cock is opened and the "thief" slowly lowered to the bottom of the tank, well, or car, the "thief" having previously been rinsed with the liquid to be sampled, the cock is closed, the "thief" is withdrawn, and the sample run into a bottle. This operation is repeated until a sample of about 1 gallon is obtained, after which the contents should be thoroughly mixed, and a portion taken to serve as a smaller sample for analysis.

It should be noted that this method cannot be used with horizontal cylindrical tanks.

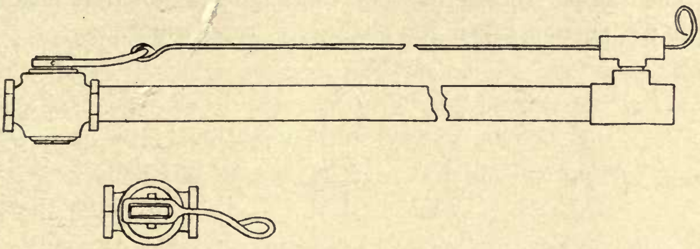

FIG. 31.—Thief sampling tube.

In the case of tar where there is always a certain amount of water or ammoniacal liquor floating on the surface, it seems best to attempt to locate the level of the water or liquor, taking a sample at this point, and then sample a lower portion of the tar which is reasonably free from water, and by calculation, estimate the total quantity of water present.

DETERMINATION OF SPECIFIC GRAVITY.

When there is no free water the gravity may be determined with a hydrometer after bringing the sample to normal temperature or by observing the temperature and correcting as follows:

$$\text{Specific gravity at } 70^\circ \text{ C.} = \text{specific gravity observed at } t^\circ \text{ C.} + (T - t) \times 0.0008.$$

It is recommended that the specific gravity be taken at 25° C. Where more accurate results are required the pycnometer bottle is recommended. These are straight sided thin glass bottles with a ground stopper the full size of the bottle and provided with a capillary hole in the center of the stopper. The bottle is dried and weighed empty and filled with water at normal temperature. It is nearly filled with tar and weighed again, it is then completely filled with water, and brought to the normal temperature, the excess water removed and the bottle dried and weighed.

$$\text{Specific gravity} = \frac{(\text{Wt. bottle} \times \text{tar}) - (\text{Wt. bottle})}{\text{Wt. water full} - \text{Wt. water added}}.$$

DETERMINATION OF WATER.

The sample should be very thoroughly agitated to insure that the portion taken for analysis is representative.

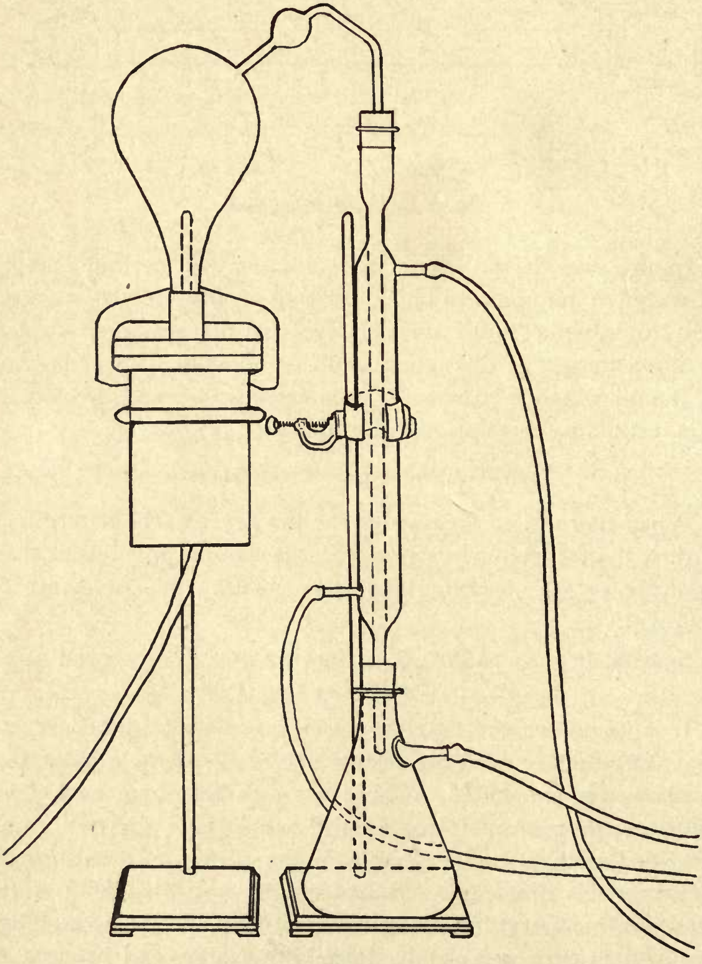

FIG. 32.

The apparatus is set up as shown in Fig. 31.

Put 25 or 30 cubic centimeters of benzol in a 250 cubic centimeter cylinder, add 200 cubic centimeters of the well mixed sample, pour into the copper still and wash out three times with benzol using 25 to 30 cubic centimeters adding washings to still.

Fasten on lid with the clamp using a gasket of manila "detail" paper, connect apparatus as shown in Fig. 27. Start ring burner at top of still and lower after the water has been driven off until the thermometer reaches 200° C.

The distillate is collected in two 100 cubic centimeter graduated cylinders.

Where an excessive amount of water is suspected the distilling head is replaced with the expansion chamber shown in Fig. 32, the side outlet and receiver is connected with a filter pump and the distillation carried out in a partial vacuum. The contents of the receiver is then transferred to a measuring cylinder.

AMMONIA.

Ammoniacal Liquor.

SAMPLING.

When the liquor is contained in a tank with straight sides, sampling is done with a "thief," which may be a bottle thief or a pipe thief. A very satisfactory bottle thief for ammoniacal liquor may be made as follows from a one-quart milk bottle.

Enough shot are put into the bottle to overcome its buoyancy and cause it to sink easily when immersed in water. The shot are held in place by pouring over them a thin paste of *Plaster of Paris.* The bottle is provided with a two-hole cork or rubber stopper through which pass two glass tubes projecting about one inch above the stopper. One tube extends just below the stopper; the other to about ¼ inch above the bottom. In use the thief is lowered at even speed through the liquor to be sampled till it strikes bottom, and then immediately raised at even speed. The speed must be such that the bottle is not completely filled when it is drawn out from the liquor. The thief is emptied, and the operation repeated till a sufficient quantity for the sample is obtained. It will be noticed that the thief does not take a portion from the liquor lying below about 8 inches from the bottom. When there seems reason for thinking that this bottom layer may be considerably different from the rest, the pipe thief should be used.

The pipe thief consists of an iron pipe of 1¼ inches to 2 inches size, as desired, long enough to reach to the bottom of the tank. Its lower end is provided with a plug-cock having a lever handle which points across the pipe when the cock is open. A rod or chain is attached to the end of the handle. The thief is slowly lowered, with the cock open to the bottom of the tank. The cock is then closed by pulling on the rod or chain, and the thief withdrawn and emptied. The operation is repeated till a sufficient sample is collected.

When liquor can be sampled during pumping, this should be done in preference to taking a sample from the tank. This is especially true with tank cars or other horizontal cylindrical tanks. A pet cock should be attached to the pipe line on the outlet of the pump by a nipple projecting into the line about one-third of the diameter of the latter. A small stream of liquor should be drawn at steady speed from the pet cock through a tube into a covered receiver of not much larger size than the sample desired. Where the question of sale is involved, an amount equal to 0.1 per cent. of the total quantity should be collected in the receiver. After shaking, a sample is taken from the latter for the laboratory.

In collecting a running sample, as described above, it is necessary that the rate of flow and the pressure in the line where the pet cock is inserted be uniform throughout the unloading of the tank. When a tank is unloaded by gravity, these conditions are not fulfilled and therefore a pet cock in the line does not give the true average sample. In such a case, however, an approximately correct sample can be obtained if several running samples are taken, each representative of a definite fraction of the whole quantity, such as one-sixth or one-eighth. Equal portions are taken from each separate sample, and mixed to form the composite sample.

In sampling from a horizontal cylindrical tank, the thief cannot be used, because equal depths of liquor at different elevations represent quite different volumes. A good approximation to a true average, however, can be made by taking several samples at varying depths, which latter are chosen to represent a division of the tank into equal parts by volume. Equal amounts are taken from the various samples, and mixed. The greater number of the samples, the more representative is the mixture. The following table shows the depths, expressed in per cent. of the diameter at which samples should be taken, when six, eight, ten and twelve samples are desired:

	For 6 samples	For 8 samples	For 10 samples	For 12 sample
Percentage	13.7	11.3	9.8	8.6
	30.0	24.4	20.7	18.3
of	43.6	35.3	30.0	26.2
	56.4	45.2	38.3	33.3
diameter	70.0	54.8	46.1	40.1
	86.3	64.7	53.9	46.7
		75.6	61.7	53.3
		88.7	70.0	59.9
			79.3	66.7
			90.2	73.8
				81.7
				91.4

These depths represent the centers of gravity of zones of equal volume.

For collecting these samples, the bottle thief is suitable. The ends of a short piece of rubber tubing with a string tied around its middle are pushed lightly over the tubes of the thief, thus sealing them. The bottle is then lowered gently to avoid disturbance of the strata, till the tops of the tubes are at the right depth for taking the first or top sample. The rubber tube is then drawn off and the thief allowed to fill. The second sample from the top is then taken, etc.

The foregoing table is intended for use on completely filled tanks. It may, however, be used for sampling partially filled tanks, without much error, if several samples are taken, and special calculation is made as follows for the top sample: The boundary between zones is assumed for this purpose to be half-way between the centers of adjoining zones. The top zone will then consist of the liquor from the surface to the first zone boundary below, and the top sample should be taken half-way between these points. The amount of this top zone sample taken for the mixed sample, should be in the ratio of the actual depth of the top zone to its full depth according to the table.

Tanks and tank cars of ammoniacal liquor, often contain tar, which may either float or sink depending on its nature. To estimate the depth of the floating tar, use a glass tube of ⅝ inch or more diameter whose lower end is fitted with a rubber stopper, which may be drawn up into the tube by a string fastened into the stopper and passed up through the tube. Lower the tube slowly through the tar layer, with the stopper suspended well below the tube end. When the tube end is well into the liquor, draw up the stopper, closing the tube. Measure the depth of the tar layer.

To measure the depth of tar in the bottom of the tank, attach a piece of cotton wicking to a rod. Wet the wicking with benzol or other light colored tar solvent, and put the rod into the tank. The tar will color the moist wicking.

Specific Gravity.

The determination of specific gravity is made by hydrometer. A regular specific gravity hydrometer, graduated to read to the third decimal place is used. However, in cases of doubt or dispute, a pycnometer (Sprengel tube) should be used.

The standard temperature for taking the gravity is 60° F. The gravity is referred to water at 60° F. A hydrometer jar of the liquor to be tested should be brought to that temperature by immersion in water, and the reading taken.

When it is desired to know accurately the weight of liquor present in a tank or tank car, the gravity must naturally be taken at the temperature at which the volume of the liquor is also measured. This may be done by taking the gravity of a freshly drawn sample at the tank; or the temperature may be noted and the regular sample brought to that temperature in the laboratory for a determination of the gravity.

The Committee recommends the general use of the specific gravity scale in reporting the gravity of ammoniacal liquor. It recognized, however, that the use of the Twaddle hydrometer is common in several of the older companies. Readings in the Twaddle scale may be changed into readings on the specific gravity scale by the use of the following formula:

Specific gravity = 1.0 divided by 0.005 Tw.

The objection to the use of the Twaddle scale, is that it is often assumed that the value of the liquor in terms of "ounce strength" may be found by multiplying the Twaddle reading by two. There is, however, no general numerical connection between the hydrometer reading of a liquor and its content of ammonia.

(In any one plant, operating regularly under the same conditions and using the same coal, it is true that an increase in the strength of the liquor will generally be accompanied by an increase in its gravity, and in such case the hydrometer reading offers a simple means of following the daily operation of condensers, scrubbers, etc.)

Since considerable changes in the reading occur when the temperature is much different from 60°, and since it is inconvenient to adjust the temperature of the liquor in works testing, the following table has been prepared to find the equivalent reading at 60° from a reading taken at a different temperature. The numbers are degrees on the Twaddle hydrometer. The table is not perfectly correct for all ammoniacal liquors but is sufficiently so for the routine testing for which it is intended.

TEMPERATURE CORRECTIONS FOR SPECIFIC GRAVITY OF AMMONIACAL LIQUOR IN DEGREES TWADDLE TEMPERATURE

40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
8.82	8.78	8.74	8.71	8.67	8.63	8.59	8.55	8.55	8.47	8.43	8.39	8.35	8.31	8.27	8.22	8.18	8.14	8.09	8.04	8.00
7.75	7.71	7.68	7.64	7.61	7.57	7.54	7.51	7.47	7.43	7.39	7.35	7.31	7.27	7.23	7.20	7.16	7.12	7.08	7.04	7.00
6.68	6.65	6.61	6.58	6.55	6.52	6.49	6.45	6.42	6.39	6.36	6.32	6.29	6.25	6.22	6.18	6.14	6.10	6.07	6.04	6.00
5.61	5.59	5.56	5.53	5.50	5.47	5.44	5.41	5.38	5.35	5.32	5.29	5.26	5.22	5.19	5.16	5.13	5.10	5.07	5.04	5.00
4.54	4.52	4.50	4.48	4.45	4.42	4.40	4.38	4.35	4.33	4.29	4.26	4.23	4.20	4.18	4.15	4.12	4.09	4.06	4.03	4.00
3.47	3.45	3.43	3.40	3.38	3.35	3.33	3.31	3.29	3.27	3.25	3.23	3.20	3.18	3.16	3.13	3.11	3.09	3.06	3.03	3.00
2.39	2.37	2.35	2.33	2.31	2.29	2.28	2.26	2.24	2.23	2.21	2.19	2.17	2.15	2.13	2.11	2.09	2.07	2.05	2.03	2.00
1.29	1.28	1.27	1.26	1.24	1.23	1.22	1.21	1.19	1.18	1.17	1.16	1.15	1.13	1.11	1.09	1.07	1.06	1.04	1.02	1.00
.20	.195	.190	.185	.173	.170	.165	.160	.155	.147	.140	.130	.115	.100	.085	.070	.059	.047	.035	.022	.000

60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
8.00	7.96	7.92	7.87	7.82	7.77	7.72	7.67	7.62	7.57	7.53	7.48	7.43	7.38	7.33	7.28	7.23	7.18	7.13	7.08	7.02
7.00	6.96	6.92	6.87	6.83	6.78	6.73	6.69	6.65	6.60	6.56	6.52	6.47	6.43	6.38	6.33	6.28	6.23	6.19	6.14	6.09
6.00	5.96	5.92	5.86	5.84	5.80	5.76	5.72	5.68	5.64	5.60	5.56	5.52	5.47	5.42	5.38	5.34	5.30	5.25	5.21	5.16
5.00	4.96	4.93	4.89	4.86	4.82	4.78	4.74	4.70	4.67	4.63	4.59	4.55	4.51	4.47	4.43	4.39	4.35	4.31	4.27	4.23
4.00	3.96	3.93	3.90	3.87	3.84	3.81	3.78	3.75	3.71	3.67	3.64	3.60	3.56	3.53	3.49	3.45	3.41	3.37	3.33	3.30
3.00	2.97	2.94	2.91	2.88	2.85	2.82	2.79	2.76	2.73	2.70	2.66	2.63	2.60	2.56	2.53	2.50	2.46	2.43	2.39	2.36
2.00	1.97	1.95	1.92	1.90	1.87	1.85	1.82	1.79	1.76	1.73	1.70	1.67	1.64	1.60	1.57	1.54	1.51	1.48	1.45	1.42
1.00	.98	.96	.93	.90	.88	.86	.84	.82	.79	.76	.73	.70	.67	.64	.61	.58	.55	.53	.50	.47
—.00	—.02	—.04	—.06	—.08	—.10	—.12	—.14	—.16	—.18	—.21	—.24	—.26	—.28	—.31	—.34	—.37	—.39	—.42	—.45	—.48

To use the table, follow down in the temperature column to the number next smaller than the hydrometer reading. The difference between the hydrometer reading and that number is to be added to the number in the same horizontal line, under the temperature of 60°. For example the hydrometer reads 4.80 at 75°. 4.43 is the next smaller number in the 75° column. Add 0.37 to 5.00, the corresponding number in the 60° column, and we have 5.37 as the corrected reading for 60°.

Ammoniacal Liquor.

DETERMINATION OF TOTAL AMMONIA.

Apparatus Required.

A 500 cubic centimeter round-bottomed long-necked flask (a Kjeldahl flask) into whose neck is set by a rubber stopper a bulb tube with the bulb portion bent to 45° off the vertical, or some other form of Kjeldahl connecting bulb, to prevent the mechanical carrying of spray into the condenser.

Inside an ordinary glass Liebig condenser jacket is slipped a block tin tube about ½ inch outside diameter, in place of the usual glass condenser tube. The tin tube can be obtained from a plumbing house. There is, however, no objection to the use of a glass condenser as shown in Fig. 28 if preferred by the chemist. About 7 inches of tin tube projects beyond the jacket and this portion is bent back on itself to an angle of 135° from the vertical and joined by rubber tubing to the connecting bulb previously mentioned.

To the lower end of the tin condenser tube is attached a plain bulb tube of about 150 cubic centimeters capacity. The lower end of this will dip into the beaker of standard acid. The object of the bulb is to prevent the accidental sucking back of the contents of the beaker. The equipment of flask and condenser should be carried on a single stand.

There will also be needed one 25 cubic centimeter pipette for sampling weak liquors; and one 100 cubic centimeter pipette and one 1,000 cubic centimeter graduated flask for use with concentrated liquors. On account of the inaccuracy of some of the volumetric apparatus on sale, the pipettes should be checked by filling them with boiled distilled water at room temperature, discharging into tared small stoppered bottles and weighing the water. The weight should not vary by more than 2 parts in 1,000 from the weight given in the tables (See circular No. 19 of the Bureau of Standards for complete tables). The water from a 25 cubic centimeter pipette calibrated for 20° C., should weigh 24.948 grams at 15° C.; 24.929 grams at 20° C.; 24.904 grams at 25° C. Water discharged

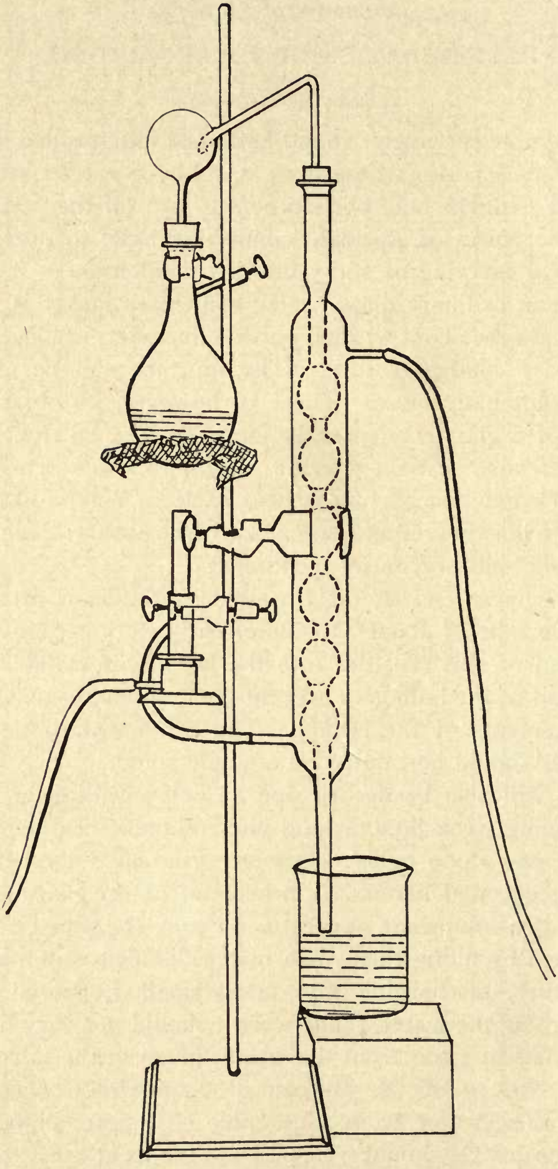

FIG. 33.

from a 100 cubic centimeter pipette, calibrated for 20° C. should weigh 99.793 grams at 15° C.; 99.718 grams at 20° C.; 99.617 grams at 25° C. New marks should be made on the pipettes if they are in error by more than the allowed amount. It should be determined also that the 1,000 cubic centimeter flask holds ten fillings from the 100 cubic centimeter pipette.

Operation A.—For liquor under 3 per cent. ammonia (ordinary weak liquor). Put 150 cubic centimeters distilled water into the 500 cubic centimeter flask and run in 25 cubic centimeters of liquor from the pipette. Add 25 cubic centimeters of 30 per cent. sodium hydroxide solution (300 grams NaOH in 700 cubic centimeters water) and a small piece of granulated zinc to prevent bumping. The addition of a small bit of paraffine will hinder troublesome foaming.

Put 50 cubic centimeters of normal sulphuric acid and 50 cubic centimeters of water in a 400 cubic centimeter beaker and support the beaker so that the bulb tube on the condenser end dips about ½ inch below the surface of the acid. Connect up the apparatus and heat up gently till the air is expelled and the boiling is steady. All the ammonia will be driven off with the first 100 cubic centimeters of distillate. From time to time lower the beaker so that the seal of the bulb tube is not much over ½ inch. When about 100 cubic centimeters has distilled over, lower the beaker clear of the tube and allow the distillate to rinse the inside of the latter. Wash the outside with a wash bottle.

Titrate the solution in the beaker with half-normal ammonium hydroxide or normal sodium hydroxide, using cochineal or methyl orange as indicator.

Calculate the number of cubic centimeters of normal acid which have been neutralized by the ammonia from the liquor. The percentage of ammonia is found by multiplying this number of cubic centimeters by the factor 0.06813 and dividing by the specific gravity of the liquor. In calculating the percentage strength, the gravity used should properly be that of the liquor at temperature of pipetting. The difference, however, may be disregarded unless the temperature varies from 60° F. by more than 10° or 12°.

B. For Concentrated Liquors.—One hundred cubic centimeters of the concentrated liquor are made up to 1,000 cubic centimeters and an aliquot of 100 cubic centimeters taken for the distillation. This is put in the distilling flask with 75 cubic centimeters of water and 25 cubic centimeters of 30 per cent. caustic soda solution. Zinc and paraffine are added as before.

The ammonia is received in 100 cubic centimeters of normal sulphuric acid in a 400 cubic centimeter beaker, or in 125 cubic centimeters for very strong liquor.

Calculate the number of cubic centimeters of normal acid neutralized by the ammonia. For percentage of ammonia multiply this number of cubic centimeters by 0.17033 and divide by the specific gravity of liquor.

C. For Waste Liquors From Ammonia Stills.—Two hundred cubic centimeters of the waste liquors are put in the distilling flask, with 25 cubic centimeters of 30 per cent. caustic soda solution together with zinc and paraffine. One hundred cubic centimeters is distilled off and received in 20 cubic centimeters of normal acid diluted with 80 cubic centimeters of water.

Calculate the number of cubic centimeters of acid neutralized by the ammonia. For percentage of ammonia, multiply this number of cubic centimeters by 0.00852.

The Committee strongly recommends reporting the amount of ammonia in liquor as a percentage, as described above. Several of the older companies, however, are in the habit of reporting in so-called "ounce-strength." Two different meanings appear to be given to this latter term. It is sometimes defined to mean the number of ounces of 100 per cent. sulphuric acid which will be neutralized on direct titration by 1 Imperial gallon (277.27 cubic inches) of this liquor. Only the free ammonia is taken into account in this test. For the determination, see the determination of free ammonia by titration, as described below.

Again "ounce-strength" is defined to mean the number of ounces of 100 per cent. sulphuric acid which will be neutralized by the total ammonia contained in 1 U. S. gallon (231 cubic inches). If figures in "ounce-strength" of this definition are sought they may be obtained from the results of the distillation analysis above described by the following calculation:

A. For Weak Liquors.—Multiply the number of cubic centimeters of acid which have been neutralized by the ammonia from the liquor, by the factor 0.26196.

B. For Concentrated Liquors.—Multiply the number of cubic centimeters by the factor 0.6549.

C. For Waste Liquors.—Multiply the number of cubic centimeters by the factor 0.03275.

It should be noted that the ounce strength as thus found is really the ounce strength of the liquor at the temperature of sampling with the pipette. The ounce strength will increase proportionately as the gravity increases with lower temperatures and *vice versa.* The difference in value for 10° F. will amount to about 1.5 parts of 1,000. The liquor, as sampled, should not therefore vary by more than 10° from 60° F.

In the method described for the determination of ammonia in ammoniacal liquor, it is usually assumed that ammonia is the only substance distilling off, which will neutralize the sulphuric acid. This is not strictly correct, for the pyridine present in the liquor will distil and will neutralize some of the acid, thereby causing the apparent ammonia found to be larger than the true value. The amount of pyridine is usually small but where high accuracy is desired, a correction should be made for it, in the following manner:

In the determination of pyridine, as described below, there is found the number of cubic centimeters of normal acid which are neutralized by the pyridine contained in a given amount of liquor. From this calculate the number of cubic centimeters of acid corresponding to the pyridine contained in the amount of liquor taken for the ammonia test. Subtract this from the number of cubic centimeters of acid neutralized in the ammonia test, and the result is the number of cubic centimeters neutralized by the ammonia alone.

To detect possible errors in the distillation test for ammonia, it is well to make a test on a pure ammonium salt. For this purpose pure ammonium sulphate or chloride should be dissolved in hot water, filtered and recrystallized. After drying at 50° C., 4.5 to 5.0 grams are put in the distillation flask with 175 cubic centimeters of water and 25 cubic centimeters of 30 per cent. caustic soda. The ammonia is received in 100 cubic centimeters of normal acid. If the equivalent of sulphate of ammonia found differs by more than 0.3 of 1 per cent. from the 100 per cent. expected, the error should be corrected. It will very likely be found in the standard solutions used.

Free Ammonia.

Free ammonia is, by definition, that which can be distilled off from liquor by boiling alone, without the use of alkali. Its determination is made exactly as the determination of total ammonia, described above, except that no caustic soda solution is used. The results are calculated in the same way and by the same factors.

For greater convenience, when the utmost accuracy is not desired, the determination of free ammonia may be made by direct titration, as described below.

For weak liquors, 25 cubic centimeters of the liquor is diluted with 100 cubic centimeters of water, and the solution titrated with normal sulphuric acid, using methyl orange as indicator. The indicator is gradually destroyed by something in the solution. If the amount of acid needed is approximately known, it is better to run in almost that amount, without adding indicator, agitate the solution till most of the gas has gone, add a few drops of indicator and bring to the end point. In any case, if there is delay in reaching the end point, a couple of drops of additional indicator must be added from time to time.

For concentrated liquors 100 cubic centimeters are diluted to 1,000 cubic centimeters, an aliquot of 100 cubic centimeters taken and mixed with 100 cubic centimeters of water. Titration is performed as for weak liquors.

When results are desired in "ounce-strength," meaning the ounces of sulphuric acid neutralized by the free ammonia in 1 Imperial gallon, as previously defined, the calculation is performed thus.

For weak liquors, multiply the number of cubic centimeters of acid used by the factor 0.31443.

For concentrated liquors, multiply the number of cubic centimeters of acid used by the factor 0.78608.

The results by direct titration check fairly well with those by distillation, being usually a trifle higher. Where speed is of more importance than high accuracy, the direct titration is preferable.

Fixed Ammonia.

To the residue left in the distillation flask, after boiling off the free ammonia are added 100 cubic centimeters of water and 25 cubic centimeters of 30 per cent. sodium hydroxide solution. The ammonia is distilled off and received in 20 cubic centimeters of normal acid, diluted to 100 cubic centimeters. Calculation of results is the same as described under "total ammonia."

Other Constituents of Liquor.

A. Pyridine:—200 cubic centimeters of weak liquor, or 25 cubic centimeters of concentrated liquor diluted to 200 cubic centimeters are neutralized with sulphuric acid of about 1:5 strength. The directions given for the direct titration of free ammonia should be followed in reaching the neutral point. Pyridine will now be combined as pyridine sulphate. Add about 10 cubic centimeters of normal ammonium hydroxide, or its equivalent, put in an ammonia distillation flask and distil off as for total ammonia, into about 25 cubic centimeters of normal sulphuric acid or its equivalent, diluted to 100 cubic centimeters with water. Collect about 100 cubic centimeters of distillate which will contain all the pyridine.

Put the distillate in an ammonia distillation flask with 10 cubic centimeters of normal sodium hydroxide solution and distil into 50 cubic centimeters of water in a 250 cubic centimeter beaker. Collect 100 cubic centimeters of distillate which will contain the pyridine together with considerable ammonia.

The beaker now contains 150 cubic centimeters. Add 6 drops of phenolphthalein indicator solution (5 grams per liter) and run in normal sulphuric acid till the pink color is just discharged. Read the burette and run in 0.13 cubic centimeter more. (A test will show that with this volume of solution and amount of indicator, the phenolphthalein color will be discharged by 0.13 cubic centimeter less of normal acid than is required to completely neutralize the ammonia when methyl orange indicator is used.) Noting the reading of the burette, add 1 drop of methyl orange and titrate to the pink color. The amount of acid used to turn the methyl orange indicates the amount of pyridine present. One cubic centimeter of acid indicates 0.079 gram of pyridine, equivalent to 0.017 gram of ammonia.

Acid Radicals.

The following methods are taken from the 1909 and previous Reports of the Chief Inspector under the Alkali, etc., Works Acts. They represent the result of work covering several years, carried on in the laboratories of the Chief Inspector in England.

Carbonate:—10 cubic centimeters of liquor (more if dilute) are diluted to 400 cubic centimeters and 10 cubic centimeters of 2N ammoniacal solution of calcium chloride are added. The whole is then heated for 1½ to 2 hours in a water bath at 100° C., the flask being closed by a Bunsen valve. (That is the flask is closed by a rubber stopper carrying a short glass tube over which is slipped a piece of rubber tubing plugged at its top end. Between the plug and the glass tube, a slit about ¼ inch long is made in the rubber tube. Gases can escape but air from outside cannot enter.) The precipitated calcium carbonate is filtered off, washed by decantation, and dissolved in N/2 hydrochloric acid. The small amount of calcium carbonate left on the filter paper is best recovered by incineration and is added to the solution. The excess of acid is titrated with N/2 sodium carbonate.

Sulphide:—10 cubic centimeters of liquor are diluted to 500 cubic centimeters, acidified with hydrochloric acid, and titrated with N/10 iodine (starch indicator). The volume of N/10 iodine required determines how much liquor to take for the actual determination of sulphide to follow. Ten cubic centimeters (or more if the sulphide is apparently small in quantity) are run into an excess of N/5 ammoniacal zinc chloride solution, diluted to about 80 cubic centimeters. The solution is warmed to coagulate the sulphide, filtered, and washed with warm water of 40° to 50° C. temperature. The zinc sulphide on the filter is washed into excess of N/10 iodine, acidified with hydrochloric acid (the last traces being washed through the filter with cold dilute acid). After vigorous shaking to complete the solution of the sulphide, the excess of iodine is titrated with N/10 thiosulphate.

Chloride:—250 cubic centimeters of liquor are boiled to expel sulphide, cooled, and made up to 250 cubic centimeters. Dilute 10 cubic centimeters of this to 150 cubic centimeters, add 25 to 50 cubic centimeters of hydrogen peroxide (3 per cent. or "10 volume" solution, free from chloride), boil for 15 minutes, add 6 drops of a 10 per cent. solution of potassium chromate, and continue the boiling 2 minutes. Should the organic matter resist oxidation, more peroxide must be added and the boiling continued with addition of potassium chromate as before. Add a slight excess of sodium carbonate, re-boil for 1 minute, filter, cool, make up to 250 cubic centimeters and titrate an aliquot portion with N/10 silver nitrate (potassium chromate indicator) after bringing to the neutral point with dilute nitric acid. A blank experiment is made with 10 cubic centimeters N/10 NaCl and the same volume of water, peroxide, and chromate, to determine the correction for traces of chloride in the reagents used. (Twenty-five cubic centimeters of peroxide should not contain more than the equivalent of 0.2 to 0.3 cubic centimeters N/10 HCl.

Thiocyanate:—1. Ferrocyanide absent—50 cubic centimeters of the solution are treated with lead carbonate to remove sulphide and the lead sulphide and carbonate filtered off and washed. To the filtrate, sodium bisulphite containing a little free sulphur dioxide is added, followed by a distinct excess of a 10 per cent. solution of copper sulphate. The solution is allowed to stand 5 to 10 minutes at 70 or 80° C. to coagulate the cuprous thiocyanate. It is then filtered and the precipitate washed with boiling water till the washings give no coloration with dilute potassium ferrocyanide. The residue is digested at 30 to 40° C. with 25 cubic centimeters of a 4 per cent. solution of sodium hydroxide (free from chloride) and filtered. To the cold filtrate are added 5 cubic centimeters of nitric acid (50 per cent. strength and free from oxides of nitrogen) followed by 1 cubic centimeter of a saturated solution of iron alum. The solution is then filtered from separated organic matter, if necessary, and titrated with N/10 silver nitrate.

Thiocyanate:—2. Ferrocyanide present—50 cubic centimeters of the liquor are slightly acidified with sulphuric acid, and ferric alum solution added in sufficient quantity to impart a decided red coloration. The solution is then warmed to 60° C., filtered from Prussian blue, and washed with water containing sodium sulphate. The filtrate is finally treated as in (1) above.

Sulphate:—250 cubic centimeters of liquor are concentrated to about 10 cubic centimeters on the water bath, 2 cubic centimeters of strong hydrochloric added, and the evaporation continued to dryness. The residue is extracted with water and the filtered solution made up to 250 cubic centimeters. One hundred cubic centimeters of this solution are acidified with hydrochloric acid, heated to boiling and barium chloride added. After standing over night, the precipitate is filtered off and weighed.

Total Sulphur:—50 cubic centimeters of liquor (100 cubic centimeters if weak) are slowly dropped into an excess of bromine (free from sulphur) covered by water moderately acidified with hydrochloric acid. The oxidized solution is evaporated to dryness on the water bath, filtered, cooled, and made up to 250 cubic centimeters. One hundred cubic centimeters are precipitated with barium chloride in the usual way.

Sulphite and Thiosulphate:—Sulphur present as sulphate, and thiosulphate, is found by subtracting from the total sulphur that present as sulphate, thiocyanate, and sulphide.

Ferrocyanide:—To 250 cubic centimeters of liquor, acidified slightly with sulphuric acid, ferric alum solution is added in sufficient excess to impart a deep red coloration. The mixture is then heated to 60° C. and filtered, the filtrate being returned to the filter if necessary until a little of it shows no blue color after adding mercuric chloride. The precipitate is washed 2 or 3 times with water containing Na_2SO_4. The filter and precipitate are then boiled for 5 minutes with 10 cubic centimeters of N sodium hydroxide, and the solution diluted to 150 cubic centimeters; 15 cubic centimeters of 3N magnesium chloride are then added to the boiling solution slowly with continual shaking in order to get a milky precipitate of magnesium hydrate. This is then boiled again and 100 cubic centimeters of boiling N/10 mercuric chloride added and the boiling continued for 5 to 10 minutes. The flask is then connected to a condenser dipping into a receiver containing 25 cubic centimeters N sodium hydroxide. Thirty cubic centimeters of 4N sulphuric acid is run from a stoppered funnel into the flask, and the contents distilled for 20 to 30 minutes, when the whole of the hydrocyanic acid is obtained in the receiver. The distillate is then titrated with N/10 silver nitrate, after addition of a little potassium iodide.

Hydrocyanic Acid:—50 cubic centimeters of the liquor are added to an excess (50 to 100 cubic centimeters) of a saturated solution of lead nitrate contained in the distillation flask of the apparatus for determining free and fixed ammonia. The mixture is distilled into 25 cubic centimeters of N sodium hydroxide into which the exit tube of the condenser dips. Thirty to 40 minutes gentle boiling, at which time about 50 cubic centimeters of liquid will have been distilled, is usually sufficient. Frothing is liable to occur and the flask should be heated therefore very carefully. At the end of the distillation a current of air is passed through the apparatus for a short time, to ensure the removal of the hydrocyanic acid. The distillate is diluted to 400 cubic centimeters, a crystal of potassium iodide added and the solution titrated with N/10 silver nitrate.

Rapid Method for Estimation of Carbon Dioxide and Hydrogen Sulphide.

In following the operation of apparatus in which a portion of the foul gases (carbon dioxide and hydrogen sulphide) are driven off from the liquor by heat, it is desirable to be able to determine those gases rapidly. For the purpose, the methods of the Alkali Inspector given above are too time-consuming. The following method is much more rapid and sufficiently accurate for control purposes.

Ammoniacal Solution of Calcium Chloride:—Dissolve 100 grams of calcium carbonate with hydrochloric acid, after adding a little water. Make alkaline with ammonia. Dissolve any precipitate that forms with hydrochloric acid, and again make alkaline. Continue this process of redissolving the precipitate till the solution finally remains clear on adding an excess of ammonia. Make the solution up to one liter.

Barium Hydroxide Solution:—Put 80 grams of good pure barium hydroxide in 2 liters of water, and dissolve as much of it as possible. After settling filter into another bottle.

Normal sulphuric acid and tenth-normal iodine solutions are also needed.

In the process which is being examined, it is very likely that the volume of the liquor will have changed between the inlet and outlet of the apparatus by the addition of steam or water. It is therefore more informing to report the foul gases present as a ratio of the equivalent of the free ammonia also present. A determination of the latter must therefore be made by direct titration.

Free Ammonia:—Pipette 10 cubic centimeters of liquor, add 50 cubic centimeters of water, and titrate with normal sulphuric acid, with methyl orange indicator.

Carbon Dioxide and Hydrogen Sulphide:—In the distilling flask of the "total ammonia" apparatus, put 200 cubic centimeters of water, and 10 cubic centimeters each of liquor, ammoniacal calcium chloride, and strong (0.900 S. G.) ammonia. In a 250 cubic centimeter flask to serve as a receiver, put 20 cubic centimeters of barium hydroxide solution, 10 cubic centimeters of strong ammonia and fill with water to one-half inch from the bottom of the neck.

The object of adding ammonia to the distilling flask is to keep the contents strongly ammoniacal during the distillation, as otherwise some of the calcium carbonate formed will be decomposed with loss of carbon dioxide. The object of adding barium hydroxide to the receiver is merely to show the possible presence of carbon dioxide in the distillate, which will occur in the distillation is conducted too long and the flask contents cease to be sufficiently ammoniacal. The barium hydroxide solution almost always shows a slight scum, due to carbonic acid in the air, which must not be mistaken for carbonic acid distilled over.

Distil, slowly at first but with a larger flame as soon as the liquid in the flask commences to boil, and continue the distillation for 5 minutes after increasing the flame. This length of distillation will distil off the hydrogen sulphide without decomposing the calcium carbonate. The residue in the flask may be tested with lead acetate paper to show the removal of hydrogen sulphide.

Transfer the liquid in the receiver to a 600 cubic centimeter beaker and dilute to about 500 cubic centimeters. Add 3 drops methyl orange, acidify with hydrochloric acid, add 5 cubic centimeters of starch solution and titrate with tenth-normal iodine.

Filter the liquid in the distilling flask through a close grained filter, wash thoroughly with water, and dissolve the precipitate in 15 cubic centimeters of normal sulphuric acid. The best way to do this is to run the acid into the washed distillation flask, to dissolve the precipitate which lodges there, and then transfer it to a beaker into which is put the filter paper containing the main portion of the precipitate. Stir well, boil, cool and titrate back with ammonia solution, using cochineal as indicator.

Since normal and tenth-normal solutions are used throughout, the ratio of the normal acid used by the calcium carbonate to that used in titrating the free ammonia, will show at once what portion of the ammonia may be considered to be combined with carbonic acid as the normal carbonate. The same is true for the titration of hydrogen sulphide by iodine, with allowance for the fact that the iodine solution is tenth-normal.

Ammonium Sulphate.

MOISTURE.

Approximately 10 grams of the salt are dried at 105° C. to constant weight.

FREE ACID.

The dry salt from the moisture determination of approximately 10 grams of a fresh sample is dissolved in about 200 cubic centimeters of water. A drop or two of methyl orange or sodium alizarin sulphonate is added and the free acid determined by titration with N/10 sodium hydroxide solution.

AMMONIA.

Ten grams are dissolved in water and diluted to 1 liter. An aliquot of 100 cubic centimeter is taken for the determination of ammonia. This is placed with 100 cubic centimeters of water in a Kjeldahl distilling flask; 10 cubic centimeters of 30 per cent. caustic soda are added with a piece of granulated zinc and the ammonia distilled over into 80 cubic centimeters of N/5 sulphuric acid. The excess acid is found by titration, etc., using sodium alizarin sulphonate or cochineal as indicator.

TARRY MATTER.

Fifty grams of salt are dissolved in cold water and filtered on a Gooch crucible which is dried at 70° C. The tar is extracted with ether and the ethereal extract is evaporated in a tared dish. The weight of dry extract is taken as total organic matter.

NAPHTHALENE.

The above weighed tarry extract is dissolved in cold alcohol and an equal weight of picric acid also in alcoholic solution is added. The naphthalene picrate is then filtered off, dried at 100° C. and weighed.

$$\text{Naphthalene picrate} \times 0.3586 = \text{naphthalene.}$$

PYRIDINE.

To a filtered solution of 50 grams of sale in 150 cubic centimeters of water in a distilling flask is added about 20 cubic centimeters of normal caustic soda, sufficient to make it slightly alkaline, but not enough to decompose it. Distil into 100 cubic centimeters of water. Nearly neutralize with hydrochloric acid and redistil into 30 cubic centimeters of water until 70 cubic centimeters have come over. Make up the distillate to a volume of 150 cubic centimeters, add 6 drops of phenolphthalein, and then run in normal acid till the pink color has just disappeared. Then add 0.13 cubic centimeter more of acid and read the burette. Add 1 drop of methyl orange and titrate to a pink color. Each cubic centimeter of acid used after adding the methyl orange equals 0.079 gram pyridine.

THIOCYANATES—PINK COLOR.

To a filtered solution of 100 grams of salt, copper sulphate and sulphurous acid are added and the solution gently warmed. After settling, the copper thiocyanate is filtered off and washed free from copper salts as shown by testing the washings with potassium ferrocyanide. The precipitate is then dissolved in nitric acid, water added, and the solution boiled for several minutes. The copper is determined in the solution as the oxide by precipitation with sodium hydroxide; or by electrolysis. The weight of copper × 1.1974 equals equivalent amount of NH_4SCN.

FERRO FERRICYANIDE—BLUE COLOR.

One hundred grams of salt are dissolved in hot water and filtered on a folded filter in a hot water funnel. Wash with hot water until free from sulphates. The residue and filter are put into a flask with about 50 cubic centimeters of water, shaken and boiled to separate the residue from the filter as much as possible. To the contents of the flask N/50 sodium hydroxide solution is added little by little until the blue is entirely decomposed, which is hastened by having the contents of the flask warm. While constantly shaking and heating, the excess sodium hydroxide is titrated with N/50 acid. The heating is quite necessary for even in the presence of an alkali, the greenish color formed by the decomposition of the blue lasts only a short time.

The end point is reached when the dark green color in the solution first appears.

One cubic centimeter N/50 NaOH equals 0.001431 gram $Fe_4Fe_3(CY_6)_3$.

ARSENIC.

Dissolve 100 grams of salt in water and filter. The arsenic will be on the filter as sulphide. Dissolve the sulphide by hot digestion with sodium sulphide, using as little as possible. Filter and wash by stirring and pressure using slightly alkaline H_2S water. Evaporate filtrate to dryness in 25 to 50 cubic centimeters hydrochloric acid (2 acid to 1 water) and add a small crystal of tartaric acid. Precipitate the arsenic from the cold solution with H_2S, allow to settle for a short time, filter on an asbestos felt and wash with acid of the same strength. This separates the arsenic from any traces of antimony that may be present from hard lead and from traces of tin which are sometimes present in distilled water which has been condensed in a tin worm.

Place the felt with the arsenic sulphide in a beaker, digest on a steam plate with red fuming nitric acid, dilute the solution with 1½ parts of water and filter out the asbestos, and evaporate to dryness with 0.1 to 0.5 gram of sodium nitrate.

Dissolve the residue in 5 cubic centimeters of cold water with 10 drops of HCl and 0.1 gram tartaric acid. Filter into a small beaker and wash with as little water as possible with a fine jet.

Make slightly alkaline with ammonia. The solution should be clear and not more than 11 cubic centimeters in volume.

Add 3 cubic centimeters magnesia mixture, make up to 20 cubic centimeters with strong ammonia and stir 5 minutes. Allow to stand over night and filter on a small filter, aiding the transfer of the precipitate within the filtrate. Wash free from chlorine with a fine jet of ammonia (1 to 3 of water) dry in an oven, remove the salt and place filter in a porcelain crucible. Add a few drops of acid ammonium nitrate solution (saturated), char carefully and repeat treatment until paper is consumed without any perceptible odor of arsenic. Transfer the remainder of the precipitate and ignite at a full red heat to constant weight. Weigh as $Mg_2As_2O_7$.

LIME.

Sampling.

A large shovelful is taken from each cart-load during the unloading of a car, and put into a covered barrel. This sample is broken down rapidly to ½-inch size, reduced by quartering to 2 quarts, sealed up in an air-tight container and sent to the laboratory. In the laboratory it is ground to a fine powder preferably in a ball mill to avoid absorption of moisture and carbon dioxide, and put in rubber stoppered weighing tubes.

DETERMINATION OF CALCIUM OXIDE.

Five grams of the finely ground lime is weighed into a 500 cubic centimeter graduated flask. Ten cubic centimeters of alcohol are added, to prevent the later caking of calcium sucrate, and the flask is filled up to the mark with a 10 per cent. cane-sugar solution. It is shaken frequently over a 4-hour period, or longer. The solution is then filtered, an aliquot of 100 cubic centimeters taken and titrated with normal hydrochloric acid, using methyl orange indicator.

Multiply five times the cubic centimeters of acid used by 0.02804. Divide by the amount of lime taken. The result is the per cent. of calcium oxide.

CYANOGEN.

Moisture.

Dry 30 grams oxide for nine (9) hours at 50° to 60° C.

Extraction of Blue.

Grind the dried oxide so that it passes through an 80-mesh sieve. Weigh out 10 grams of this and introduce into a 250 cubic centimeter flask. Add 50 cubic centimeters of a 10 per cent. caustic potash solution and let stand for 15 to 16 hours at ordinary temperature, shaking frequently. At the end of this time, make up to 225 cubic centimeters (5 cubic centimeters for the oxide). Shake vigorously and filter through a dry filter. Take 100 cubic centimeters of the filtrate and run it into a boiling solution of ferric chloride—50 cubic centimeters. This ferric chloride solution consists of 60 grams ferric chloride and 100 cubic centimeters HCl made up to 1,000 cubic centimeters. After the blue settles a little, filter and wash with boiling water, until the blue, together with the filter paper is put into a beaker and 25 cubic centimeters of the caustic potash solution is added, and, after complete decomposition, made up to 250 cubic centimeters and then filtered through a dry filter. Take 100 cubic centimeters of this filtrate, acidify with 10 per cent. sulphuric acid (test with litmus) and add excess of 10 cubic centimeters acid. Titrate with standard zinc sulphate solution, the operation being the same as in the standardization of the zinc solution. From the number of cubic centimeters zinc sulphate used, the value of this in prussiate can be calculated.

Calculation.—Multiply your standard by number of cubic centimeters $ZnSO_4$ used, and divide by 1.6, multiply this result by 100. This gives per cent. of Prussian blue as $K_4Fe(CN)_6$ in dry sample.

This result multiplied by 100 minus the moisture per cent. gives the result in terms of the undried oxide.

ZINC SULPHATE SOLUTION.

Weigh out 10 grams zinc sulphate C. P. and make up to 1 liter, after adding 10 cubic centimeters concentrated sulphuric acid.

POTASSIUM FERROCYANIDE SOLUTION.

Weigh out exactly 5 grams potassium ferrocyanide (C. P. and with exact quantity of water of crystallization. If this is more or less, a correction has to be made). Make up to 250 cubic centimeters.

STANDARDIZING THE ZINC SOLUTION.

Measure out 25 cubic centimeters of the ferrocyanide solution into a beaker. Add about 50 cubic centimeters of water and acidify with 10 cubic centimeters of a 10 per cent. sulphuric acid solution. Now from a burette run in the zinc solution.

As an indicator, use a 3 per cent. solution of ferric alum, using Schleichner & Schnell's drop reaction paper No. 601. One drop of the ferric alum solution is brought on to the paper, and near this spot a drop of the solution being titrated is placed, so that by extension the two spots just touch each other. The end point of the titration is reached when the blue coloration at the point where the two drops meet does not appear for the space of 1 minute. From the number of cubic centimeters of zinc sulphate solution used, the value of this in prussiate can be calculated.

In titrating the oxide solution, acidify the 100 cubic centimeters with 10 per cent. sulphuric acid, after adding methyl orange No. 3 to the solution, and add an excess of 10 cubic centimeters acid. Titrate with the standard zinc solution, the operation being the same as the standardization of the zinc solution.

The original Knublauch method involved the use of copper sulphate.

The Feld-Witzeck Method.

Two grams of the dried and finely pulverized oxide are taken and titrated for 5 minutes in a glass mortar with 1 cubic centimeter of normal solution of ferrous sulphate and 5 cubic centimeters of eight times normal solution of caustic soda. Then 50 cubic centimeters of three times normal solution of magnesium chloride are added with constant stirring, and the whole is washed into a flask—the volume of liquid being brought to about 220 cubic centimeters. After boiling for 5 to 10 minutes, 100 cubic centimeters of boiling decinormal solution of mercuric chloride are poured into the boiling liquid, and the boiling continued for 10 minutes. The flask is then connected with the condenser, 30 cubic centimeters of four times normal sulphuric acid are added, and the liquid is distilled for 20 to 30 minutes. The distillate is collected in 20 cubic centimeters of twice normal solution of caustic soda. If it is cloudy, 0.5 gram of lead carbonate is added to it in a measuring flask, which is filled to the mark, and an aliquot portion is taken for the titration, after the precipitate has been filtered off.

The titration is carried out according to Liebig's method with decinormal solution of silver nitrate and the addition of 5 cubic centimeters of one-fourth normal solution of potassium iodide. The appearance of a yellowish milky cloudiness indicates the end of the reaction. *(Journal of Gas Lighting & Water Supply, Aug. 3, 1915, p. 244.)*

Apparatus for Distillation.—A round bottom flask is provided with a double bored rubber stopper which contains a separatory funnel and distilling column. The latter is connected with a condenser which dips into an Erlenmeyer flask also provided with a double bored rubber stopper, the second hole is connected with a 3-bulb tube containing sodium hydroxide. (*Allen's Commercial Organic Analysis, Vol. VII, p. 521.*)

The Committee recommends the use of the Feld-Witzeck Method.

CHAPTER III.

IMPURITIES IN GAS.

Determination of Hydrogen Sulphide.

The hydrogen sulphide is determined by leading the gas through a suitable absorption apparatus containing a solution of lead nitrate. The resulting lead sulphide is filtered off, oxidized in a porcelain crucible with nitric acid, treated with a drop of sulphuric acid, evaporated to dryness, ignited and weighed.

For works control where great accuracy is second and speed first consideration, the H_2S burette is the most widely used method and gives within small errors best results, and can be recommended as sufficiently accurate for all practical purposes.

The apparatus employed is shown in Fig. 34. It consists of a burette provided at the top with a 2-way and at the bottom with a 1-way cock, communicating at top through one of the outlets with a 10 cubic centimeter glass stoppered cylinder graduated into 1/10 cubic centimeter. There are only two graduations on the burette proper, one at the 100 cubic centimeter mark, and the other 50 millimeters from the bottom cock, dividing the remaining space into two divisions of about 5 cubic centimeters and 10 cubic centimeters respectively. A levelling bulb is attached to the lower cock at *E*, and the burette mounted on a stand as indicated.

Chemicals.

The following chemicals are necessary:

1. *Standard Iodine Solution.*—One cubic centimeter of this solution should contain 0.0017076 gram iodine, which is equivalent to 100 grains of sulphureted hydrogen per 100 cubic feet of gas.

2. *Starch Solution.*—Rub into a thin paste about 1 teaspoonful of wheat starch with a tablespoonful of water. Pour into a pint of boiling water, stir, allow to stand until cold, and

pour off the clear solution for use. Make a fresh solution every few days.

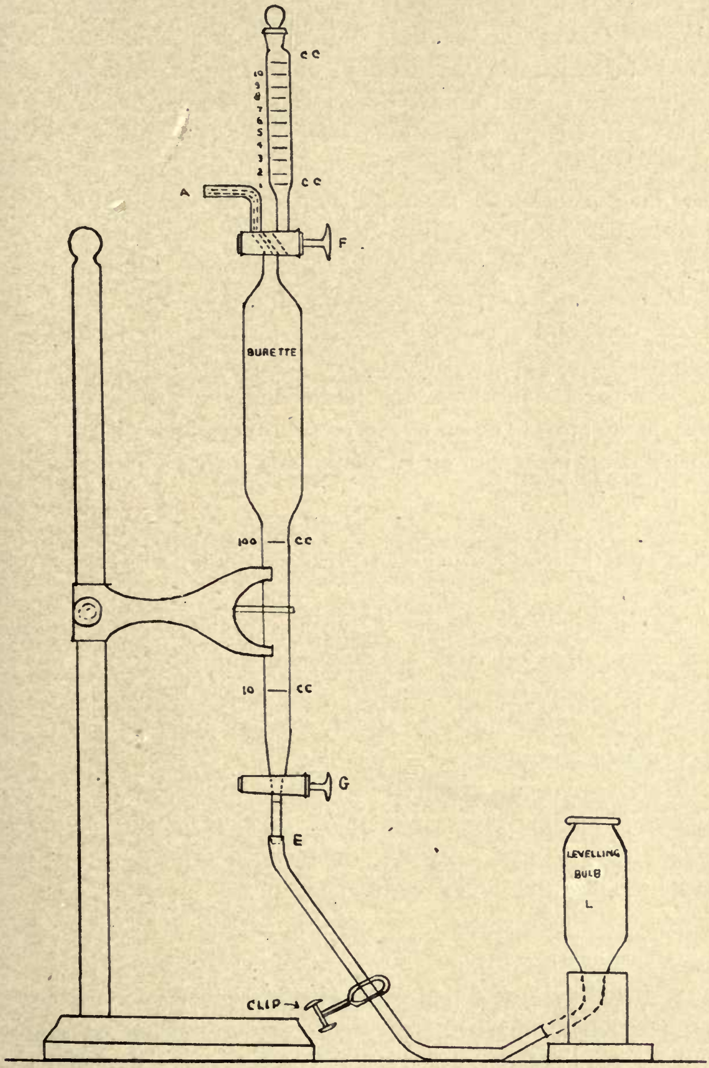

FIG. 34.

To Make Analysis.

Fill levelling bulb *L* with starch solution and turn cocks so that on raising the levelling bulb the starch solution will fill the burette and run out through the gas inlet tube *A*. Close lower cock *C*, and attach rubber tube through which the gas to be tested is passing to inlet tube *A*. Open lower cock, and lower levelling bulb until the starch solution just passes the 100 cubic centimeter mark on the stem of the burette. Close lower cock, then close top cock *F*, and disconnect from gas supply. Open lower cock and bring starch solution to 100 cubic centimeter mark by raising levelling bulb, then close lower cock and open top cock to air momentarily to obtain atmospheric pressure in the burette. Close top cock and by opening lower cock and lowering the levelling bulb draw the starch out of the burette down to the 10 cubic centimeter mark. Close lower cock, place clip on rubber tubing near *E*, and disconnect levelling bulb from *E*.

We now have 100 cubic centimeters of gas measured at atmospheric temperature and pressure, under a negative pressure.

Fill graduated cylinder *C* with standard iodine solution, noting reading on same. Admit iodine solution into the burette very gradually through *F*, shaking well between each addition. Continue until the starch solution assumes a faint, but permanent blue color.

Note reading on graduated cylinder, which subtracted from previous reading gives amount of solution used. This multiplied by 100, gives directly number of grains of hydrogen sulphide per 100 cubic feet of gas.

Precautions.

1. It will be found that even with gas entirely free from sulphureted hydrogen an appreciable amount of iodine solution will be required to color the starch solution a permanent blue. Therefore a certain constant, previously determined on each fresh bottle of starch solution, should be subtracted from all

readings. In order to determine this constant, suck starch solution into the burette up to the 10 cubic centimeter mark, this being the amount used in each determination, close lower cock and carefully drop into the burette iodine solution from the cylinder, shaking between each addition, until the starch solution assumes a permanent blue color. Note amount of iodine added, which will be about 0.2 cubic centimeter to 0.3 cubic centimeter and subtract this from total amount of iodine solution required in each determination.

2. The blue color must not be confused with the opalescent milky appearance due to the separation of free sulphur, nor with a red color which will disappear on shaking.

3. For extremely accurate work, introduce a correction factor for temperature and pressure, bringing the gas to 60° F and 30″.

In special cases where the highest accuracy is required and time can, therefore, be no factor, the following method is the most suitable:

The gas to be tested is first purified from such impurities as may interfere with the work, such as tar, by passing it through a U-tube filled with cotton and then into a gas wash bottle containing an ammoniacal solution of silver nitrate. (It is best to use two bottles in series to prevent any H_2S to go by when the first bottle should become saturated by a high H_2S content in the gas, stopping the operation when the second solution is showing precipitate of silver sulphide.) The ammonia absorbed by the gas from the train is removed by another bottle containing H_2SO_4 before entering the meter. Where insufficient gas pressure exists it is best to use suction to pull the gas through. The solution and precipitated Ag_2S etc. is next transferred to a beaker and filtered and washed. The silver acetylene formed is next decomposed by filling the filter with diluted HCl, forming silver chloride and acetylene; again wash with water and remove the silver chloride with dilute NH_4OH and again with water.

The filter and contents are next placed in a Rose crucible, dryed and burned. After all the filter paper has been burned and the sulphide roasted, the silver is reduced in a stream of hydrogen to metallic silver. From the weight of the metallic silver the H_2S is calculated by multiplying the weight with 0.1578 or with 0.14875 for sulphur.

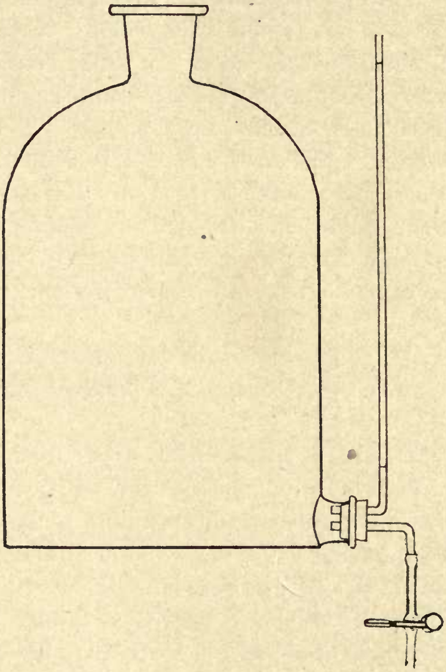

FIG. 35.

Another quicker although not quite as accurate method has been in use in various modifications. It is based on the method of determining sulphur in steel. The gas freed from tar by passing it through cotton is bubbled through an ammoniacal solution of cadmium chloride contained in a gas washing bottle using a graduated aspirating bottle for measuring the gas or a meter. The operation is as follows:

To the gas outlet by means of a short rubber tube connect a U-tube filled with cotton, connect this with two gas washing bottles (200 cubic centimeters capacity), containing 50 cubic centimeters of an ammoniacal solution of cadmium chloride, in series. If a meter is used for measuring the gas another bottle containing dilute sulphuric acid, to remove the ammonia from the gas before entering the meter, must be placed behind the absorption bottles. This can be omitted where a graduated aspirating bottle is used. This bottle (see Fig. 35) is graduated by filling it with water to a mark scratched on the glass *L* in the stopper at the top, the water is next drawn out through the bottom stopper also fitted with a glass *L* and closed with a piece of rubber tubing and pinch-cock. 3,537.5 cubic centimeters = to ⅛ cubic foot of the water are drawn off and the bottle marked. This is best accomplished by having a 2-hole stopper at the bottom, the second hole being fitted with a glass tubing bent short at right angles and reaching to the top. The bottle being perfectly level, the second mark is made on this tube insuring more accurate measuring. Where a meter is used from 0.1 to 0.15 cubic foot of gas are passed. In both cases the gas should be passed at a very slow speed, not more than 0.5 cubic foot per hour.

The contents of the washing bottles are next transferred to a 600 cubic centimeter beaker, the bottles first washed with distilled water and then with a little dilute hydrochloric acid, sufficient dilute HCl added to the beaker to make acid, indicated by clearing of solution, starch solution added and titrated with standardized iodine solution, and the H_2S calculated from the iodine used.

Qualitative Test.

For qualitative test the following method is in general use:

A strip of white filter paper is dipped in a solution containing 5 per cent. by weight of lead acetate, the excess solution being removed from the test paper with a blotter. The paper is exposed while moist for 1 minute to a current of gas flowing at the rate of approximately 5 cubic feet per hour in an apparatus as shown in Fig. 31 and described below, or in other similar apparatus.

The gas may be considered free from hydrogen sulphide if the paper thus exposed is not distinctly darker than another paper moistened with the same solution but not exposed to the gas.

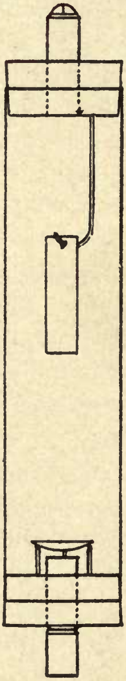

FIG. 36.—Apparatus for exposing test paper.

The apparatus for exposing the paper as shown in Fig. 36 is made from a cylindrical gas chimney 8 inches long, and 1¾ inches in diameter. The pillar of a gas burner from which the lava tip has been removed is inserted through the lower stopper, and a small glass, 1 to 1¼ inches in diameter is supported above the pillar to prevent the gas from impinging directly on the test paper. The watch glass may be supported on three glass pegs, ½ to 1 inch high, being held in place with small bits of wax. The gas is burned from an ordinary open flame burner on the upper stopper, this burner being so selected that it will pass 5 cubic feet per hour at the ordinary pressure of the gas supply. The test paper is hung on a glass hook so that it is held midway between the watch glass and the bottom of the upper stopper.

This apparatus may be attached permanently to a wall bracket, or a Bunsen burner may be inserted through the lower stopper in place of the pillar so that the apparatus can conveniently be attached at any outlet with a rubber hose.

AMMONIA.

Methods of Operation.

The apparatus as shown in Fig. 37 consists of two all glass modified Woulff bottles. These should be placed before the governor and meter if the ammonia determination is made in connection with the sulphur determination.

Place in the absorption apparatus an accurately measured portion (about 25 cubic centimeters) of a standard solution of sulphuric acid prepared as directed below, and add 2 drops of the indicator solution. The acid should be measured from a pipette or a burette and may then be diluted with the distilled water until the volume is obtained which gives the best operation with the particular apparatus in use. Connect the apparatus with the gas supply, and with a meter on the outlet of the bottle pass the gas to be tested, at the rate of 0.5 to 0.6 cubic foot per hour, for 2 to 5 hours, according to convenience and accuracy required. Somewhat greater accuracy is secured by the longer test. When the requisite amount of gas has passed, the supply is shut off and the color of the solution noted to determine whether the acid has been neutralized, as shown by the indicator. If neutralized, add more H_2SO_4 to make slightly acid. The acid remaining unneutralized is determined as follows: The content of the apparatus is rinsed into a beaker with distilled water, using the smallest amount possible to secure complete removal of the acid, and the solution is titrated with a standard solution of sodium hydroxide.

A solution of sodium alizarin sulphonate is recommended as an indicator. The solution of sodium alizarin sulphonate for use is made by dissolving 1 gram of the material in 100 cubic centimeters of water and filtering off the undissolved portion. In titrating, the end point is reached when the color changes from greenish yellow to light brown. The color further changes to red, but the first change is the proper one for this work. The change is sharp.

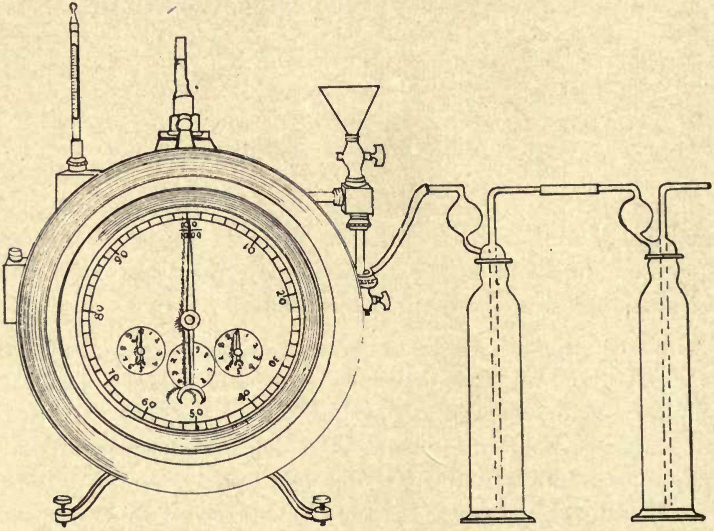

FIG. 37.

Preparation of Solutions.

The sulphuric acid may be conveniently made of such strength that 1 cubic centimeter neutralizes approximately 0.005 gram of ammonia, and its exact strength is determined by standardization. To 2 liters of distilled water add between 1.25 and 1.50 cubic centimeters of pure concentrated sulphuric acid and mix thoroughly by shaking. This solution must be carefully preserved in a glass stoppered bottle to avoid contamination and evaporation. For the standardization of the acid a 50 cubic centimeter portion is accurately measured into a 400 cubic centimeter beaker, diluted to 250 cubic centimeters and treated with 10 per cent. barium chloride solution in the manner already given. The weight of barium sulphate (in grams) obtained by this process is multiplied by 2.25 and then divided by the number of cubic centimeters of solution taken as sample. The result is then expressed in grains of ammonia equivalent to 1 cubic centimeter of the acid.

The sodium hydroxide solution for titrating the excess of the acid is prepared by dissolving approximately 1.8 grams of sodium hydroxide in 2 liters of water and mixing thoroughly. To obtain the ratio of the acid to the alkali, measure out the same amount of acid as is ordinarily titrated in a determination and add distilled water until the volume of solution is about equal to that obtained in washing out the apparatus after a determination, add 2 drops of indicator solution and complete the titration with the alkali. For convenience the strength of the alkali may be made equivalent to the acid by dilution or further addition of alkali.

TOTAL SULPHUR.

The referee's form of apparatus is recommended on account of its wide use and general ease of manipulation. The apparatus is shown in Fig. 38.

The entire apparatus consists of a pressure governor, U water gauge, meter and sulphur apparatus; these being connected in the order given. If the gas used for the sulphur tests is also used for the ammonia test, the ammonia absorber is connected between the source of the gas supply and the pressure governor. For connecting the various parts of the apparatus rubber tubing is not satisfactory. It is usually most convenient to make permanent connections from governor to gauge, gauge to meter, and meter to burner; these can be of glass tubing with rubber connections wired on, except the connection of meter to burner. For the latter it is best to braze or screw a metal tube to the burner inlet (about 6 to 8 inches is a convenient length) so that if the burner strikes back during a test the connection is not broken at the base of the burner and gas allowed to escape or take fire at this point.

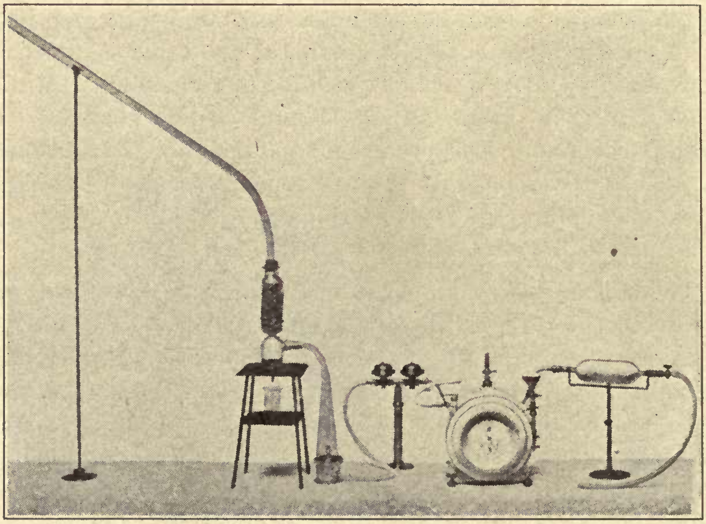

FIG. 38.

The meter and governor used may be of either the wet or dry type. The usual precautions as to levelling and proper adjustment should, of course, be observed. The pressure on the governor should be so adjusted once for all that when the gas is turned on full at the supply cock the burner will pass gas at the desired rate.

The connection between meter and burner, as well as the meter itself, should be frequently tested to show the absence of leaks. Any leaks, even very small ones, may cause appreciable errors in the test, since the rate of gas consumption is small.

Method of Operation.

After all connections and adjustments of the apparatus have been made the gas should be burned from the apparatus for several hours to saturate the meter and governor water and to purge the connections. Before each test the line may be purged in this way by burning the gas for about a half-hour, a burner which will pass 5 cubic feet or more per hour being substituted for the regular test burner.

When the line is thus purged, the regular burner is put in place and ammonium carbonate placed on the burner. As much ammonium carbonate is used as will find place about the burner pillar. The ammonium carbonate should be in large lumps which have been freed from effervescent portions. It is usually desirable to rinse out condenser and chimney tubes just before starting the test, in order to prevent dust which might have collected there between the tests from contaminating the condensate. When all parts, including the flask to collect the condensate, are in place, the trumpet tube is set over the burner and quickly connected with the condenser, the meter reading being noted at the instant the trumpet tube is put in place. This reading and the time, meter, temperature, barometer and manometer readings are recorded in the test record.

The gas is burned at ½ cubic foot per hour.

If the sulphate is to be determined gravimetrically, it is generally desirable to burn at least 2½ or 3 cubic feet of gas for a test.

When it is desired to burn more than 3 cubic feet of gas for a test, it is necessary to replenish the supply of ammonium carbonate. To do this the gas is shut off and the trumpet tube allowed to cool so that it may be handled comfortably.

A fresh supply of carbonate is then added, the burner relighted, and the trumpet tube replaced quickly. If more than a few thousandths of a cubic foot of gas are burned with the trumpet tube off, the amount so burned should be deducted from the total used for the test. A fresh supply of carbonate must be added in this manner after every 3 cubic feet of gas burned in the Referee's apparatus.

When sufficient gas has been burned, the supply is cut off and the apparatus allowed to cool. The time, meter reading, meter temperature, and barometer are recorded again at the close of the test. The trumpet tube is then washed once and the condenser four times. Each portion of wash water is 50 cubic centimeters and is added all at once to thoroughly flush the condenser.

The sulphate in the condensed liquid and wash water is determined by precipitation with barium chloride. From sulphate found and corrected volume of gas burned, the sulphur content of the gas (in grains of sulphur per 100 cubic feet of gas) is calculated.

Determination of Sulphate in the Solution Obtained.

In the more common procedures for the gravimetric sulphate determination, the precipitation of the barium sulphate is made in nearly neutral solution. This method may be used as follows:

To the solution which is diluted or concentrated to about 300 cubic centimeters add 2 or 3 drops of paranitrophenol or methyl orange solution and neutralize with hydrochloric acid, adding this solution dropwise, and finally add 2 cubic centimeters of the 1:1 acid in excess. Heat to boiling, add 10 per cent. barium chloride solution, boil 5 minutes, allow to stand on a steam bath for a half-hour or longer, filter through a good close-grained paper, and wash with hot water until a few drops of filtrate collected in a test-tube no longer form a precipitate with silver nitrate. In a weighed platinum crucible char the paper with low Bunsen flame and finally ignite until the precipitate appears white. Cool the crucible in a desiccator and weigh. The precipitation when made in the presence of a fixed amount of acid is always affected in equal degree by the solubility of the barium sulphate in the acid. Under the conditions given, the loss from this source is negligible for the present work.

DETERMINATION OF NAPHTHALENE IN GAS.

Absorption of Naphthalene by Picric Acid.

Pass the gas to be tested first through N/1 H_2SO_4, next through an empty bottle, then through three bottles each containing 100 to 150 cubic centimeters of saturated picric acid solution and excess of undissolved picric acid, (2) and finally through a gas meter for measurement. Stop the operation when a naphthalene picrate precipitate begins to appear in the second picric acid wash bottle.

Preparing Benzol Solution of Naphthalene-Picrate and Picric Acid.

Transfer the picric acid solution and precipitate to a liter separatory funnel, the residues being washed in with naphthalene-free benzol. Shake gently the funnel contents until the precipitate is completely dissolved in the benzol. Reject the aqueous layer and draw the benzol solution into a 250 cubic centimeter measuring flask. Make up to the mark with benzol and thoroughly mix.

Determination of Total Picric Acid.

Titrate 50 cubic centimeters of this solution—preferably in a 200 or 250 cubic centimeter separatory funnel for shaking is necessary—with N/5 NaOH using methyl red as indicator. This titrates both the free and combined picric acid.

If $T =$ cubic centimeters N/5 NaOH required for this total titre.

Then $5T =$ cubic centimeters N/5 NaOH required for total titre of the whole solution.

(To prepare methyl red indicator, dissolve 2 grams methyl red in 1 liter of a mixture of two parts grain alcohol and one part water.)

Determination of Free Picric Acid.

The free picric acid present is determined by the following procedure:

From a burette draw $\frac{1200}{T}$ cubic centimeters of the benzol solution into a 100 cubic centimeter flask and evaporate to dryness to remove the benzol, proceeding carefully according to the following directions. The flask is placed in a hot water bath and a current of air passed over (not in) the benzol solution, at no time allowing the level of the hot water to be above the level of the benzol solution. The flask should be gently shaken during the evaporation to keep the walls moistened and to avoid overheating any part. (4) Keep the flask about 1 minute in the hot water after the residue appears dry, then remove, but continue the air current until the odor of benzol can no longer be detected.

Dissolve the residue in the flask with 10 cubic centimeters of 95 per cent. alcohol, heating gently if necessary, then precipitate the naphthalene-picrate by adding distilled water slowly, with agitation, until the volume is exactly 100 cubic centimeters. The temperature of this solution must be cooled to 20° C.—in no case more than 2° higher or lower.

Filter through a dry filter into a 100 cubic centimeter cylinder and titrate 90 cubic centimeters of the filtrate with N/5 NaOH using methyl red as indicator. The cubic centimeters N/5 NaOH taken divided by 0.9 give the titre required for the free picric acid in $\frac{1200}{T}$ cubic centimeters of the original benzol solution.

If F = cc. N/5 NaOH required for this $\frac{1200}{T}$ cc.

Then $F \times \frac{250}{\frac{1200}{T}}$ = NaOH required for the free picric acid in the whole benzol solution.

Calculation of the Naphthalene from the Picric Acid Titres.

The difference between the total titre and the free acid titre is the titre of the picric acid combined as naphthalene-picrate, and this latter titre, multiplied by its naphthalene equivalent, gives the grams naphthalene in the gas sample taken, as follows:

$$\left[\overset{\text{Total titre}}{5\,T} - \left(\overset{\text{Free acid titre}}{F} \times \frac{250}{\frac{1200}{T}}\right)\right] \times \overset{\substack{\text{Grams naphthalene}\\ \text{equivalent to 1 cc.}\\ \text{N/5 NaOH}}}{0.0256} = \text{Grams naphthalene in gas sample.}$$

or, simplified $0.0053T\ (24 - F)$ = grams naphthalene in gas sample, and $\frac{0.0053\,T\ (24-F)}{\text{cu. ft. gas taken}}$ = grams naphthalene per cu. ft. gas. which × 15.43 = grains per cu. ft.

Notes on the Method.

(1) The reactions involved in the method are the following:

$$\frac{\text{Naphthalene}}{C_{10}H_8} + \frac{\text{Picric acid}}{C_6H_2(NO_2)_3OH} = \frac{\text{Naphthalene picrate}}{C_6H_2(NO_2)_3OH.C_{10}H_8 + H_2O}$$

$$\frac{\text{Picric acid}}{C_6H_2(NO_2)_3OH} + NaOH = \frac{\text{Sodium picrate}}{C\ H\ (NO)\ ONa} + H_2O$$

$$C_6H_2(NO_2)_3OH.C_{10}H_8 + NaOH = C_6H_2(NO_2)_3ONa + C_{10}H_8 + H_2O.$$

(2) To absorb the naphthalene completely the picric acid solution must be fully saturated, and to insure this an excess of crystals must be present.

(3) The reason for taking $\frac{1200}{T}$ cubic centimeters of the benzol solution for the free picric acid test is that this is the quantity which contains the right amount of total picric acid (1.1 grams) to saturate the 100 cubic centimeters of solution to which it is finally made up, and this saturation is essential to prevent decomposition of the naphthalene picrate present at the stated temperature (20° C.).

(4) Naphthalene picrate is easily decomposed by heat, evolving naphthalene and leaving behind free picric acid.

Reagents—N/5 NaOH.

Saturated picric acid solution of known strength (100 cubic centimeters picric acid should be equivalent to 28-35 cubic centimeters N/5 NaOH).

Methyl red or lacmoid indicator.

Standardizing of the Picric Acid.

Filter 500 cubic centimeters of strongly saturated picric acid solution. Take 100 cubic centimeters of filtrate and titrate against N/5 NaOH, using methyl red or lacmoid indicator. Between 28 and 35 cubic centimeters N/5 NaOH should be required. Let titre equal "A."

Test.

Wash 15 to 50 cubic feet of gas through the remaining 400 cubic centimeters of picric acid. The gas should first pass through a dilute H_2SO_4 solution, next an empty bottle and then through at least two picric acid wash bottles. The gas should be washed at the rate of 1 or 2 cubic feet per hour.

As rubber absorbs naphthalene the connections between bottles, and to the supply pipe, must be so made that little or no rubber is exposed to the gas. (Glass to glass.)

Determination.

Mix the picric acid solution and filter. Reject the first 50 cubic centimeters. Take the next 100 cubic centimeters and titrate against N/5 NaOH. Let titre equal B. Let C equal the N/5 NaOH equivalent of naphthalene in one-fourth of gas used. Then $A - B = C$.

One cubic centimeter N/5 NaOH equals 0.0256 gram naphthalene.

Therefore: $4 \times c \times 0.0256$ equals grams naphthalene in gas tested.

For Example.

In a test, 69 cubic feet of gas were washed. Titre *A* required 31.8 cubic centimeters N/5 NaOH. Titre *B* required 30.4 cubic centimeters N/5 NaOH.

31.8 — 30.4 equals 1.4.

4 x 1.4 x 0.0256 equals 0.14336 grams naphthalene. 0.14336 divided by 69 equals 0.00208 grams $C_{10}H_8$ per cubic foot gas used.

Remarks.

Grams naphthalene per cubic foot x 1543 = grains naphthalene per 100 cubic feet.

$$\left(\frac{C \times 158}{\text{Cu. ft. gas}} = \text{grains naphthalene per 100 cu. ft.}\right)$$

A picric acid solution containing 12 grams per liter picric acid is saturated at 15° C. though it can be colled several degrees lower without separation of picric acid. If the latter separation takes place during the test a serious error may result, consequently the solution must not be too strong for the temperature to which it may be exposed and a 12 grams per liter solution is recommended for ordinary temperature (15° to 25° C.).

Since the naphthalene content is calculated from a small difference between two large titres the latter must be carefully and exactly performed. The best indicator appears to be methyl red.

DETERMINATION OF CYANIDE IN GAS.

In each of a series of three Muencke gas washing bottles are placed 20 cubic centimeters of a strong solution of caustic soda (1:3), to which is added 50 cubic centimeters of suspended ferrous hydroxide. The ferrous hydroxide used is prepared by adding 40 cubic centimeters of the caustic solution to 60 cubic centimeters of a 10 per cent. solution of ferrous sulphate, allowing the precipitate of ferrous hydroxide to settle, decanting off the solution containing sodium sulphate, and making the volume of suspended ferrous hydroxide up to 150 cubic centimeters with water. About 5 cubic feet of gas are passed for each test, at the rate of approximately 2.5 cubic feet per hour. The contents of the three bottles are then transferred to a flask, boiled for 15 minutes, allowed to cool, and filtered. The filtrate is made up to 500 cubic centimeters and an aliquot part 100 cubic centimeters acidulated with sulphuric acid, an excess of ferric alum added and the precipitated Prussian blue collected and washed until free from sulphates. The precipitate with the filter is at once placed in an evaporator, water added, and the contents heated nearly to boiling, the amount of Prussian Blue being then directly determined by titrating with N/50 NaOH. (The end point is reached when the last trace of blue disappears.)

If 5 cubic feet of gas is used in the test then:

1 cubic centimeter N/NaOH = 2.3315 pounds of $K_4Fe(CN)_6.3H_2O$,

or, 1 cubic centimeter N/NaOH = 2.8660 pounds of $Na_4Fe(CN)_6.12H_2O$ per 10,000 cubic feet of gas.

1 cubic centimeter N/50 NaOH = 0.04663 pound of $K_4Fe(CN)_6.3H_2O$,

or, 1 cubic centimeter N/50 NaOH = 0.05732 pounds of $Na_4Fe(CN)_6.12H_2O$ per 10,000 cubic feet of gas.

DETERMINATION OF CO_2 IN GAS.

(See under gas analysis.)

DETERMINATION OF CS_2 IN GAS.[1]

The gas is first passed through cotton to remove tar and then dried by passing it over calcium chloride and then through three wash bottles containing a strong solution of NaOH covered with an ethereal solution of triethylphosphine until a red coloration appears in the third bottle. The gas should be passed very slowly, not over 0.5 cubic foot an hour and not more than 2 cubic feet of gas should be used. After the

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[1] This method although not in general use is very promising and worthy of consideration for further use.

third bottle becomes red, the contents of the three bottles are transferred to a beaker and filtered through a weighed filter paper, washed and dried. The weight of the $(C_2H_2)_3PCS_2$ multiplied by 0.392 gives the weight of CS_2.

DETERMINATION OF IRON CARBONYL.[1]

Iron carbonyl may be determined by passing the gas through concentrated nitric acid or bromine water and determining the iron in solution (due to the decomposition of the carbonyl) by first evaporating with the addition of H_2SO_4 until white fumes of acid are coming off, then dilute with water, reduce with zinc, and titrate with standard permanganate. This amount of iron multiplied with 3.5 gives the weight of iron carbonyl. Since the carbonyl is present in very minute quantities large volumes of gas (at least 100 cubic feet) have to be treated to obtain any tangible results.

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[1] This method although not in general use is very promising and worthy of consideration for further use.

CHAPTER IV.

TESTS OF TAR PRODUCTS AND LIGHT OILS.

1. Crude Gas Benzols.

a. Bulb Distillation.

APPARATUS.

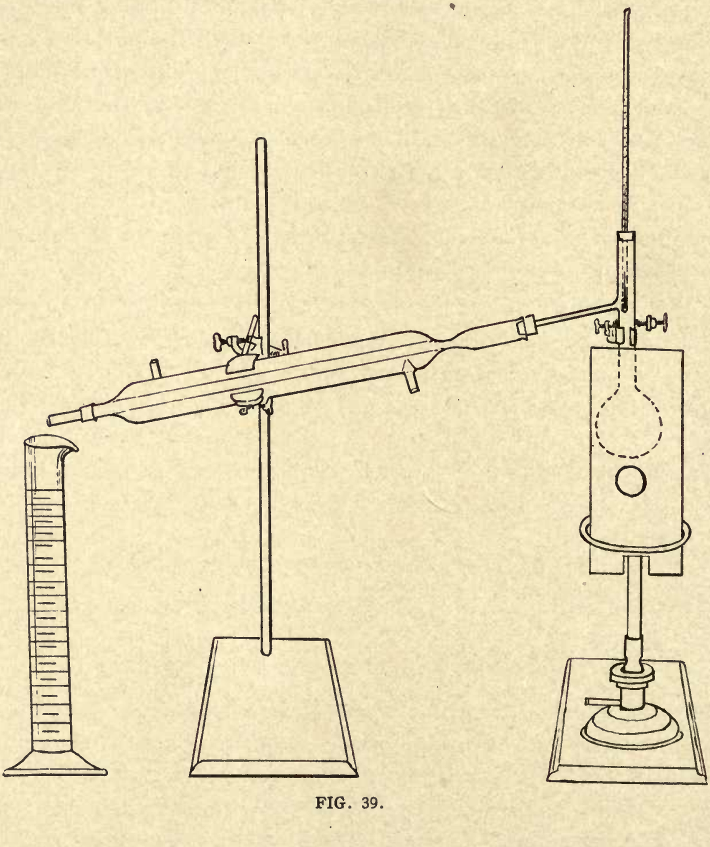

FIG. 39.

Flask: The flask used shall be the standard Engler flask, as described in the various standard works upon petroleum, such as Redwood, Holde, etc.

"Engler employs a globular flask 6.5 centimeters in diameter, with a cylindrical neck 1.6 centimeters in internal diameter and 15 centimeters in length, from the side of which a vapor tube 10 centimeters in length extends at an angle of 75° downwards to the condenser. The junction of the vapor tube with the neck of the flask should be 9 centimeters above the surface of the oil when the flask contains its charge of 100 cubic centimeters of oil. The observance of the prescribed dimensions is considered essential to the attainment of uniformity of results." (Redwood, 3rd Ed., Vol. II, p. 205, 1913.)

The flask shall be supported in a ring of asbestos having an opening 1½ inches in diameter in its center.

The flask, burner, etc., shall be surrounded by a shield.

Condenser: The condenser shall consist of a tube of thin glass 24 inches in length, set at an angle of 75° with the flask surrounded by a water-jacket of the through type.

The thermometer shall conform to the following requirements:

The thermometer shall be made of resistance glass of a quality equivalent to suitable grades of Jena or Corning makes. It shall be thoroughly annealed. It shall be filled above the mercury with inert gas which will not act chemically on or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale. There shall be a reservoir above the final graduation large enough so that the pressure will not become excessive at the highest temperatures. The thermometer shall be finished at the top with a small glass ring or button suitable for attaching a tag. Each thermometer shall have for identification the makers' name, a serial number, and the letters "A. S. T. M. DISTILLATION."

The thermometer shall be graduated from 0° to 400° C. at intervals of 1° C. Every fifth graduation shall be longer than the intermediate ones, and every tenth graduation beginning at zero shall be numbered. The graduation marks and numbers shall be clear-cut and distinct.

The thermometer shall conform to the following dimensions:

Total length, mm.	385	maximum
Diameter of stem, mm.	7,	tolerance 0.5
Diameter of bulb, mm.	5	minimum, and shall not exceed that of the stem
Length of bulb, mm.	12.5,	tolerance 2.5
Distance 0° to bottom of bulb	30,	tolerance 5
Distance 0°-400°	295,	tolerance 10

The accuracy of the thermometer when delivered to the purchaser shall be such that when tested at full immersion the maximum error from 0°-200° C. shall not exceed 0.5°; 200°-300° C., it shall not exceed 1° C.; 300°-375° C., it shall not exceed 1.5° C.

The sensitiveness of the thermometer shall be such that when taken at a temperature of 26° C. and plunged into a free flow of steam, the meniscus shall pass the 90° C. mark in not more than six seconds.

The thermometer shall be inserted through a tight-fitting cork in the neck of the flask, so that the top of the thermometer bulb will be on a level with the bottom of the side outlet in the neck of the flask and in the center of the neck.

METHOD OF DISTILLATION.

The flask, connected with the condenser, shall be filled with 100 cubic centimeters of the material at 15.5° C., which shall be measured in the 100 cubic centimeter receiving cylinder. The same cylinder may be used without drying as the receiving vessel for the distillate. The flask shall be heated directly by a suitable burner.

The distillation shall proceed at the rate of not less than 4 nor more than 5 cubic centimeters per minute, into the receiving cylinder. The temperature at which the first drop leaves the lower end of the condenser shall be considered the initial boiling-point.

Readings of the quantity in the receiver shall be taken when the next 10° point is reached, and for every even 10° thereafter. For example, if initial boiling-point occurs at 104°, then the first reading of the quantity in the receiver shall be made at 110°, and thereafter at 120°, 130°, etc.

The distillation shall be continued until the point is reached where the last drop is vaporized, when a puff of white vapor usually appears in the bottom of the flask. The temperature at this point shall be considered the end or dry point of distillation.

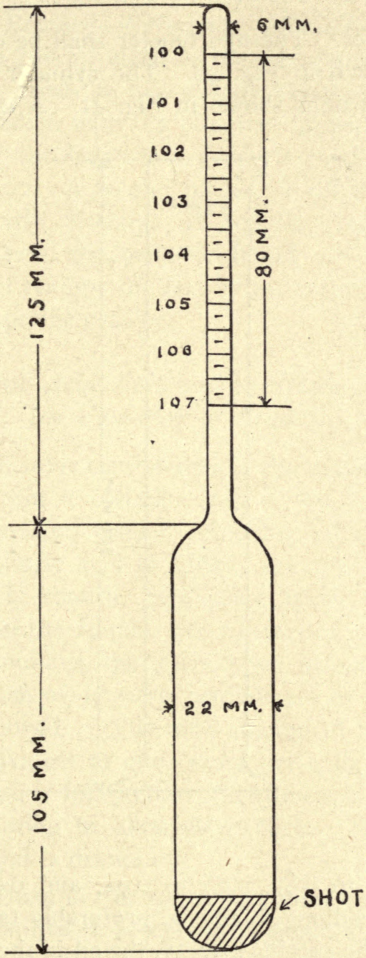

FIG. 40.

The total yield of distillate shall not be less than 97 per cent.

(This method is adapted with some modification from report of Sub-Committee, D—1, *A. S. T. M.*, 1915).

b. Specific Gravity.

1. *Hydrometer:* The hydrometer shall be of the form and dimensions shown in Fig. 40. The cylinder shall be of the form and dimensions shown in Fig. 41. A set of three with ranges of 0.79 to 0.87, 0.86 to 0.94, and 0.93 to 1.01, will suffice. The readings should be preferably taken at 15.5° C. Before taking the specific gravity, the oil in the cylinder should be thoroughly stirred. Care should be taken that the hydrometer does not touch the sides or bottom of the cylinder when the reading is taken, and that the oil surface is free from froth and bubbles. If the specific gravity is determined at a higher

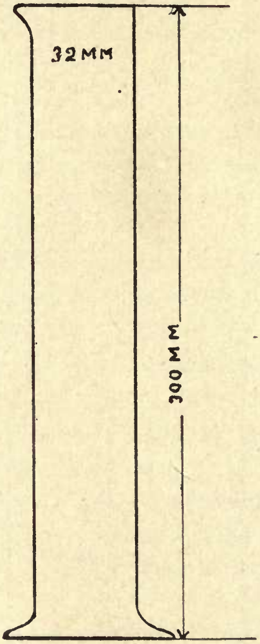

FIG. 41.

temperature than 15.5° C., correction should be made by adding 0.001 for each degree Centigrade excess of temperature. (This correction figure is only an approximate one, and should not be used when exact work is desired.)

2. *Westphal Balance—Reference Method:* The balance should be set up and adjusted so that the plummet when suspended to swing freely in air, exactly balances the beam. A reading is then taken with the plummet immersed in water at 15.5° C., and if the balance is properly made and adjusted, this should be 1.00. A second reading in oil at 15.5° C. gives the specific gravity directly. If for any reason the water reading is not 1.00, the balance should not be adjusted in water, but the oil reading divided by the water reading should be taken as the specific gravity.

c. Wash with Acid, Followed by Steam Distillation for Valuation of Crudes.

Three hundred cubic centimeters of the material to be tested are measured from a cylinder into a 500 cubic centimeter Squibb type separatory funnel. About 4 cubic centimeters of 66° Baumé sulphuric acid is added, and the contents of the funnel thoroughly shaken, care being taken to avoid piling up of pressure in the funnel, due to heat of reaction. After settling for 15 minutes, the lower layer of acid is drawn off and a second wash of 17 cubic centimeters of acid is applied, and likewise removed. (The total amount of acid used is approximately equivalent to one pound per gallon of material.) The last acid wash is followed by a treatment with 10 per cent. caustic soda solution to alkaline reaction. This soda is allowed to settle and is drawn off.

The treated benzol is run into a 500 cubic centimeter short-neck bulb and distilled in a current of steam until no more oil is visible in the distillate. The flask containing the treated benzol should be kept warm enough by a burner during the course of the distillation to prevent undue condensation of steam. The volume of oil distillate is measured, and divided by three, gives the percentage of refined benzols in the crude gas benzol.

(Steam distillation is necessary here to avoid possible decomposition. A redistillation by method 1-a may be made if there is any indication of the presence of wash oil in the distillate.)

2. HOLDER OILS (DRIP OILS).

a. Bulb Distillation.

Same as 1-a, with the exception that the distillation is not continued to the drying point, but only to the point where 95 per cent. of the material is distilled off.

b. Specific Gravity.

Same as 1-b. If the specific gravity is determined at a higher temperature than 15.5° C., correction should be made by adding 0.00088 for each degree Centigrade excess of temperature.

c. Distillation with Dephlegmator.

One hundred cubic centimeters of the oil are placed in a flask equipped with Hempel distilling tube, supplied with solid glass beads of 4.8 to 5.5 millimeters diameter to a depth of 75 millimeters, and distilled, noting the cubic centimeters distillate at 170° C. and 200° C. The first fraction represents approximately crude benzol, toluol and solvent, and the 170-200° fraction heavy naphtha.

NOTE.—A 6-bulb Lebel column or 12-bulb Young pearhead flask may be substituted for the Hempel tube in this test.

d. Naphthalene.

The residue above 200° left in the flask (*c*) is transferred to a copper beaker and cooled to 15.5° C. for 15 minutes. The mass is filtered on a perforated funnel in a suction pump and sucked dry. The naphthalene in the filter is then pressed between paper in a letter press to remove all oil, and weighed.

This test is not very accurate.

3. BENZOLS AND REFINED NAPHTHAS.

a. Bulb Distillation.

Same as 1-*a,* with the exception of tests on pure benzol and pure toluol. With these materials, readings of the per cent. distilled are taken every 0.2° C. and a thermometer of the following specifications may be used:

Dimensions:—

Total length, mm.	370—400
Diameter, mm.	6.5—7.5
Bulb length, mm. (max.)	10
Bulb diameter, mm.	4.5—5.5

Scale.—Scale to start not less than 75 millimeters above bottom of bulb, and to be from 240 to 270 millimeters long.

General.—The thermometer shall be furnished with an expansion chamber at the top and have a ring for attaching tags.

Range.—60° to 140° C., in fifths of a degree.

Accuracy.—To be correct to one-fifth degree Centigrade.

b. Specific Gravity.

Same as 1-*b.*

c. Sulphuric Acid Wash Test.

ACID WASHING TEST FOR BENZOL, TOLUOL, SOLVENT NAPHTHA, ETC.

Semet-Solvay Company's Modification of The Barrett Company's Method. Adopted by The Barrett Company on July 1, 1916.

(Revised.)

The set of color standards consists of 15 bottles (French squares, stoppered, 1 ounce capacity), each containing one of the colored solutions made up as given below and the bottle sealed.

When making a test for amount of acid washing a similar bottle is used. Seven cubic centimeters of 96 per cent. C. P. sulphuric acid is put in first, and then approximately 21 cubic centimeters of the material to be tested is added; shake thoroughly for 15 to 20 seconds and allow to stand for the specified time; compare the resulting color of the acid layer with the standard set and determine which number it corresponds to.

In pure benzol and pure toluol testing the benzol or toluol layer must remain white, and the color of the acid layer after standing 15 minutes, but not be darker than No. 4.

For 90 per cent. benzol and all grades of benzol and toluol other than pure, the benzol and toluol layer must remain white, and the color of the acid layer after standing 15 minutes must not be darker than No. 6.

For xylol, the xylol layer must remain white and the color of the acid layer after standing 15 minutes must not be darker than No. 6.

For solvent naphtha the acid layer color only is noted, and after 5 minutes standing it must not be darker than No. 14.

It is well to note that the above schedule shows the limit of color allowable in the sales specifications; and it is to be expected that to consistently pass the test, works practice should call for a limit of at least one number lighter in each case.

The solutions for the standards are made up as follows:

The following basic solutions are used:

A. 59.4965 grams $CoCl_2.6H_2O$ (nickel free) is made up to 1,000 cubic centimeters with a mixture of 25 cubic centimeters 31 per cent. HCl and 975 cubic centimeters H_2O.

B. 45.054 grams $FeCl_3.6H_2O$ made up to 1,000 cubic centimeters with a mixture of 25 cubic centimeters 31 per cent. HCl and 975 cubic centimeters H_2O.

C. 3.5 volumes of solution A + 36.5 volumes solution B + 90 volumes of H_2O.

D. 3.5 volumes of solution A + 36.5 volumes of solution B (No water is added.)

E. Solution of K_2CrO_4 saturated at 21° C.

F. One volume of a solution of $K_2Cr_2O_7$ saturated at 21° C. + 1 volume of H_2O.

As standard color solutions to be used for comparison the following are made up and numbered from 0 to 14:

No. 0.—Pure water.
No. 1.—1 volume of solution C + 1 volume of H_2O.
No. 2.—5½ volumes of solution C + 2 volumes of H_2O.
No. 3.—Solution C as such.
No. 4.—1 volume of solution D + 1 volume of H_2O.
No. 5.—5½ volumes of solution D + 2 volumes of H_2O.
No. 6.—Solution D as such.
No. 7.—5 volumes of solution E + 2 volumes of water.
No. 8.—Solution E as such.
No. 9.—7 volumes of solution E + ½ volume of solution F.
No. 10.—6½ volumes of solution E + 1 volume of solution F.
No. 11.—5½ volumes of solution E + 2 volumes of solution F.
No. 12.—1 volume of solution E + 1 volume of solution F.
No. 13.—2 volumes of solution E + 5 volumes of solution F.
No. 14.—Solution F as such.

(These standard solutions should, in all cases, remain stoppered to prevent evaporation.)

To make the test place approximately 7 cubic centimeters of C. P. sulphuric acid and 21 cubic centimeters of the light oil to be tested in one of these standard bottles, shake thoroughly and stand aside for 15 minutes (in all cases excepting the test for solvent naphtha, in which 5 minutes is the limit.) At the end of 15 minutes compare the color produced in the sample with that of the standard solution by looking through the tube towards the light.

In making up the standard color comparison solutions, put in an amount of colored solution equivalent to the amount of acid used in the test, and on top of it put the amount of benzol used in the test. This gives an apparent exact duplicate of a wash test. In all cases, except solvent naphtha, the light oil should remain white, the color test being applied only to the color of the acid. In the case of solvent naphtha no specification is made as to the color of the solvent naphtha itself, since it will not be white, but the color of the acid compared with this standard color solution determines the degree of washing.

For pure benzol and toluol, standard sample No. 4 has been adopted as the greatest amount of color allowable for these grades. For all commercial grades, such as 90 per cent. benzol, 50 per cent. benzol and commercial toluol, No. 6 is the lowest color limit. For solvent naphtha No. 14 has been adopted.

d. Solidifying Point (for pure benzol only).

Fifty cubic centimeters are taken in a test tube with the thermometer in the liquid, and cooled with stirring until separation of crystals occurs. At this point there is a constant temperature for a considerable period, which is taken as the solidifying point. If the material supercools, the temperature rises as the crystals separate, and the highest point reached is taken as the solidifying point.

e. Unnitrifiable Hydrocarbons.

Place 100 cubic centimeters of material in a flask of about 500 cubic centimeters capacity, provided with a dropping funnel and a long tube (drawing) for condensing any hydrocarbon volatilizing. Prepare a mixture of 150 grams nitric acid of specific gravity 1.4, and 180 or 200 grams sulphuric acid, specific gravity 1.84, which must be allowed to cool before use. Run this, drop by drop, through the tap-funnel into the benzol, shaking this up almost constantly. As soon as the temperature rises, cool the flask by immersing it in a dish full of water. When all the acid has been added, and when no further rise of temperature takes place spontaneously, heat the flask gently for an hour or two (during this time the tube is best replaced by a proper reflux condenser). Allow the whole to settle, and separate the lower acid layer by means of a separating funnel from the crude nitrobenzol. Dilute the acid with several times its bulk of water; any oily liquid separating after a few hours' rest is added to the nitrobenzol. Wash the crude nitrobenzol three times with its own bulk of water, once with a very dilute solution of caustic soda (if this solution is employed too concentrated, an emulsion is formed which is very awkward to manage), and again with water, taking care that no oil is lost in separating the washings. The well-settled liquor can be at once tested for its specific gravity, which in the case of 90 per cent. benzol ought to be 1.20; with 50 per cent. benzol 1.19 at 15°; but this is not decisive, as the nitrobenzol is not quite free from water, and some benzol may have escaped nitrification. The liquor is therefore distilled from a fractionating flask till the temperature has reached 150°, and the distillate is once more nitrated, but this time with large excess of the acid mixture; anything remaining undissolved may be regarded as unnitrifiable hydrocarbons. Theoretically, 100 parts of benzol furnish 157.6 of nitrobenzol; 100 parts of toluol, 148.9 of nitrotoluol.

(Taken from Lunge's Coal Tar and Ammonia.)

NOTE:—This method is not accurate with material containing small quantities of paraffine.

4. TAR.

a. Water.

Measure 50 cubic centimeters of coal tar naphtha or light oil (which must be tested to determine that it is free from

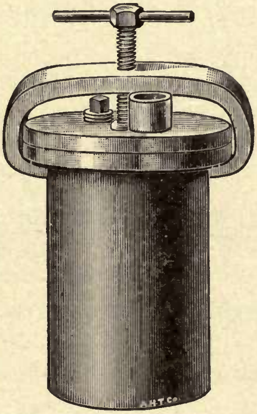

FIG. 42.

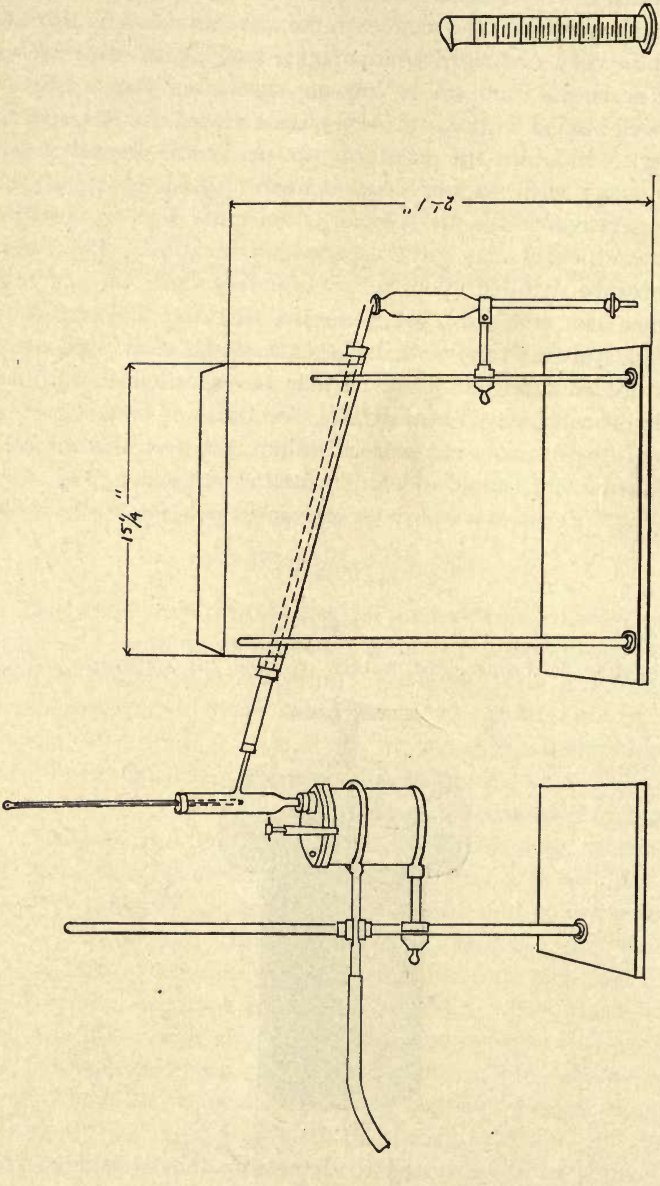

FIG. 43.

water, whenever a new supply is required) in a 250 cubic centimeter measuring cylinder. (No objection is raised to measuring the tar direct into the still or in other ways, but the measurement must be made as described in case of dispute.) Add 200 cubic centimeters of the tar. Transfer contents of cylinder to copper still and wash the cylinder with 50-75 cubic centimeters more of naphtha, adding the washings to contents of the still. Attach lid and clamp, using a paper gasket and set up apparatus (Fig. No. 42). Apply heat by means of the ring burner and distil until the vapor temperature, as indicated by the thermometer (in this and all other tests care must be used to have the thermometer set exactly as shown in drawing) has reached 205° C. The distillate is collected in the separatory funnel, to which 15-20 cubic centimeters of benzol have been previously added. This effects a clean separation of the water and oil. The reading is made after twirling the funnel and allowing to settle for a few minutes. The percentage is figured by volume.

NOTE.—In case a large percentage of water is present, a vacuum head as shown in Fig. 32, Chap. II, "Tar," may be used to advantage.

b. Distillation.

Apparatus.—The apparatus shall consist of the following standard parts:

(*a*) *Flask.*—The distillation flask shall be a 250 cubic centimeter Engler distilling flask, having the following dimensions:

Diameter of bulb, cm.	8.0
Length of neck, cm.	15.0
Diameter of neck, cm.	1.7
Surface of material to lower side of tubulature, cm.	11.0
Length of tubulature, cm.	15.0
Diameter of tubulature, cm.	0.9
Angle of tubultaure	75°

A variation of 3 per cent. from the above measurements will be allowed.

The thermometer shall conform to the following requirements:

The thermometer shall be made of resistance glass of a quality equivalent to suitable grades of Jena or Corning makes.

It shall be thoroughly annealed. It shall be filled above the mercury with inert gas which will not act chemically on or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale. There shall be a reservoir above the final graduation large enough so that the pressure will not become excessive at the highest temperatures. The thermometer shall be finished at the top with a small glass ring or button suitable for attaching a tag. Each thermometer shall have for identification the makers' name, a serial number, and the letters "A. S. T. M. DISTILLATION."

The thermometer shall be graduated from 0° to 400° C. at intervals of 1° C. Every fifth graduation shall be longer than the intermediate ones, and every tenth graduation beginning at zero shall be numbered. The graduation marks and numbers shall be clear-cut and distinct.

The thermometer shall conform to the following dimensions:

Total length, mm.	385	maximum
Diameter of stem, mm.	7,	tolerance 0.5
Diameter of bulb, mm.	5	minimum, and shall not exceed that of the stem
Length of bulb, mm.	12.5,	tolerance 2.5
Distance 0° to bottom of bulb	30,	tolerance 5
Distance 0°-400°	295,	tolerance 10

The accuracy of the thermometer when delivered to the purchaser shall be such that when tested at full immersion the maximum error from 0°-200° C. shall not exceed 0.5°; 200°-300° C., it shall not exceed 1° C.; 300°-375° C., it shall not exceed 1.5° C.

The sensitiveness of the thermometer shall be such that when taken at a temperature of 26° C. and plunged into a free flow of steam, the meniscus shall pass the 90° C. mark in not more than six seconds.

(*c*) *Condenser.*—The condenser tube shall have the following dimensions:

Length of tube, mm.	500
Width of tube, mm.	12 to 15
Width of adaptor end of tube, mm.	20 to 25

(*d*) *Stands.*—Two iron stands shall be provided, one with a universal clamp for holding the condenser, and one with a light grip arm with a cork-lined clamp for holding the flask.

(*e*) *Burner and Shield.*—A Bunsen burner shall be provided with a tin shield 20 centimeters long by 9 centimeters in diameter. The shield shall have a small hole for observing the flame.

(*f*) *Cylinders.*—The cylinders used in collecting the distillate shall have a capacity of 25 cubic centimeters and shall be graduated in tenths of a cubic centimeter.

Setting up the Apparatus.—The apparatus shall be set up as

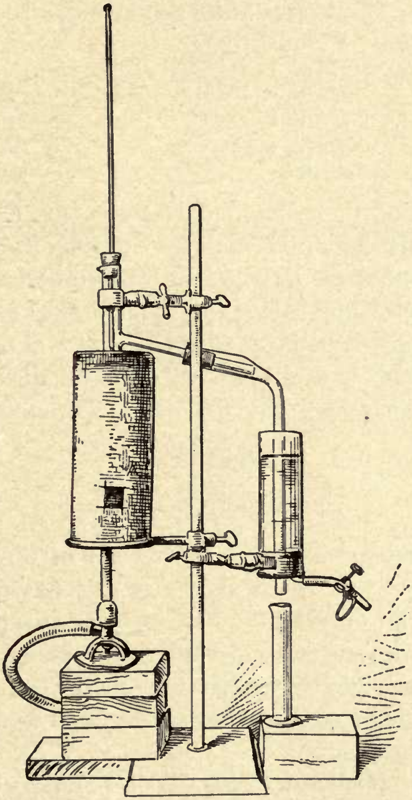

Fig. 44.—Apparatus for the distillation of tar.

shown in Fig. 44, the thermometer being placed so that the top of the bulb is opposite the middle of the tubulature. All connections should be tight.

Method.—One hundred cubic centimeters of the dehydrated material to be tested shall be placed in a tared flask and weighed. After adjusting the thermometer, shield, condenser, etc., the distillation is commenced, the rate being so regulated that 1 cubic centimeter passes over every minute. The receiver is changed as the mercury column passes the fractionating point.

The following fractions should be reported:

Start of distillation to 110°C.
110°C. to 170°C.
170°C. to 235°C.
235°C. to 270°C.
270°C. to 315°C.
315°C. to 355°C.
Residue

To determine the amount of residue, the flask is weighed again when distillation is complete. During the distillation the condenser tube shall be warmed when necessary to prevent the deposition of any sublimate. The percentages of fractions should be reported both by weight and by volume.

(This method is adapted with some modification from report of Subcommittee on Distillation, Committee D-4, A. S. T. M., 1911.)

c. Specific Gravity.

1. *Hydrometer.*—Same as 1-b. A set of three with ranges of 1.07 to 1.15, 1.14 to 1.22, and 1.21 to 1.30 will suffice. The hydrometer can only be used on tars for rough work, and is used at any convenient temperature. If the specific gravity is determined at a higher temperature than 15.5° C., correction should be made by adding 0.000685 for each degree Centigrade excess of temperature.

2. *Modified Hubbard Bottle.*—For accurate work with the bottle, the test should be made on dry tar only. The type of

bottle used is shown in Fig. 45. The following weights are noted:

a. Weight of empty bottle.
b. Weight of bottle filled with water to the mark of 15.5° C.
c. Weight of bottle partly filled with tar.
d. Weight of bottle with tar and water adjusted to the mark at 15.5° C.

The specific gravity then is $\frac{c - a}{(b - a) - (d - c)}$

FIG. 45.

NOTE.—Freshly distilled water should be used in this work.

d. Free Carbon.

APPARATUS.

Extractor.—The extraction apparatus is shown in Fig. 46.

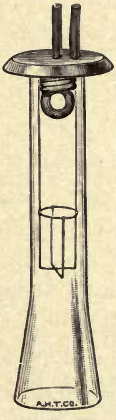

FIG. 46.

Filter Cups.—The filter cups or thimbles are made of Schleicher and Schull No. 575 hardened filter paper, which comes in cut circles. The size used is 15 centimeters in diameter. To make a cup, two circles should be taken and one cut down to a diameter of about 14 centimeters. A round stick about 1 inch in diameter is used as a form. The stick is placed in the center of the circles of filter paper, the smaller inside; the papers are then folded symmetrically around the stick to form a cup of about 2½ inches in length. A very little practice enables the operator to make these evenly and quickly. After being made, they are soaked in benzol to remove any grease due to handling, drained, dried in a steam oven and kept in a desiccator until used.

Method.—If tar is to be assayed, it must be dried before testing, and after drying it is passed hot through a 30-mesh sieve to remove foreign substances.

For materials of 5 per cent. or more carbon content, 5 grams should be taken for the test. With lesser percentages, 10 grams should be used. The amount is weighed out in a 100 cubic centimeter beaker, and digested with about 50 cubic centimeters of chemically pure toluol on the steam bath for a period not to exceed 30 minutes. If the solution is kept hot and constantly stirred, the digestion can be completed very rapidly. A filter cup, prepared as described, is weighed in a weighing bottle and placed in a carbon filter tube over a beaker or flask. The toluol-tar mixture is now decanted through the thimble and washed with hot chemically pure toluol until clean, using some form of policeman which is unaffected by toluol for the purpose of detaching any carbon which may adhere to the beaker. The cup is finally given a washing with hot chemically pure benzol and then, after draining is covered with a cap of filter paper or alundum, and placed in the extracting apparatus in which chemically pure benzol is used as a solvent. The extraction is continued until the descending benzol is colorless. The thimble is then removed, the cap taken off, dried in the steam oven, and weighed in the weighing bottle after cooling in the desiccator. The balance used for this work should be accurate to at least a half milligram.

NOTE.—If desired, carbon bisulphide may be used instead of benzol and toluol as a solvent, but the results may not be comparable.

5. TAR LIGHT OILS.

a. Bulb Distillation.

Same as 2-*a*.

b. Tar Acids.

The distillate from (*a*) is placed in a separatory funnel (Fig. 47). If the light oil is not liquid at room temperature, it should be kept in a constant temperature bath at a point high enough to insure all solid matter remaining in solution. After the material in the funnel has come to constant temperature, the reading is noted and 50 cubic centimeters of a 10 per cent. caustic soda solution added. It is then shaken and allowed to settle, the soda drawn off, the oil allowed to come to its original temperature, and the shrinkage noted. This process is repeated with successive portions of 30 cubic centimeters each of the same soda solution, until no further shrinkage is noted. The total shrinkage is taken as the percentage of tar acids.

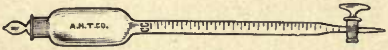

FIG. 47.

(This test is empirical, and it would be desirable to have a more accurate method).

c. Distillation with Dephlegmator.

Same as 2-*c*. In this case the extracted oil from the tar acid determination is used instead of the original.

d. Naphthalene.

Same as 2-*d*. Made on residue above 200° from 5-*c*.

e. Specific Gravity.

Same as 1-*b*. A set of two hydrometers with ranges of

0.86 to 0.94, and 0.93 to 1.01, will suffice. If the specific gravity is determined at a higher temperature than 15.5° C., correction should be made by adding 0.0009 for each degree Centigrade excess of temperature.

Reference method, same as 1-*b* (2).

6. TAR MIDDLE OILS.

a. Bulb Distillation.

Same as 2-*a*.

b. Specific Gravity.

Same as 1-*b*. A set of two hydrometers with ranges of 0.93 to 1.01, and 1.00 to 1.08 will suffice. If the specific gravity is determined at a higher temperature than 15.5° C., correction should be made by adding 0.00085 for each degree Centigrade excess of temperature.

Reference method, same as 1-*b* (2).

c. Tar Acids.

Same as 5-*b*.

d. Naphthalene.

Same as 2-*d*.

7. TAR HEAVY OILS (CREOSOTE OILS).

a. Distillation.

Retort.—This shall be a tubulated Jena glass retort of the usual form with a capacity of 250 to 290 cubic centimeters.

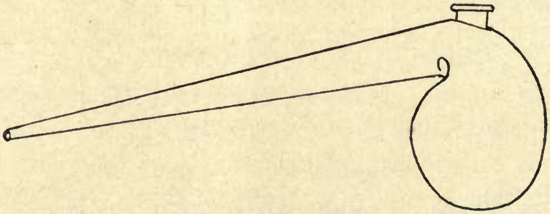

FIG. 48.

The capacity shall be measured by placing the retort with the bottom of the bulb and the end of the offtake in the same horizontal plane, and pouring water into the bulb through the tubulature until it overflows the offtake. The amount remaining in the bulb shall be considered its capacity. (See Fig. 48.)

Condenser Tube.—Any suitable form of glass tubing may be used. (Fig. 49.)

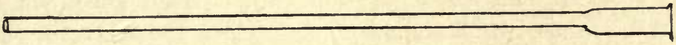

FIG. 49.

Shield.—To be made of asbestos (Fig. 50) shall be used to protect the retort from air currents and to prevent radiation. This may be covered with galvanized iron, as such an arrangement is more convenient and more permanent.

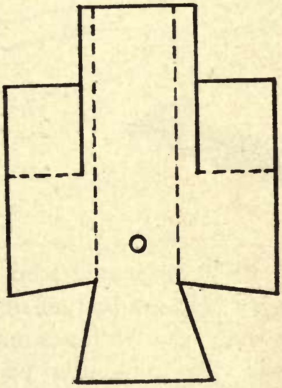

FIG. 50.

Receivers.—Erlenmeyer flasks of 50 to 100 cubic centimeters capacity are most convenient forms.

The thermometer shall conform to the following requirements:

The thermometer shall be made of resistance glass of a quality equivalent to suitable grades of Jena or Corning makes.

It shall be thoroughly annealed. It shall be filled above the mercury with inert gas which will not act chemically on or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale. There shall be a reservoir above the final graduation large enough so that the pressure will not become excessive at the highest temperatures. The thermometer shall be finished at the top with a small glass ring or button suitable for attaching a tag. Each thermometer shall have for identification the makers' name, a serial number, and the letters "A. S. T. M. DISTILLATION."

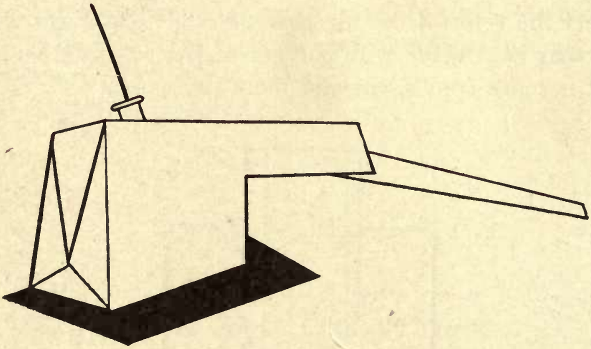

FIG. 51.

The thermometer shall be graduated from 0° to 400° C. at intervals of 1° C. Every fifth graduation shall be longer than the intermediate ones, and every tenth graduation beginning at zero shall be numbered. The graduation marks and numbers shall be clear-cut and distinct.

The thermometer shall conform to the following dimensions:

Total length, mm.	385	maximum
Diameter of stem, mm.	7,	tolerance 0.5
Diameter of bulb, mm.	5	minimum, and shall not exceed that of the stem
Length of bulb, mm.	12.5,	tolerance 2.5
Distance 0° to bottom of bulb	30,	tolerance 5
Distance 0°-400°	295,	tolerance 10

The accuracy of the thermometer when delivered to the purchaser shall be such that when tested at full immersion the maximum error from 0°-200° C. shall not exceed 0.5°; 200°-300° C., it shall not exceed 1° C.; 300°-375° C., it shall not exceed 1.5° C.

The sensitiveness of the thermometer shall be such that when taken at a temperature of 26° C. and plunged into a free flow of steam, the meniscus shall pass the 90° C. mark in not more than six seconds.

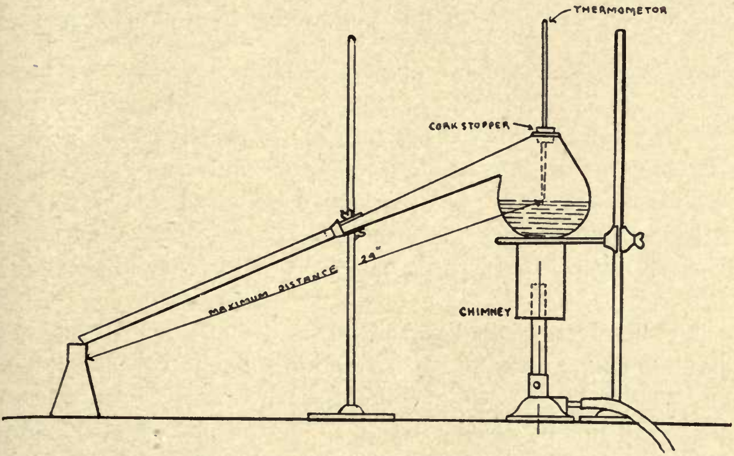

FIG. 52.

Assembling.—The retort shall be supported on a tripod of rings over two sheets of 20-mesh gauze 6 inches square. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the tubulature with the bottom of the bulb ½ inch from the surface of the oil in the retort. The exact location of the thermometer bulb shall be determined by placing a vertical rule graduated in division not exceeding 1/16 inch back of the retort when the latter is in position for the test, and sighting the level of the liquid and the point for the bottom of the thermometer bulb. The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than 24 nor more than 20 inches. The burner should be protected from draughts by a suitable shield or chimney.

Method.—Exactly 100 grams of oil shall be weighed into the retort, the apparatus assembled and heat applied. The distillation shall be conducted at the rate of at least one drop and not more than two drops per second, and the distillate collected in weighed receivers. The condenser tube shall be warmed whenever necessary to prevent accumulation of solid distillates. Fractions shall be collected at the following points:

Up to 170°C.
170 to 200°C.
200 to 210°C.
210 to 235°C.
235 to 270°C.
270 to 315°C.
315 to 355°C.

The receivers shall be changed as the mercury passes the dividing temperature for each fraction. The last receiver shall be removed at 355° C., and the drainage from the condenser, etc., shall not be considered as a part of the fraction. For weighing the receivers and fractions, a balance accurate to at least 0.05 gram shall be used. During the process of distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer.

When any measurable amount of water is present in the distillate, it shall be separated as nearly as possible and reported separately, all results being calculated on a basis of dry oil. When more than 2 per cent. of water is present, water-free oil shall be obtained by separately distilling a larger quantity of oil, returning to the oil any oil carried over within the water, and using dried oil for the final distillation. A copper tar still is a convenient means of obtaining water-free oil.

(This method is adapted with some modification from report of Sub-Committee on Preservatives, Committee D-7, A. S. T. M., 1915.)

Other methods for the distillation of creosote oil have been described by the National Electric Light Association, the Forest Service, and Lunge (Coal Tar and Ammonia).

b. Specific Gravity.

1. Same as 1-*b*. A set of two hydrometers with ranges of 1.00 to 1.08 and 1.07 to 1.15 will suffice. If the specific gravity is determined at a higher temperature than 15.5° C., correction should be made by adding 0.0008 for each degree Centigrade excess of temperature.

2. Westphal Balance—Reference Method. See 1-*b* (2). A reading is taken with the plummet immersed in water at 38° C., and a second reading in oil at 38° C. The specific gravity is the oil reading divided by the water reading, times 0.9939 (the density of water at 38° C. divided by the density at 15.5° C.).

c. Tar Acids.

Same as 5-*b*. As most creosote oils are not liquid at ordinary temperatures, it is customary to determine the tar acids at a constant temperature of 60° C.

8. PITCH.

a. Distillation.

Same as 4-*b*.

b. Specific Gravity.

Apparatus.—This consists entirely of a platinum pan having a total weight of about 7 grams.

Method.—The pan is suspended above the balance pan by a fine, waxed silk thread, and the weight in air and water at 15.5° C. determined. It is then filled with pitch and weighed both in air and in water at 15.5° C.

Formula.—Let $a =$ weight of pan in air.
$b =$ weight of pan in water.
$c =$ weight of pan plus pitch in air.
$d =$ weight of pan plus pitch in water.

$$\text{The specific gravity} = \frac{c - a}{(b \quad c) - (a \quad d)}$$

a. Modified Hubbard Bottle.—Same as 4-*c*.

c. Free Carbon.

Same as 4-*d*. In case the pitch is hard enough, it should be ground before making the test, and the residue in the extraction thimble should be examined for extraneous matter, such as sticks of wood or pieces of bagging.

d. Melting Point.

Apparatus shown in Fig. 53.

1. Pitches having melting-points from 43° to 77° C.

Pitches of this consistency can ordinarily be molded at room temperature, or if necessary, cold or hot water can be used to harden or soften them. The molds should always be scrupulously clean, but may be moistened if necessary.

A clean-shaped ½-inch cube of the pitch to be formed in the mold, placed on the hook of No. 12 B. & S. gauge copper wire (diameter 0.0808 inch), and suspended in the 600 cubic centimeter beaker, so that the bottom of the pitch is 1 inch above the bottom of the beaker. (A sheet of paper placed on the bottom of the beaker and conveniently weighted will prevent pitch from sticking to the beaker when it drops off.) The pitch is to remain five minutes in 400 cubic centimeters of freshly boiled distilled water at a temperature of 15.5° C. before heat is applied; heat to be applied in such a manner that the temperature of the water is raised 5° C. each minutes; the temperature recorded by the thermometer at the instant the pitch touches the bottom of beaker to be considered the melting-point.

2. Pitches having melting-points below 43° C.

Same method as described in (1), except that at the start the water should have a temperature of 4° C. The cubes can be conveniently formed in water at the temperature specified.

3. Pitches have melting-points above 77° C.

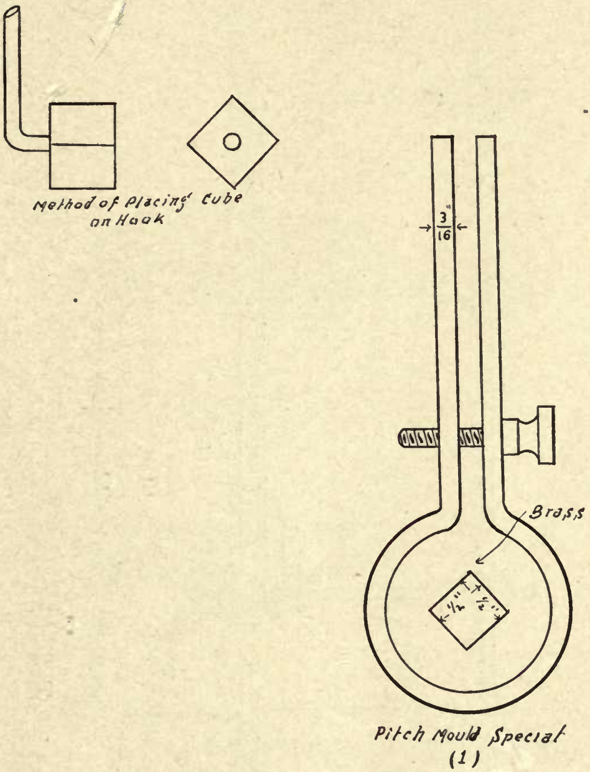

FIG. 53.

It is usually necessary to heat these pitches in order to form the cube. For this purpose a copper cup of approximately 50 cubic centimeters capacity, 1½ inches deep and 1½ inches diameter, provided with wooden handle, can be used. The cup should be half-filled with pitch and heated carefully, avoiding noticeable evolution of vapors, and the heating should not be continued any longer than absolutely necessary. An oil bath may be used for this purpose.

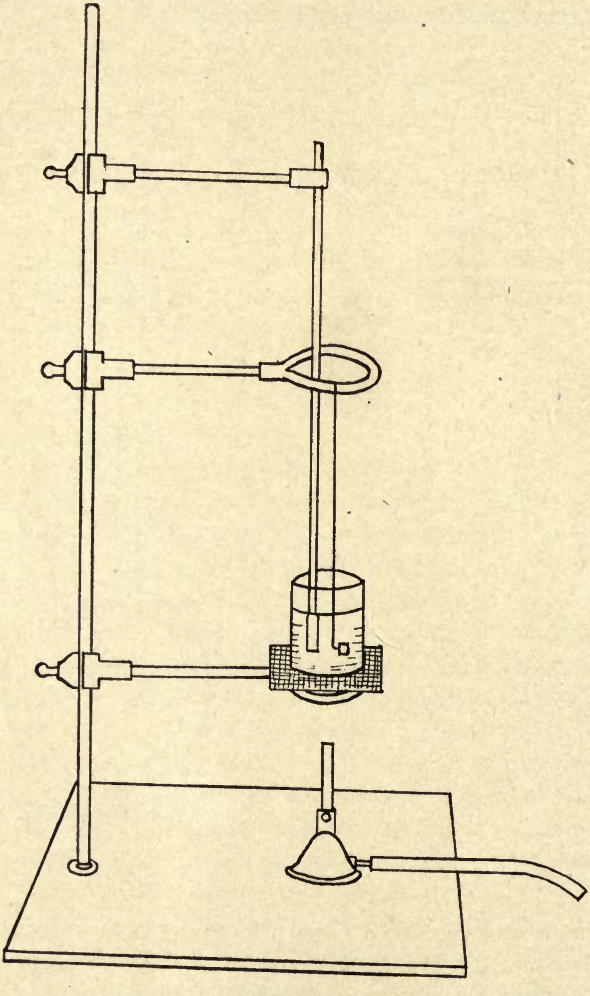

FIG. 54.

For these pitches an air bath is substituted for the water bath. The hook is shorter, so that the cube is suspended on a line running through the center of the observation windows, the thermometer bulb being at the same level. The temperature of the oven is raised 5° C. each minute, as usual, and the temperature recorded by the thermometer at the instant the pitch drops to the bottom of the oven, is considered the melt-

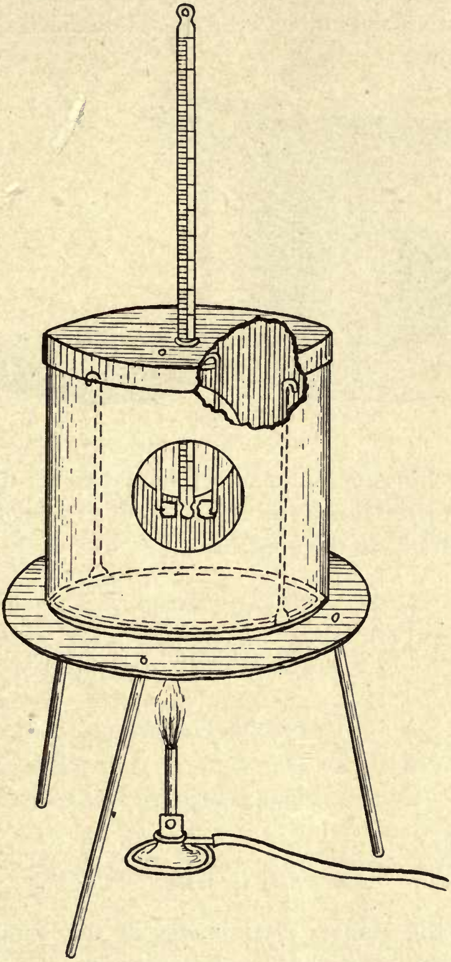

FIG. 55.

ing-point. To make results by this method comparable with results obtained in water, 6.5° C. should be added to the observed melting-point. (*Important.*—Results by this method are not directly comparable with results obtained in water, but are always lower.)

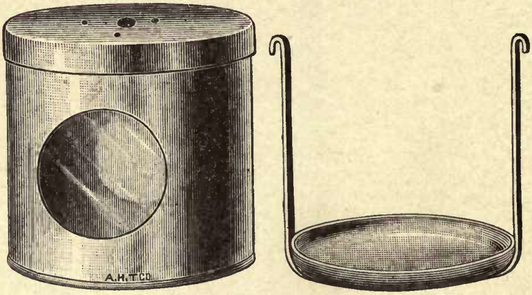

FIG. 56.

NOTE.—Melting-point apparatus should be set up in a place free from drafts, and if necessary, protected by means of a shield set apart from the apparatus.

9. ROAD TARS.

a. Distillation.

Same as 4-*b*.

b. Specific Gravity.

Same as 8-*b*.

c. Free Carbon.

Same as 4-*d*.

d. Viscosity.

Taken in the Engler viscosimeter at the temperature required by specifications. The full quantity, 250 cubic centimeters, is placed in the apparatus and raised to the temperature at which it is desired to make the test. One hundred cubic centimeters are then permitted to flow into a graduated flask of the above capacity, and the time of flow in seconds noted.

e. Float Test.

Apparatus.—Consists of two parts, an aluminum float or saucer, and a conical brass collar. (Fig. 57.)

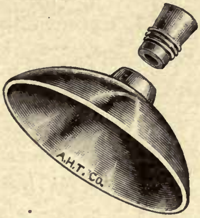

FIG. 57.

Method.—The brass collar is placed upon a brass plate, the surface of which has been amalgamated, and filled with the bituminous material under examination, after it has been softened sufficiently to flow freely by gentle heating. The collar must be level-full, and as soon as the bitumen has cooled sufficiently to handle, it is placed in ice water at 4° C. for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at the desired temperature.

As the plug of bitumen in the brass collar becomes warm and fluid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface of same.

The time elapsing between placing the apparatus on the water and when the water breaks through the bituminous material is noted by means of a stop watch.

10. NAPHTHALENE SALTS (CRUDE NAPHTHALENE).

a. Water.

Weigh 200 grams into a copper still, add 100 cubic centimeters of water-free naphtha and distil up to 210° C. vapor temperature. Note volume of water as in similar test on tar.

b. Solidifying Point.

If water is present it must be removed by proper distillation, as in creosote oil. About 20 cubic centimeters of melted naphthalene are taken in a test-tube of thin glass about 1 inch in diameter by 6 inches long. The contents are thoroughly liquified and then allowed to cool, stirring constantly with an accurate thermometer. As permanent crystals begin to form, a constant temperature is held for a short time; this is taken as the solidifying point. Often, if the material supercools, the temperature rises as the solids separate; in this case the highest point attained on the rise is recorded. The higher the solidifying point is, the longer the period of constant temperature, and hence the sharper the test.

c. Distillation.

Weigh 100 grams of dried naphthalene into a regular 200 cubic centimeter side-neck distilling bulb. Connect to a 24-inch condenser tube (from the water-in-tar-testing apparatus). *Water cooling should not be used.* Use a standard creosote oil distillation test thermometer and collect the distillate in a 100 cubic centimeter graduated cylinder. Conduct the test as in the regular bulb distillation of naphthas or light oils, noting the first drop, the cubic centimeters distilled every 10° C. up to 210° C.; then every 5° C. to 230° C. and every 10° C. up to the decomposition point. This is indicated by the appearance of white fumes in the flask. During the course of the test, the condenser tube should be kept warm enough to keep the distillate liquid by playing a flame over it.

CHAPTER V.

MISCELLANEOUS.

WATER ANALYSIS.

Sampling.

A sample of water should not be taken except when the supply is being drawn on at the normal operating rate. All taps or connections through which the sample passes must be thoroughly flushed out. The vessel to contain the sample should be cleaned with care and then thoroughly rinsed several times with the water to be sampled. Metal containers and earthenware jugs may contaminate the sample. A 1-gallon bottle with a ground glass stopper is the best container for samples of water.

Total Solids.—Evaporate 250 cubic centimeters to dryness in a platinum dish (weighed), dry in an air oven at 100° C. Cool and weigh.

Organic and Volatile Matter.—Ignite the contents of the dish at a low red heat. Cool and weigh. The loss will be organic and volatile matter.

Mineral Solids.—Subtract the weight of the dish from the weight just found above. The difference will be the weight of the mineral solids. The results found above in milligrams multiplied by 4 will be the parts per million.

Alkalinity or Temporary Hardness.—Measure 100 cubic centimeters of the water into a 250 cubic centimeter glass-stoppered bottle, add 2.5 cubic centimeters Erythrosine solution (0.1 gram of the sodium salt in 1 liter distilled water), and 5 cubic centimeters chloroform. Add N/50 H_2SO_4 in small quantities, shaking vigorously at each addition. The rose color gradually disappears, and is finally entirely discharged by a drop or two of the acid. A white paper held behind the bottle facilitates the detection of any color remaining as the end-point is reached. The number of cubic centimeters of the acid used multiplied by 10 gives the number of parts per million alkalinity in terms of $CaCO_3$.

Incrustants or Permanent Hardness.—Measure 200 cubic centimeters of the water into a Jena glass Erlenmeyer flask, boil 10 minutes to expel free CO_2. Add 25 cubic centimeters of N/10 soda reagent (equal parts of N/10 NaOH and N/10 Na_2CO_3), and boil to a volume of 100 cubic centimeters. Cool and rinse into a 200 cubic centimeter graduated flask, make up to the mark with boiled distilled water. Filter, and reject the first 50 cubic centimeters. Titrate 100 cubic centimeters of the remainder for excess of soda reagent with N/20 H_2SO_4, using Erythrosine as an indicator as above. If S equals the cubic centimeters of N/20 H_2SO_4 equivalent to the soda reagent used, and N equals the cubic centimeters of N/20 H_2SO_4 required for the excess or back titration, then the incrustants in parts per million $CaCO_3$ will be: $12.5\ (S - 2N)$. Total hardness is the sum of the alkalinity and incrustants.

Mineral Analysis. NOTE.—The volume taken for analysis depends on the quantity of total solids present in the water. The calculations of the following method are based on a volume of 1 liter of water.

Method.—Evaporate 1 liter in a platinum dish to about 5 cubic centimeters. Filter into a 200 cubic centimeter graduated flask. Wash with successive small quantities of hot distilled water by putting the water into the dish, rinsing it around and pouring it on the filter.

The solution in the flask contains probably Cl, SO_3, Mg, alkalies, and Ca.

The residue in the dish and on the filter contains probably SiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$, and $MgCO_3$.

Treatment of the Solution.—Cool the flask and fill to the mark with distilled water. Mix well and divide into three parts.

Part a.—Fifty cubic centimeters equivalent to 250 cubic centimeters original water. Determine Cl with standard $AgNO_3$. Milligrams Cl multiplied by 4 gives parts Cl per million.

Part b.—Fifty cubic centimeters equivalent to 250 cubic centimeters original water. Slightly acidify with HCl and determine SO_3 by precipitating with $BaSO_4$. $BaSO_4$ multiplied by 0.343 equals SO_3. Milligrams SO_3 multiplied by 4 gives parts SO_3 per million.

Part c.—One hundred cubic centimeters equivalent to 500 cubic centimeters original water. Slightly acidify with HCl. Make faintly alkaline with NH_4OH, boil, and add ammonium oxalate, allow to stand over night, filter, wash, ignite, and weigh the CaO. CaO multiplied by 0.715 equals Ca. Milligrams Ca multiplied by 2 equals parts Ca per million. Evaporate the filtrate to dryness in a weighed platinum dish, add a few drops of H_2SO_4 and ignite until white fumes are all driven off. Cool and weigh as $MgSO_4 + Na_2SO_4$. Dissolve in warm water, filter if necessary, acidify slightly with HCl. Place beaker in a dish cooled with ice, add 5 cubic centimeters sodium phosphate, then make strongly alkaline with ammonia. Stir for about 3 minutes and set aside over night. Filter, and wash with water containing 10 per cent. NH_4OH and 10 per cent. NH_4NO_3. Dry in an oven. Ignite in a porcelain crucible. Weigh as $Mg_2P_2O_7$. $Mg_2P_2O_7$ multiplied by 0.362 gives MgO. Milligrams MgO multiplied by 2 gives parts MgO per million. $Mg_2P_2O_7$ multiplied by 1.0814 gives $MgSO_4$, which deducted from the contents of the dish found above gives Na_2SO_4. Na_2SO_4 multiplied by 0.324 gives Na_2. Milligrams Na_2 multiplied by 2 gives parts Na per million in the water.

NOTE.—The chlorine found may be checked in two ways:

1. By dissolving the contents of the dish in mineral solids in H_2O, and titrating with standard $AgNO_3$.

2. By taking 100 cubic centimeters of the original water, boiling out the Co_2, cooling and titrating with standard $AgNO_3$.

Calculations from above:

Calculate Na to NaCl.
Cl remaining to $MgCl_2$.
Cl remaining to $CaCl_2$.
Mg remaining to $MgSO_4$.
SO_3 remaining to Na_2SO_4.

Residue in Dish and on Filter Paper.—Place filter and contents in the dish, dry over a Bunsen burner flame, carefully burn paper, and ignite to burn off carbon. Add a little HCl and rinse around the dish. Evaporate to dryness, redissolve in a little acid, and evaporate again to dryness. Take up again with a little acid, add water, boil and filter into a 200 cubic centimeter graduated flask. Wash thoroughly. Dry, ignite, and weigh the filter in a platinum crucible; this gives SiO_2; milligrams of which equals parts per million in the original water. Cool the flask and contents, fill to the mark with distilled water and mix well. Divide this solution into two parts.

Part a.—Fifty cubic centimeters equivalent to 250 cubic centimeters of original water. Determine SO_3 as $BaSO_4$, as before described. $BaSO_4$ multiplied by 0.343 equals SO_3. Milligrams SO_3 multiplied by 4 equals parts per million in original water.

Part b.—One hundred fifty cubic centimeters equivalent to 750 cubic centimeters original water. Add a few drops of HNO_3 and boil. Make faintly alkaline with ammonia and boil until odor of ammonia has gone. Filter off Al and Fe hydroxides, wash, dry, ignite and weigh as $Al_2O_3 + Fe_2O_3$. Milligrams of Al_2O_3 divided by Fe_2O_3 multiplied by 4/3 equal parts per million in the original water.

Filtrate.—Boil, add ammonium oxalate, and allow to stand for 4 hours, filter, wash with hot water, dry, ignite in a platinum crucible, finishing over a blast lamp to constant weight. Milligrams CaO multiplied by 4/3 equal parts CaO per million in the original water.

Filtrate.—Concentrate to about 50 cubic centimeters adding HNO_3 to destroy the NH_4Cl if necessary, precipitate $Mg_2P_2O_7$ as usual. $Mg_2P_2O_7$ multiplied by 0.362 gives MgO, milligrams of which multiplied by 4/3 equal parts per million in the original water.

Calculations from above:

Calculate SO_3 to $CaSO_4$.
Calculate CaO remaining to $CaCO_3$.
Calculate MgO to $MgCO_3$.

PAINTS.

Analysis of Red Holder Paint.

Weigh out 0.5 gram of the dry pigment after extraction of the vehicle in a porcelain casserole and add 50 cubic centimeters HCl (1:1). Boil gently for 15 minutes, evaporate to dryness on the sand bath, moisten with concentrated HCl, and evaporate again. Moisten again with concentrated HCl, add 100 cubic centimeters of water and boil gently for a few minutes. Filter, wash, ignite and weigh as silica, SiO_2, etc. Add a few drops of H_2SO_4 to the residue and a little HCl, and evaporate gently on a sand bath under the hood. The loss in weight represents SiO_2; any residue remaining should be fused with potassium bisulphate and dissolved in HCl and filtered. Any residue remaining on the filter is $BaSO_4$, which is ignited and weighed. The filtrate is added to the filtrate from the silica. This procedure is only necessary in case of a large per cent. of insoluble. Otherwise, report as insoluble matter. The combined filtrates are made up to 250 cubic centimeters and an aliquot portion taken, made alkaline with NH_4OH, boiled, filtered, washed, ignited, and weighed as Fe_2O_3 and Al_2O_3. Take another portion and precipitate with ammonia as before. Filter and wash, and dissolve the precipitate on the paper with 10 per cent. H_2SO_4 into a flask. Add a few pieces of zinc, stopper flask with a stopper fitted with a Bunsen valve and allow to stand until all the iron is reduced. Then filter off the zinc and add 10 cubic centimeters H_2SO_4, and titrate with N/10 $KMnO_4$, calculating to Fe_2O_3. The difference between these gives Al_2O_3. The filtrate from the iron and alumina is heated to boiling, ammonium oxalate added, set aside on the sand bath over night, filtered, ignited and weighed as CaO. If any magnesium is present, precipitate with sodium hydrogen phosphate in the filtrate from the calcium as usual. Determine SO_3 water of hydration, and CO_2 as usual in separate samples.

Method of Analysis of Green Pigments.

Weigh out 1 gram into a 200 cubic centimeter Jena beaker and ignite gently to decompose the Prussian blue. Cool the beaker, add 25 cubic centimeters (1 : 1) HCl, boil to dissolve the iron oxide and expel the excess of acid. Dilute with water and filter off the insoluble matter.

Insoluble Part.—Ignite in a platinum crucible and weigh. Add fusing mixture and fuse to decompose the clay and barium sulphate. Extract the fusion with water, dissolve the insoluble residue in HCl and determine the barium as sulphate in the acid solution.

Soluble Part.—Nearly neutralize the acid with ammonia and precipitate the lead as sulphide with H_2S. Filter off the precipitate, dissolve in HNO_3, and determine the lead as sulphate or chromate. Boil the filtrate to expel H_2S and precipitate the iron, aluminum and chromium with ammonia. Filter off the precipitate and in the solution determine the calcium as usual. Dissolve the combined hydrates in HCl and dilute the solution to 100 cubic centimeters with water. Take 50 cubic centimeters and reprecipitate the metals with ammonia. Filter, ignite and weigh as oxides. Oxidize the chromium in the second 50 cubic centimeter portion by a careful addition of Na_2O_2. Boil the solution to decompose the excess of peroxide, dilute with water and filter off the ferric hydrate. The filtrate will contain the chromium as chromate and aluminum as aluminate of sodium.

Dissolve the ferric hydrate in acid, reduce with zinc and titrate with N/10 $KMnO_4$. Acidify the chromium solution with H_2SO_4, add excess of ferrous sulphate and titrate the unoxidized iron with $KMnO_4$ N/10. From the amount of $FeSO_4$ used up to reduce the chromate, calculate the per cent. of chromium. Calculate the iron and chromium to oxides and subtract from the weight of the combined oxides. The alumina is found by difference. Calculate the iron to Prussian blue, and chromium to lead chromate. Determine the soluble SO_3 and water of hydration in separate samples.

PAINT VEHICLES.

Method of Analysis of a Mixture Consisting of Benzene, Turpentine, Fatty Oils, Rosin Oil, and Petroleum.

1. Distil off and collect the benzene and turpentine, using either a current of CO_2, Note A, or of steam, Note B. Separate them by fractional distillation, Note C, by the action of HNO_3, Note D, or of H_2SO_4, Note E.

2. Saponify the fatty oils in the residue, Note F, with caustic KOH in the usual manner. Dissolve the saponified matter in water, Note G, and the unsaponified oils in ether. Separate carefully, washing the aqueous solution with ether, and the ethereal solution with water.

3. Evaporate off the ether and weigh the rosin oil and petroleum oil. Treat with HNO_3, Note H, extract the residual petroleum oil with ether, evaporate the latter and weigh. Rosins, if present, would be saponified with the fatty oils, and might be estimated in the soap solution by Gladding's method. Tar oil would probably accompany the rosin oil in the above scheme.

NOTE *A*.—Turpentine can be distilled according to H. J. Phillips, *Chem. News,* 63, 275, and *Jour. Chem. Ind.* 10, 577, at about 220° using about 150 grams of the sample and passing through it a current of CO_2 to prevent oxidation of the linseed oil. The temperature required by this method is higher than that used in steam distillation, and in most cases the latter would probably be preferable.

NOTE B.—In the steam distillation, use about 25 grams of the sample in a 400 cubic centimeter flask with a few pieces of glass or metal to prevent bumping. Maintain at a temperature of about 110° and when the turpentine is all removed, continue the heating long enough to remove the last portions of water. The weight of the residue may then be taken to check the results. The distillate is allowed to stand, the turpentine and benzene are separated from the water and weighed, and to the result is added 0.100 gram of turpentine for every 30 cubic centimeters of water in the distillate. According to McIlhiney, *Jour. Am. Chem. Soc.*, 16, 348, this method gives very accurate results.

NOTE C.—In case of a mixture of turpentine with light benzene, a rough separation may be effected by fractional distillation, since the turpentine distils mainly between 150° to 180°. A method which is not affected by the boiling-point of benzene is that of separation by means of acids.

NOTE D.—The HNO_3 method for separating benzene and turpentine, due to Burton, *Am. Chem. Jour.*, 12, 102, is thus described by Phillips, *Eng. Chem.*, p. 273: A balloon flask of 750 cubic centimeters capacity is fitted with a two-hole cork stopper. Connect with a dropping funnel and an inverted condenser. About 300 cubic centimeters fuming HNO_3 of 1.4 specific gravity are placed in the flask and 100 cubic centimeters of the turpentine to be tested are measured into the dropping funnel. The flask is surrounded by cold water and the turpentine allowed to drop slowly into the HNO_3. As each drop strikes the acid, a violent action takes place with the evolution of red fumes. Shake occasionally, and when all the turpentine has been added, allow to stand until all action is over. Transfer to a separatory funnel and wash with hot water. Finally separate and measure and weigh the benzene.

NOTE E.—Armstrong's method for the separation of benzene from turpentine, *Jour. Soc. Chem. Ind.*, 1, 480, depends upon the polmerization of the latter by H_2SO_4. This method is given by Allen, *Com. Org. Analy.*, 11, 441, but it is more time consuming than the HNO_3 process and probably no more accurate.

NOTE F.—This residue may be dried and weighed. If it shows signs of alteration as a result of the steam distillation, another portion may be freed from turpentine by exhaustion of the air and gentle heating. In this case, it is necessary after removing most of the turpentine, to add a little petroleum ether of very low boiling-point. This, in distilling, carries the last of the turpentine with it. A residue prepared in this way may be found in better condition for further examination than one obtained by steam distillation.

NOTE G.—If the amount of fatty oil is not found by difference, it can be estimated by separating the fatty acids, weighing and them, and estimating the corresponding weight of glycerides. If resin is present, the resin acids are determined by Gladding's method. If the fatty oils present are not more than two in number, an approximate estimate of the amount of each may be deducted from the determination of such constants as Hubl, Koettsdorfer, and acetyl figures on the separated fatty acids.

NOTE H.—According to McIlhiney, *Jour. Am. Chem. Soc.*, 16, 385, the following process gives fairly accurate results:

Fifty cubic centimeters HNO_3 of 1.2 specific gravity are heated to boiling in a flask of 700 cubic centimeters capacity. The source of heat is removed and 5 grams of the oil to be analyzed added. The flask is then heated on the water bath with frequent shaking for 15 to 20 minutes, and about 400 cubic centimeters of cold water added. After the liquid has become entirely cold, 50 cubic centimeters of petroleum ether are added and the flask agitated. The petroleum oil is unchanged and dissolves in the ether. This solution is poured into a separatory funnel, leaving the lumps of solid resin as far as possible in the flask. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a tared flask. The resin is washed with another portion of petroleum ether, which is added to the first. The ether is then evaporated and the oil weighed. Since mineral oils lose about 10 per cent. in this way, the weight of oil found must be divided by 0.9 to obtain the correct value.

FIRE CLAY AND REFRACTORIES.

Chemical Analysis.

Since the heat resistance as well as the strength of refractories depends largely on its chemical composition, an analysis can in most cases help to distinguish between good, mediocre or bad refractories. It will also help to ascertain the cause of failures.

Aside from physical tests it is of utmost importance to ascertain the chemical composition of refractories. The following elements or rather their oxides, etc., are to be considered silica, alumina, ferrous and ferric oxides, calcium, magnesium, alkalies, also in clay, manganese oxide, sulphur trioxide, carbon dioxide, silica. Dissolving in acids is in most cases impossible. It is therefore advisable to fuse in a platinum crucible 1 gram of the very finely powdered sample and 5 grams of a fusing mixture (sodium carbonate 4 parts, potassium nitrate 1 part). The fusion is complete as soon as the evolution of the gas ceases. The crucible is next transferred to a porcelain casserole and the fusion dissolved in hot water to which a few drops of hydrochloric acid are added from time to time. After the fusion has been dissolved, remove platinum crucible carefully, washing inside and outside well into the casserole. Care must be taken that the content of the casserole is acid. Evaporate to dryness, bake for a short time at about 120° C. until all the HCl has been driven off. Wash the precipitate on the filter paper about 3 to 5 times with hot dilute HCl and then with hot water until no more precipitate is formed by adding a drop of silver nitrate to the filtrate collected in a test-tube, after removing beaker containing the bulk of filtrate. Dry both filter papers in a tared platinum crucible, burn and weigh the SiO_2. The silica should be perfectly white. If there is any indication of color due to impurities it is best to add a few drops of sulphuric acid to the silica and then add drop by drop hydrofluoric acid until no more reaction takes place. Add a slight excess and evaporate to dryness, heat over a Bunsen burner, cool and weigh. Deduct this weight from the weight of crucible and precipitate. This gives the correct weight of SiO_2. The residue in the platinum crucible generally consists of iron oxide. It is dissolved in HCl and added to the bulk of filtrate from SiO_2. The filtrate is next transferred to a 500 cubic centimeter graduated flask and made up to 500 cubic centimeters and well stirred. One hundred cubic centimeters of the solution are transferred to a beaker, about 10 cubic centimeters of sulphuric acid added, and the whole evaporated until all the HCl has been driven off. It is next diluted with water and reduced with zinc. (The most satisfactory method is a Jones reducteur, but stick zinc will do where a Jones reducteur is not available) and titrated with a standard solution of potassium permanganate. The iron factor of the permanganate multiplied by 1.429 gives the factor for Fe_2O_3. The results multiplied by 5 gives the per cent. of iron oxide in the sample.

Phosphoric Acid.—In another 100 cubic centimeters of the solution the phosphoric acid is determined by precipitation with molybdic acid solution. (For preparing the solution see analysis of iron and steel.) Twenty to 25 cubic centimeters are added to the 100 cubic centimeters of the filtrate from the silica and transferred to a 300 cubic centimeter Erlenmeyer flask. After vigorously shaking for 5 minutes, the flask is stood aside for the precipitate to settle. After the solution has cleared it is filtered through a close-grained paper, the flask and precipitate are washed with a dilute solution of ammonium sulphate made slightly acid with sulphuric acid. After washing it is redissolved in ammonia into the flask in which it had been precipitated. It is then reduced with zinc and titrated with standard permanganate solution as under iron (for factor see Iron and Steel).

Alumina.—To the remaining 300 cubic centimeters add, after transferring to a 600 cubic centimeter beaker, sufficient ammonia to have a slight excess of the latter, boil off excess and filter off the precipitated iron and aluminum oxides, wash with water, dry and burn off in a tared porcelain crucible. From the weight, subtract the iron oxide and phosphoric acid previously determined. The rest is alumina.

Calcium.—To the filtrate from the iron and aluminum oxides add a solution of ammonium oxalate, and heat to boiling. The precipitated calcium oxalate is filtered off and washed. The filter paper is next transferred to a weighed porcelain crucible, a few drops of sulphuric acid are added, and it is then dried and burned. The calcium oxide is calculated from the weight of the calcium sulphide thus formed.

Magnesia.—In the filtrate from the calcium oxalate the magnesia is determined. The filtrate is first concentrated to about 250 cubic centimeters. It is then cooled and placed in a dish containing ice water. A solution of sodium ammonium phosphate and about 30 cubic centimeters ammonia are added, and the solution vigorously stirred. Care should be taken not to touch the sides of the beaker with the rod. The solution is left standing for about 10 hours, and the magnesium pyrophosphate is then filtered and washed with a dilute solution of ammonium nitrate made slightly alkaline with ammonia. The precipitate of magnesium pyrophosphate is next dried and burned and weighed as $Mg_2P_2O_7$ from which the MgO is calculated.

Alkalies.—For the alkalies place 2 grams of the finely divided sample into a platinum dish, moisten with about 2 cubic centimeters of concentrated sulphuric acid, then add hydrofluoric acid until reaction ceases. Add a small excess and heat to drive off excess, until white fumes of sulphurous acid are given off. Cool, add water, and wash into a beaker. Add 10 cubic centimeters of hydrochloric acid and boil. Precipitate iron and alumina with ammonia, and then add a solution of ammonium oxalate to precipitate calcium, boil and filter off precipitate and wash with hot water. Discard filter paper and precipitate. Evaporate filtrate in a weighed platinum dish and after the solution has been evaporated to dryness, heat over a Bunsen flame. The residue consists of alkaline and magnesium sulphates; calculate the magnesium previously determined to sulphate and deduct from weight of dish. The difference between this corrected weight and the original weight of the dish are alkaline sulphates.

Sulphur Trioxide.—Two grams of the finely divided sample are for 12 hours digested in hydrochloric acid, to which potassium chlorate is added. It is finally taken down to dryness, redissolved in HCl, and the insoluble part filtered off. The filtrate is heated to boiling, barium chloride added, and then cooled. After the solution has cleared the barium sulphate is filtered, washed, transferred to a weighed crucible and burned. From the weight, the sulphur trioxide is calculated.

Titanium.

To determine titanic acid, treat 2 grams of the finely ground clay in a large platinum crucible with hydrofluoric acid and 5 cubic centimeters of sulphuric acid. Evaporate off the hydrofluoric acid and heat carefully until the greater part of the sulphuric acid is volatilized. Allow the crucible to cool, add 10 grams of sodium carbonate, and fuse for 30 minutes at the highest temperature obtainable by a Bunsen burner. Run the fused mass well up on the sides of the crucible, and allow it to cool. Treat the fused mass with water, transfer it to a beaker, and filter. Wash the insoluble matter slightly on the filter, dry, ignite, and fuse it again with sodium carbonate. Dissolve in water as before, and filter. By this method of treatment nearly all of the alumina will be dissolved and separated from the titanic acid. Fuse the insoluble matter left on the filter with sodium carbonate. Dissolve in hot water, filter off insoluble ferric oxide, etc., acidulate with HCl, add a few drops of acid ammonium sulphite, boil off all smell of sulphurous acid, and pass hydrogen sulphide through the hot solution to precipitate any arsenic that may be present. Pass a current of carbonic acid through the solution to expel the excess of hydrogen sulphide, filter off the arsenious sulphide, and to the filtrate add a sufficient amount of ferric chloride solution to combine with all the phosphoric acid as ferric phosphate and leave a slight excess. Add a slight excess of ammonia, which should throw down a red precipitate, while the solution is alkaline to test-paper; then add acetic acid to slightly acid reaction, boil, filter off the ferric phosphate and ferric oxide, and wash with hot water. Acidulate the filtrate with HCl, add ammonia until a permanent precipitate forms, redissolve with a few drops of hydrochloric acid, add a filtered solution of 20 grams of sodium acetate and one-sixth the volume of the solution of acetic acid (1.04 specific gravity) and heat to boiling. The titanic acid is precipitated almost immediately in a flocculent condition and quite free from iron. Boil a few minutes, allow the titanic acid to settle, filter, wash with hot water containing a little acetic acid, dry, ignite, and weigh as titanic acid, which contains 60.05 per cent. titanium. Should the precipitate contain an appreciable amount of ferric oxide, fuse with bisulphate and reprecipitate in the same way.

The essential points in this method are: 1. Separation of the titanic acid from the mass of ferric oxide by ammonium acetate in the deoxidized solution. 2. Separation from all the phosphoric acid and the greater part of the alumina by fusion with sodium carbonate, by which means a sodium titanate insoluble in water is formed, and at the same time sodium phosphate and aluminate soluble in that menstruum. 3. Separation of the last traces of alumina from the ferric oxide, lime, etc., by precipitating the titanic acid in the thoroughly deoxidized solution in the presence of a large excess of acetic acid and some sulphurous acid, the sulphuric acid being all in the form of sodium sulphate. The addition of a large excess of sodium acetate, by which this latter condition is effected, converts all the sulphate into acetates, and precipitates the titanic acid almost instantaneously as a hydrate, which is flocculent, settles quickly, shows no tendency to run through the filter, and is washed with the greatest ease. It sometimes happens that a little ferrous oxide is precipitated with the titanic acid, and the latter, after ignition, appears discolored; in this case fuse with a little sodium carbonate, add sulphuric acid to the cold fused mass, dissolve, and repeat the precipitation with sodium acetate in the presence of sulphurous and acetic acids exactly as in the first instance.

The above titanium method is taken from "The Chemical Analysis of Iron," by Blair.

Sutton gives the following volumetric method:

H. L. Wells and W. L. Mitchell, in a contribution to the *Jour. Amer. Chem. Soc.* 1895, 878, allude to a volumetric method of determining titanic acid by Pisani (*Compt. Rend. lix.* 289) which does not appear to have been found satisfactory. Marignac (*Zeit., anal. Chem.* vii. 112) applied Pisani's method in the estimation of titanic acid in the presence of niobic acid, special conditions being adopted to avoid the reduction of the latter.

The authors have modified Pisani's process as improved by Marignac, and employ it for the determination of iron together with the titanic acid in ores. Sulphuric acid solutions are used, and the liquid is protected from the air during cooling and titration by means of a current of carbon dioxide.

Process.—Five grams of the pulverized ore are treated with 100 cubic centimeters of concentrated hydrochloric acid in a covered beaker, using a gradually increasing heat, and adding more acid if necessary.[1] When there is no further action, 50 cubic centimeters of a mixture of equal volumes of sulphuric acid and water are added, and the liquid evaporated until it fumes strongly. After cooling, 200 cubic centimeters of water are added, the whole heated until the sulphates dissolve, and the liquid filtered into a liter flask. If anything besides silicious matter is left on the filter paper, it should be fused with potassium bisulphate, treated with concentrated sulphuric acid, and the sulphates dissolved in hot water and added to the main solution.

The liquid in the flask is made up to the mark with water, and four portions of 200 cubic centimeters each taken, two in Erlenmeyer flasks (500 cubic centimeters), and the other two in ordinary 350 cubic centimeter flasks. Each of these represents 1 gram of the ore.

To determine the iron, H_2S is passed into the solutions in the ordinary flasks to saturation, after which they are boiled until all the H_2S has been removed, care being taken to avoid any contact of the solution with the air by covering the mouths of the flasks with crucible lids. The flasks are then quickly filled to the neck with cold recently-boiled water, rapidly cooled, transferred to large beakers, and titrated with standard potassium permanganate.

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[1] For refractories it appears advisable to treat with HFl and H_2SO_4, and then continue as above.

To the solutions in the Erlenmeyer flasks 25 cubic centimeters of concentrated sulphuric acid are added, and 3 or 4 rods of pure zinc, about 5 millimeters long and 6 or 7 millimeters in diameter are suspended in the liquid by means of a platinum wire attached to the loop of a porcelain crucible lid, which is inverted over the mouth of the flask. The liquid is then gently boiled for 30 or 40 minutes. Then, without interrupting the boiling, a rapid current of CO_2 is introduced under the cover. The flask is now rapidly cooled, the zinc washed with a jet of water and removed, and the solution titrated with permanganate, while the current of CO_2 is still being passed in. The difference between the permanganate used in this case and that required for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid (TiO_2).

The most convenient strength for the permanganate solution is one of 7.9 grams per liter, corresponding to about 0.014 gram of metallic iron.

In the determination of iron by reduction with sulphureted hydrogen, no effect is produced on cold permanganate solution by the precipitated sulphur present, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling.

The results of test analyses of recrystallized potassium titanofluoride were somewhat low, but probably quite as good or better than any gravimetric method.

LUBRICATING OIL.

A good lubricant should meet the following, generally accepted requirements:

(1) It must be free from corrosive elements such as acids, either of mineral, animal or vegetable origin.

(2) It must have body enough to form and retain a filament of the lubricant over the lubricated parts to prevent direct contact of the metal.

(3) A minimum coefficient of friction.

(4) High boiling-point to insure the proper flash and fire points.

(5) Freedom from grit or tarry matter.

(6) Must not gum, due to presence of readily oxidizable oils.

(7) Must not contain thickener.

(8) Must have a low volatility at comparatively high temperatures.

(9) Must not become too thin when heated.

(10) Should not freeze or become thickened by moderately low temperatures.

To determine the above qualities the following chemical, physical, and mechanical tests are applied:

Chemical Tests:

1. Iodine Absorption.
2. Acidity.
3. Color Reactions.
4. Saponification.
5. Soap Test.
6. Tarry Matter and Grit.

Physical Tests:

1. Flash and Fire Tests.
2. Viscosity.
3. Specific Gravity.
4. Cold Test.
5. Index of Refraction.

Mechanical Test:

1. Coefficient of Friction.

Twenty-five grams of iodine and 30 grams of mercuric chloride are each dissolved in 500 cubic centimeters of 95 per cent. alcohol, uniting the two solutions, and allowing to stand several hours before use. It is then standardized by 10/N thiosulphate sodium solution. The process of the determination of the iodine absorption of an oil is as follows: One-tenth to 0.5 gram of the fat or oil is dissolved in 10 cubic centimeters of purest chloroform in a well-stoppered flask, and 20 cubic centimeters of the iodine solution added. The amount must be finally regulated so that after not less than two hours digestion the mixture possesses a dark brown tint; under any circumstances it is necessary to have a considerable excess of iodine (at least double the amount absorbed ought to be present), and the digestion should be from 6 to 8 hours. Some potassium iodide solution is then added, and the whole diluted with 150 cubic centimeters of water, and 10/N thiosulphate solution delivered in until the color is nearly discharged. Starch is then added, and the titration finished in the usual way.

Acidity: (*a*) Fatty Acids in Compounded Oils.—Dissolve 10 grams of the oil in 50 cubic centimeters of absolute alcohol and warm, add a drop of phenolphthalein and titrate with N/50 soda solution until red appears. Calculate Mg. NaOH required to neutralize 1 gram of oil.

(*b*) Free Acid in Mineral Oil.—In a separatory funnel shake 25 cubic centimeters of the oil with 50 cubic centimeters of hot water, to which a drop of methyl orange has been added. The water must not turn red.

Color Reaction: Heidenreich's test is as follows: A clear glass plate is placed over a piece of white paper; 10 drops of the oil under examination are placed thereon, and 1 drop of concentrated sulphuric acid is added.

The color produced when the acid comes in contact with the oil is noticed as well as the color produced when the two are stirred with a glass rod. Many oils give off characteristic odors during the reaction, especially neatsfoot oil, whale oil, and menhaden oil.

Massie's test is thus performed:

Nitric acid of 1.40 specific gravity, free from nitrous acid is mixed in a test-tube with ⅓ its volume of the oil, and the whole agitated for 2 minutes.

The color of the oil after separation from the acid is the indication.

In mixture of oils, the characteristic colors produced, by either Heindenreich's or Massie's test are often clouded, and in many instances no inference can be drawn, yet with single oils the reactions are often distinctive and sufficiently strong to give confirmatory results.

In cod liver oil, or whale oil, when mixed with mineral or even vegetable oil, the characteristic brilliant violet color produced with sulphuric acid cannot be mistaken. This color, due to the presence of cholic acid, is found in most of the fish oils, but is much more pronounced in cod liver oil.

	Heidenreich's Test		Massie's Test
Lard Oil	Yellow	Brown	Yellow
Tallow Oil	Yellow	Orange	Colorless
Neatsfoot Oil	Yellowish	Red-brown	Red
Oleo Oil	Colorless	Orange	Pink
Elain Oil	Light green turning to brown	Brown	Orange Red
Sperm Oil	Brown with purple streaks	Reddish brown	Red
Whale Oil	Red-violet	Brown	Dark red
Dog-fish Oil	Violet	Dark Brown	Orange
Cod liver Oil	Red-violet	Dark Brown	Orange-red
Crude Cottonseed	Brilliant red	Brown	Brown
Ref'd Cottonseed	Reddish brown	Red	Orange-red
Rape Oil	Yellow-brown	Brown	Orange
Castor Oil	Light yellow to brown	Pale brown	Orange
Olive Oil	Light green	Greenish to light brown	Yellow to greenish
Rosin	Brown	Brown	Orange
Earth Nut Oil	Yellow to Orange	Greenish	Reddish

Saponification: (*a*) Separation of the Mineral Oil.—Ten grams of the oil are weighed in a dry weighed beaker (250 cubic centimeters), and to it are added 75 cubic centimeters of an alcoholic solution of potash (60 grams of potassium hydroxide to 1,000 cubic centimeters of 95 per cent. alcohol), and the contents evaporated until all the alcohol is driven off. In this process, if any animal or vegetable oil is present, it is formed into a soap by the potash, while the mineral oil is unacted upon. Water (75 cubic centimeters) is now added and the material well stirred to insure complete solution of the soap, and then it is transferred to a separatory funnel, 75 cubic centimeters of sulphuric ether added, corked, the liquid violently agitated and allowed to stand for 12 hours. Two distinct liquids are now seen, the lower, the solution of the soap, the upper the ether solution (colored, if mineral oil is present, colorless if not). The aqueous solution is drawn off in a No. 3 beaker, the ethereal solution remaining in the separatory funnel. The former is placed on a water bath, heated for ½ hour, and until all traces of ether (which is absorbed by the water in a very small amount) is gone. The solution is allowed to cool, diluted somewhat with water, and made acid with dilute sulphuric acid. Any animal or vegetable oil present will be indicated by a rise of the fatty acids to the surface of the liquid. (In this reaction the sulphuric acid decomposes the soap, uniting with the potash to form sulphate of potash and liberating the fatty acids of the oil.)

If it is desired to weigh the fatty acids, proceed as follows:

Weigh carefully about 5 grams of pure white beeswax, place it in the beaker upon the surface of the oil and water, and bring the contents nearly to boiling; the melted wax and fatty acids unite; allow to cool, remove the wax, wash with water, dry between folds of filter paper, and weigh. The increase in weight of the wax over its original weight gives the weight of the fatty acids of the animal or vegetable oil in the lubricating oil.

(*b*) Saponification Value.—This is expressed by the number of milligrams of potassium hydrate necessary to saponify 1 gram of the oil. From 2.5 to 10 grams of the oil, according to the percentage of saponifiable matter supposed to be present, are boiled with 25 cubic centimeters of N/2 alcoholic potash in a 200 cubic centimeter Jena Erlenmeyer flask. A reflux condenser is used, and the boiling may require from 5 to 8 hours. The excess of alkali is titrated with N/2 HCl, using phenolphthalein. The strength of the N/2 KOH is determined by boiling 25 cubic centimeters in similar flasks alongside of those in which the oil is treated and for the same length of time.

Tarry Matter and Grit.—Shake 10 cubic centimeters of the oil with 90 cubic centimeters of petroleum ether in a test tube, holding 125 cubic centimeters. No deposit should appear after standing for 1 hour.

Flash and Fire Test.—In a porcelain evaporating dish filled with sand, place a platinum crucible, suspend a thermometer reading at least 600° F. from a support directly above the crucible so that the mercury bulb will reach to about the middle of the crucible, care being taken not to touch the sides. Fill the crucible with oil, completely covering the bulb of the thermometer but allowing room for the oil to expand without overflowing on heating. Adjust the flame so that the temperature of the liquid in the dish rises at the rate required for the liquid being tested, and when the temperature reaches a desired point, apply the test flame by passing it slowly, entirely across the dish, about a half inch above the level of the liquid and just in front of the thermometer. Allow the liquid to rise in temperature until another testing point is reached and then apply the test flame again in the same manner. Proceed in this way until the vapor from the liquid above it ignites with a slight flash. The temperature shown by the thermometer when this is the case is the flashing point of the liquid. Continue the heating and testing in the same manner until a point is reached where the liquid takes fire. The reading of the thermometer when this is the case is the burning point of the liquid.

The test flame can best be adjusted by using a jeweler's blowpipe and allowing enough gas to flow to produce a flame of 2 to 3 millimeters long.

Viscosity.—The viscosity is generally determined by the rate of flow at a specified temperature through an opening of accurate standard size. It is recorded in seconds for a specified temperature and volume.

By comparison with standards an oil may be rated as to its viscosity thus giving one of the values required for a lubricant. Engler's apparatus—probably the first used for this purpose—is made of metal (copper). This instrument is the standard for determining the viscosity of oil in Germany, and is also a standard in this country. It is recommended by the United States Bureau of Standards for use unless another form of viscosimeter is called for in the specification.

In using this instrument, the viscosity of an oil is stated in seconds required for 200 cubic centimeters of the oil to run into the flask. Two hundred and forty cubic centimeters of the oil being placed in the viscosimeter, water usually requiring from 50 to 53 seconds at 20° C. Heat can be applied to the water bath, the viscosity being determined at any temperature up to 100° C. Higher temperatures to 360° C. can be secured by filling the outer vessel with paraffine instead of water. Engler recommends that all viscosities be compared with water thus: If water requires 52 seconds for delivery of 200 cubic centimeters into the receiving flask, and the same amount of the oil under examination requires 130 seconds, the ratio is determined by $\frac{132}{52} = 2.50$, the oil thus having a viscosity of 2.5 times that of water.

The American Society for Testing Materials, Report of Committee D-2, state as follows:

In case it is desired to correct for specific gravity of the oil, the following formula which gives the results in specific viscosity can be used:

$$\text{Sp. viscosity} = \text{Sp. grav.} \times \frac{\text{time of efflux of oil}}{\text{time of efflux of water}} \times 7.32.$$

If it is necessary to use a quantity of oil less than 240 cubic centimeters, the following quantities can be employed and multiplied by the corresponding factor:

Amount of oil put in, cc.	45	50	60	120
Amount of oil run out, cc.	25	40	50	100
Factor to change to 200 cc. run out and 240 cc. put in	5.55	3.62	2.79	1.65

The Committee recommends the use of the Saybold viscosimeter. In this country it is the most widely used standard and has the advantage that small samples of 125 cubic centimeters are sufficient for the test. This instrument is shown in Fig. 58. The tests are carried out in practically the same way as in the Engler, only that a flask graduated to 60 cubic centimeters is used for the receiver, and the seconds required for the oil to fill the flask to the 60 cubic centimeter mark indicate the viscosity.

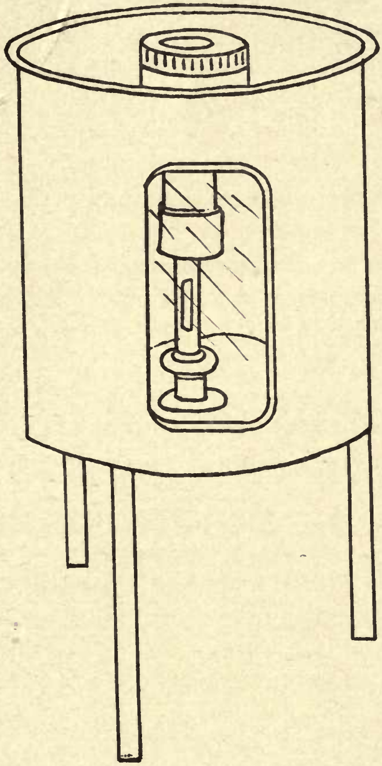

FIG. 58.

Specific Gravity.—Lubricating oils are practically always reported in degrees Baumé. It is, therefore, sufficient to read the gravity by means of a hydrometer, correcting for temperature. If the oil is too thick to float the hydrometer, heat to 90° or 100° F. The following table can be used for temperature corrections:

°F	60	62	64	66	68	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	100
Hydrometer.																					
20°B.	20.0	19.9	19.8	19.6	19.5	19.4	19.3	19.2	19.1	19.0	18.9	18.8	18.7	18.6	18.5	18.4	18.2	18.1	18.0	17.8	17.7
21	21.0	20.9	20.8	20.6	20.5	20.4	20.3	20.2	20.1	20.0	19.9	19.8	19.7	19.6	19.5	19.4	19.2	19.1	19.0	18.8	18.7
22	22.0	21.9	21.7	21.6	21.5	21.4	21.3	21.1	21.0	20.9	20.8	20.7	20.6	20.5	20.4	20.3	20.2	20.1	19.9	19.8	19.7
23	23.0	22.9	22.7	22.6	22.5	22.4	22.3	22.1	22.0	21.9	21.8	21.7	21.6	21.5	21.4	21.3	21.2	21.1	20.9	20.8	20.7
24	24.0	23.9	23.7	23.6	23.5	23.4	23.2	23.1	23.0	22.9	22.8	22.6	22.5	22.4	22.3	22.2	22.1	21.9	21.8	21.7	21.6
25	25.0	24.9	24.7	24.6	24.5	24.4	24.2	24.1	24.0	23.9	23.8	23.6	23.5	23.4	23.3	23.2	23.1	22.9	22.8	22.7	22.6
26	26.0	25.9	25.7	25.6	25.5	25.3	25.2	25.1	25.0	24.8	24.7	24.6	24.5	24.4	24.2	24.1	24.0	23.9	23.7	23.6	23.5
27	27.0	26.9	26.7	26.6	26.5	26.3	26.2	26.1	26.0	25.8	25.7	25.6	25.5	25.4	25.2	25.1	25.0	24.9	24.7	24.6	24.5
28	28.0	27.9	27.7	27.6	27.5	27.3	27.2	27.1	26.9	26.8	26.7	26.5	26.4	26.3	26.2	26.0	25.9	25.8	25.6	25.5	25.4
29	29.0	28.9	28.7	28.6	28.5	28.3	28.2	28.1	27.9	27.8	27.7	27.5	27.4	27.3	27.2	27.0	26.9	26.8	26.6	26.5	26.4
30	30.0	29.9	29.7	29.6	29.5	29.3	29.2	29.0	28.9	28.8	28.6	28.5	28.4	28.2	28.1	28.0	27.8	27.7	27.6	27.5	27.3
31	31.0	30.9	30.7	30.6	30.5	30.3	30.2	30.0	29.9	29.8	29.6	29.5	29.4	29.2	29.1	29.0	28.8	28.7	28.6	28.5	28.3
32	32.0	31.9	31.7	31.6	31.4	31.3	31.2	31.0	30.9	30.7	30.6	30.4	30.3	30.2	30.0	29.9	29.7	29.6	29.5	29.3	29.2
33	33.0	32.9	32.7	32.6	32.4	32.3	32.2	32.0	31.9	31.7	31.6	31.4	31.3	31.2	31.0	30.9	30.7	30.6	30.5	30.3	30.2
34	34.0	33.8	33.7	33.5	33.4	33.3	33.1	33.0	32.8	32.7	32.5	32.4	32.2	32.1	32.0	31.8	31.6	31.5	31.4	31.2	31.1
35	35.0	34.8	34.7	34.5	34.4	34.3	34.1	34.0	33.8	33.7	33.5	33.4	33.2	33.1	33.0	32.8	32.6	32.5	32.4	32.2	32.1
36	36.0	35.8	35.7	35.5	35.4	35.2	35.1	34.9	34.8	34.6	34.5	34.3	34.2	34.0	33.9	33.7	33.5	33.4	33.3	33.1	33.0
37	37.0	36.8	36.7	36.5	36.4	36.2	36.1	35.9	35.8	35.6	35.5	35.3	35.2	35.0	34.9	34.7	34.5	34.4	34.3	34.1	34.0
38	38.0	37.8	37.7	37.5	37.4	37.2	37.1	36.9	36.8	36.6	36.4	36.3	36.1	36.0	35.8	35.6	35.5	35.3	35.2	35.0	34.9
39	39.0	38.8	38.7	38.5	38.4	38.2	38.1	37.9	37.8	37.6	37.4	37.3	37.1	37.0	36.8	36.6	36.5	36.3	36.2	36.0	35.9
40	40.0	39.8	39.7	39.5	39.4	39.2	39.0	38.9	38.7	38.5	38.4	38.2	38.1	37.9	37.7	37.6	37.4	37.2	37.1	36.9	36.8
41	41.0	40.8	40.7	40.5	40.4	40.2	40.0	39.9	39.7	39.5	39.4	39.2	39.1	38.9	38.7	38.6	38.4	38.2	38.1	37.9	37.8
42	42.0	41.8	41.7	41.5	41.3	41.2	41.0	40.8	40.7	40.5	40.3	40.2	40.0	39.8	39.7	39.5	39.3	39.2	39.0	38.9	38.7
43	43.0	42.8	42.7	42.5	42.3	42.2	42.0	41.8	41.7	41.5	41.3	41.2	41.0	40.8	40.7	40.5	40.3	40.2	40.0	39.9	39.7
44	44.0	43.8	43.7	43.5	43.3	43.1	43.0	42.8	42.6	42.5	42.3	42.1	42.0	41.8	41.6	41.4	41.3	41.1	40.9	40.8	40.6
45	45.0	44.8	44.7	44.5	44.3	44.1	44.0	43.8	43.6	43.5	43.3	43.1	43.0	42.8	42.6	42.4	42.3	42.1	41.9	41.8	41.6
46	46.0	45.8	45.7	45.5	45.3	45.1	44.9	44.8	44.6	44.4	44.2	44.1	43.9	43.7	43.6	43.4	43.2	43.0	42.9	42.7	42.6
47	47.0	46.8	46.7	46.5	46.3	46.1	45.9	45.8	45.6	45.5	45.2	45.1	44.9	44.7	44.6	44.4	44.2	44.0	43.9	43.7	43.6
48	48.0	47.8	47.6	47.4	47.3	47.1	46.9	46.7	46.5	46.4	46.2	46.0	45.8	45.7	45.5	45.3	45.2	45.0	44.8	44.6	44.5
49	49.0	48.8	48.6	48.4	48.3	48.1	47.9	47.7	47.5	47.4	47.2	47.0	46.8	46.7	46.5	46.3	46.2	46.0	45.8	45.6	45.5
50	50.0	49.8	49.6	49.4	49.3	49.1	48.9	48.7	48.5	48.3	48.1	48.0	47.8	47.6	47.4	47.3	47.1	46.9	46.7	46.5	46.4

Cold Test.—Twenty cubic centimeters of the oil are transferred to a narrow bottle or test tube, stoppered with a rubber stopper, through which is inserted a thermometer, the bulb of which remains an inch or more into the oil.

The bottle is placed in a mixture of ice and salt, or other freezing compound, and retained there until the oil becomes solid. It is then removed and allowed to warm until the contents become somewhat thinner in consistency. The bottle is inclined from side to side until the oil begins to flow, when the temperature is taken.

At this particular temperature the oil is neither at its normal fluidity, nor is it solid, and while this method does not correctly indicate the exact temperature of the solidifying-point, it does show the point at which the oil ceases to flow readily, the important one to the oil inspector.

These methods are in part taken from Stillman's "Analysis of Lubricating Oil."

SOLDER.

Tin and Antimony Determination.

Tin Determination.—Dissolve 0.5 gram of very finely divided sample (best done with hacksaw) in 50 cubic centimeters of concentrated hydrochloric acid till action ceases, passing a stream of CO_2 gas, during the whole operation to prevent oxidation, cool, still, passing CO_2. Add starch paste and titrate with 10/N iodine solution. Cubic centimeters used x 1.18 = per cent. tin.

Antimony Determination.—Dissolve 0.5 gram metal in hydrochloric acid (as in tin determination, except not using CO_2 gas). After action ceases, add small quantities of iodine crystals. Boil off excess iodine, cool, dilute to 150 cubic centimeters (put in 500 cubic centimeter flask), add 50 cubic centimeters of Rochelle salt solution (10 — 20 grams salt in the 50 cubic centimeters of water, keep cold, and nearly neutralize with sodium bicarbonate, then completely neutralize with sodium hydrate, keep cold (using litmus paper). Add quickly concentrated sodium bicarbonate solution till milky. Add starch paste and titrate with 10/N iodine solution. Cubic centimeters used x 1.2 = per cent. antimony.

Lead is seldom determined but instead is taken by difference. It may, however, be determined by the method described under Babbitt.

One-tenth normal iodine solution: 6.35 grams iodine and 9 grams of potassium iodine to 500 cubic centimeters of water.

HARD LEAD AND BABBITT.

To determine antimony in hard lead, the method for Babbitt metal can be used.

To Determine Copper and Lead.—Five-tenth gram of the finely divided sample in nitric acid adding 0.5 gram of chemically pure copper (to avoid sponging of the lead on the cathods) evaporate until almost dry and redissolve in 88 cubic centimeters of nitric acid with 50 cubic centimeters of distilled water, filter, wash well with water and electrolyze (see Copper Alloys), deduct the 0.5 gram C added from your weight of the cathods, the remainder in the C in the Babbitt. The increase of the weight of the annode multiplied by 0.868 x 2 x 100 gives the lead as metallic lead.

COPPER ALLOYS.

Weigh out 1 gram of the clean borings into a 250 cubic centimeter beaker, dissolve in 20 cubic centimeters of diluted nitric acid and evaporate to dryness.

Redissolve with 10 cubic centimeters concentrated nitric acid and 40 cubic centimeters of water and filter off the oxide of tin, running the filtrate into a 250 cubic centimeter beaker, wash well with distilled water and fill the beaker to within ½ inch of the top.

The solution is then electrolyzed by placing two platinum electrodes previously weighed and connected with a 4-volt direct current (storage battery or Edison Laland cells are best fitted for the purpose) at a rate of about ½ ampere per hour. After about 10 to 12 hours all of the copper will be deposited on the negative electrode as metallic copper, the lead on the positive electrode as black peroxide. The electrolyte is then quickly removed by lowering the beaker and washed by replacing it with a beaker of distilled water and then a beaker of alcohol. The electrodes are then dried and weighed. The increase gives the per cent. of copper direct; the lead is calculated by multiplying the weight of the oxide with 0.868.

The oxide of tin is burned off and weighed. The weights multiplied by 0.7881 gives the per cent. of metallic tin.

To the electrolyte from the electrolysis, ammonia is added until decidedly ammoniacal, boil off excess and filter off any iron hydroxide present, burn off and weigh. If zinc is present, precipitate with hydrogen sulphide, filter and burn to zinc oxide, weigh and calculate to metallic zinc.

In alloys containing nickel, the electrolyte after the copper has been deposited and weighed is made alkaline with an excess of ammonia and the electrode coated with the copper replaced and a current of 6 volts passed through it to deposit the nickel as metallic nickel. It is advisable to use the copper plated cathod, since the nickel when deposited direct on the platinum is hard to remove.

LIME.

In works practice the analysis is confined to determine the quality of the lime as a binder for mortar and as an alkaline for setting free ammonia from its fixed salts.

A high percentage of calcium oxide is most desirable and the determination of CaO therefore suffices for most purposes.

In selecting the sample, about a bucket full of lumps are quickly broken up into pieces the size of a pea, and quartered down until one-quarter fills approximately a pint bottle; precaution should be taken to prevent the sample from absorbing moisture or CO_2 from the air.

One hundred grams of this sample are weighed into a 1 liter flask. The sample is next slaked and the flask filled to the mark with water and well shaken.

One hundred cubic centimeters of this milk of lime without letting it settle are transferred to another liter flask again filled to the mark and well shaken. Fifty cubic centimeters of this solution are transferred to an Erlenmeyer flask of 250 cubic centimeters capacity, adding a few drops of phenacetolin as an indicator, and titrated with normal hydrochloric acid solution until the solution becomes a faint pink. The caustic lime is calculated from the number of cubic centimeters of HCl neutralized.

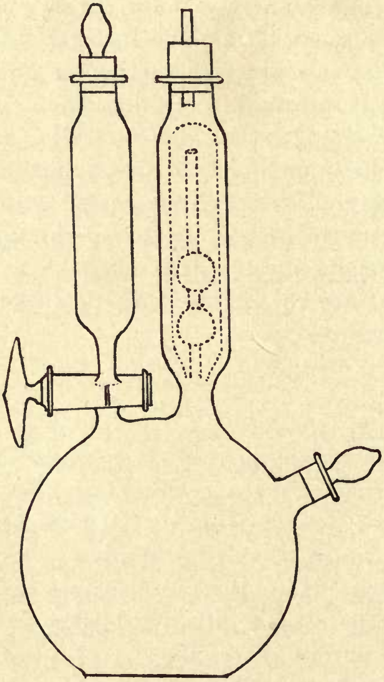

FIG. 59.

The titration is then continued until the solution changes first to red and finally to yellow, the second titration giving the carbonate of lime. It is sometimes desirable to determine the unburned lime by determining the CO_2 and calculating it therefrom. It can best be done by means of an alkalimeter. See Fig. 59.

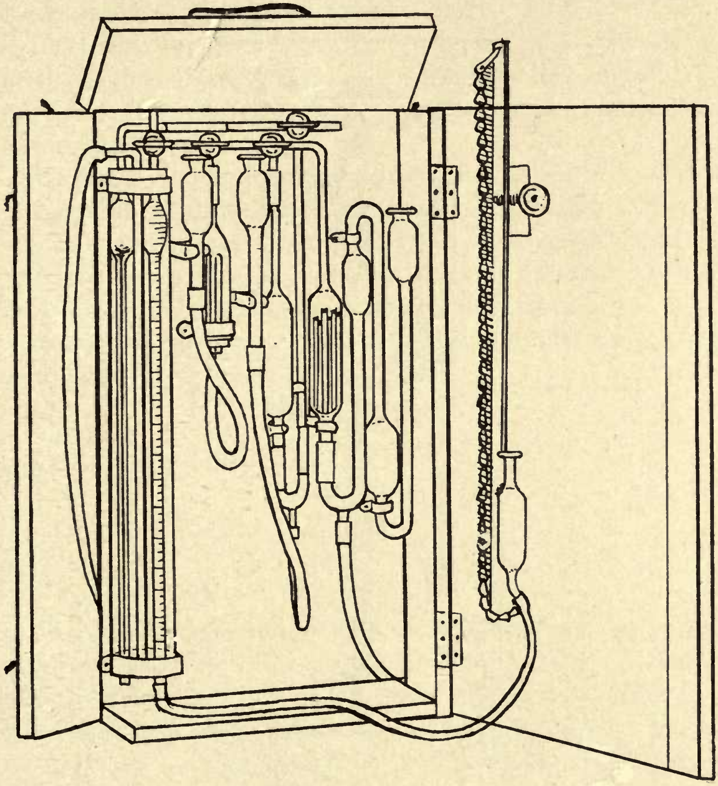

FIG. 60.

The latter consists of a glass vessel having a glass stoppered opening at the side through which the sample is introduced, a separatory funnel with a glass stopper at one side of the top and a gas scrubbing tube at the other.

To use the apparatus the gas scrubbing tube is first filled ⅓ full with concentrated sulphuric acid. The separatory funnel is then filled with diluted HCl (½ acid, ½ water) and the apparatus weighed.

Then approximately 5 grams of the powdered sample are introduced through the glass stoppered opening and the whole is again weighed. The acid in the separating funnel is next

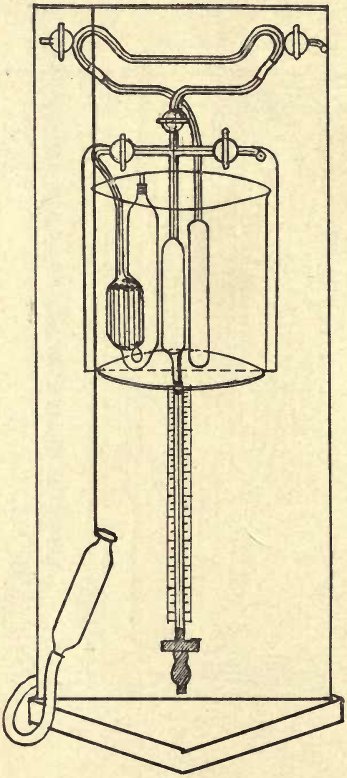

FIG. 61.

run into the vessel through the stop-cock, and after the reaction ceases, the flask is slightly warmed. After cooling it is again weighed. The difference between the second and third weights represents the CO_2 driven off. By dividing the difference between the first and second weight (the weight of the sample), into the third and mutliplied by 100, the percentage of CO_2 is found and the percentage of calcium carbonate can be calculated therefrom.

MAGNESIUM.

For the determination of magnesium follow scheme under Refractories or Water Analysis.

Efficiency Test. For Use in Ammonia Still.—Five grams of the sample are placed in a Kjeldahl flask and slaked. The flask is next connected with the condenser of an ammonia distilling apparatus.

Through a separatory funnel are then added 10 grams of ammonium sulphate previously dissolved in water. The ammonia liberated on boiling is absorbed in a beaker containing standard sulphuric acid. The operation is the same as in the determination of ammonia in ammoniacal liquors.

From the ammonia thus determined, the efficiency of the lime can be determined as follows:

$a = NH_3$ found

$b = CaO$ used

$$\frac{\left(\frac{a \times 56}{34}\right)}{b}$$

CO_2 IN AIR.

For the determination of CO_2 in air, there are two apparatuses generally used, the one is Haldane's (Fig. 60) and the other Petterson's (Fig. 61). These apparatuses differ from the Orsat apparatus that the gas volume can be read as close as 0.001 of a cubic centimeter and CO_2 can, therefore, be determined in 0.0001 by volume.

CEMENT.

STANDARD SPECIFICATIONS FOR CEMENT, AS PUBLISHED BY THE AMERICAN SOCIETY FOR TESTING MATERIALS.

Adopted, 1904; Revised, 1908, 1909.

GENERAL OBSERVATIONS.

1. These remarks have been prepared with a view of point-

ing out the pertinent features of the various requirements and the precautions to be observed in the interpretation of the results of the tests.

2. The Committee would suggest that the acceptance or rejection under these specifications be based on tests made by an experienced person having the proper means for making the tests.

Specific Gravity.

3. Specific gravity is useful in detecting adulteration. The results of tests of specific gravity are not necessarily conclusive as an indication of the quality of a cement, but when in combination with the results of other tests may afford valuable indications.

Fineness.

4. The sieves should be kept thoroughly dry.

Time of Setting.

5. Great care should be exercised to maintain the test pieces under as uniform conditions as possible. A sudden change or wide range of temperature in the room in which the tests are made, a very dry or humid atmosphere, and other irregularities vitally affect the rate of setting.

Constancy of Volume.

6. The tests for constancy of volume are divided into two classes, the first normal, the second accelerated. The latter should be regarded as a precautionary test only, and not infallible. So many conditions enter into the making and interpreting of it that it should be used with extreme care.

7. In making the pats the greatest care should be exercised to avoid initial strains due to molding or to too rapid drying-out during the first 24 hours. The pats should be preserved under the most uniform conditions possible, and rapid changes of temperature should be avoided.

8. The failure to meet the requirements of the accelerated

tests need not be sufficient cause for rejection. The cement may, however, be held for 28 days, and a retest made at the end of that period, using a new sample. Failure to meet the requirements at this time should be considered sufficient cause for rejection, although in the present state of our knowledge it cannot be said that such failure necessarily indicates unsoundness, nor can the cement be considered entirely satisfactory simply because it passes the tests.

SPECIFICATIONS.

General Conditions.

1. All cement shall be inspected.

2. Cement may be inspected either at the place of manufacture or on the work.

3. In order to allow ample time for inspecting and testing, the cement should be stored in a suitable weather-tight building having the floor properly blocked or raised from the ground.

4. The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment.

5. Every facility shall be provided by the Contractor and a period of at least 12 days allowed for the inspection and necessary tests.

6. Cement shall be delivered in suitable packages with the brand and name of manufacturer plainly marked thereon.

7. A bag of cement shall contain 94 pounds of cement net. Each barrel of Portland cement shall contain four bags, and each barrel of natural cement shall contain three bags of the above net weight.

8. Cement failing to meet the 7-day requirements may be held awaiting the results of the 28-day tests before rejection.

9. All tests shall be made in accordance with the methods proposed by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, presented to the Society January 21, 1903, and amended January 20, 1904, and

January 15, 1908, with all subsequent amendments thereto. (See addendum to these specifications.)

10. The acceptance or rejection shall be based on the following requirements:

Natural Cement.

11. *Definition.*—This term shall be applied to the finely pulverized product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

FINENESS.

12. It shall leave by weight a residue of not more than 10 per cent. on the No. 100, and 30 per cent. on the No. 200 sieve.

TIME OF SETTING.

13. It shall not develop initial set in less than 10 minutes; and shall not develop hard set in less than 30 minutes, or in more than 3 hours.

TENSILE STRENGTH.

14. The minimum requirements for tensile strength for briquets 1 square inch in cross section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

Neat Cement.

Age	Strength
24 hours in moist air	75 pounds
7 days (1 day in moist air, 6 days in water)	150 pounds
28 days (1 day in moist air, 27 days in water)	250 pounds
One Part Cement, Three Parts Standard Ottawa Sand.	
7 days (1 day in moist air, 6 days in water)	50 pounds
28 days (1 day in moist air, 27 days in water)	125 pounds

CONSTANCY OF VOLUME.

15. Pats of neat cement about 3 inches in diameter, ½ inch thick at center, tapering to a thin edge, shall be kept in moist air for a period of 24 hours.

(*a*) A pat is then kept in air at normal temperature.

(*b*) Another is kept in water maintained as near 70° F. as practicable.

16. These pats are observed at intervals for at least 28 days, and, to satisfactorily pass the tests, shall remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating.

Portland Cement.

17. *Definition.*—This term is applied to the finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, and to which no addition greater than 3 per cent. has been made subsequent to calcination.

SPECIFIC GRAVITY.

18. The specific gravity of cement shall not be less than 3.10. Should the test of cement as received fall below this requirement, a second test may be made upon a sample ignited at a low red heat. The loss in weight of the ignited cement shall not exceed 4 per cent.

FINENESS.

19. It shall leave by weight a residue of not more than 8 per cent. on the No. 100, and not more than 25 per cent. on the No. 200 sieve.

TIME OF SETTING.

20. It shall not develop initial set in less than 30 minutes; and must develop hard set in not less than 1 hour, nor more than 10 hours.

TENSILE STRENGTH.

21. The minimum requirements for tensile strength for briquets 1 square inch in cross section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

Neat Cement.

Age	Strength
24 hours in moist air	175 pounds
7 days (1 day in moist air, 6 days in water)	500 pounds
28 days (1 day in moist air, 27 days in water)	600 pounds
One Part Cement, Three Parts Standard Ottawa Sand.	
7 days (1 day in moist air, 6 days in water)	200 pounds
28 days (1 day in moist air, 27 days in water)	275 pounds

CONSTANCY OF VOLUME.

22. Pats of neat cement about 3 inches in diameter, ½ inch thick at the center, and tapering to a thin edge, shall be kept in moist air for a period of 24 hours.

(*a*) A pat is then kept in air at normal temperature and observed at intervals for at least 28 days.

(*b*) Another pat is kept in water maintained as near 70° F. as practicable, and observed at intervals for at least 28 days.

(*c*) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel for 5 hours.

23. These pats, to satisfactorily pass the requirements, shall remain firm and hard, and show no signs of distortion, checking, cracking, or disintegrating.

SULPHURIC ACID AND MAGNESIA.

24. The cement shall not contain more than 1.75 per cent. of anhydrous sulphuric acid (SO_3), nor more than 4 per cent. of magnesia (MgO).

ADDENDUM.

METHODS FOR TESTING CEMENT.[1]

Recommended by the Special Committee on Uniform Tests of Cement of the American Society of Civil Engineers.

SAMPLING.

1. *Selection of Sample.*—The selection of samples for testing should be left to the engineer. The number of packages sampled and

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[1] Accompanying Final Report of Special Committee on Uniform Tests of Cement of the American Society of Civil Engineers, dated January 17, 1912.

the quantity taken from each package will depend on the importance of the work and the facilities for making the tests.

2. The samples should fairly represent the material. When the amount to be tested is small it is recommended that 1 barrel in 10 be sampled; when the amount is large it may be impracticable to take samples from more than 1 barrel in 30 or 50. When the samples are taken from bins at the mill 1 for each 50 to 200 barrels will suffice.

3. Samples should be passed through a sieve having twenty meshes per linear inch, in order to break up lumps and remove foreign material; the use of this sieve is also effective to obtain a thorough mixing of the samples when this is desired. To determine the acceptance or rejection of cement it is preferable, when time permits, to test the samples separately. Tests to determine the general characteristics of a cement, extending over a long period may be made with mixed samples.

4. *Method of Sampling.*—Cement in barrels should be sampled through a hole made in the head, or in one of the staves midway between the heads, by means of an auger or a sampling iron similar to that used by sugar inspectors; if in bags, the sample should be taken from surface to center; cement in bins should be sampled in such a manner as to represent fairly the contents of the bin. Sampling from bins is not recommended if the method of manufacture is such that ingredients of any kind are added to the cement subsequently.

CHEMICAL ANALYSIS.

5. *Significance.*—Chemical analysis may serve to detect adulteration of cement with inert material, such as slag or ground limestone, if in considerable amount. It is useful in determining whether certain constituents, such as magnesia and sulphuric anhydride, are present in inadmissible proportions.

6. The determination of the principal constituents of cement, silica, alumina, iron oxide, and lime, is not conclusive as an indication of quality. Faulty cement results more frequently from imperfect preparation of the raw material or defective burning than from incorrect proportions. Cement made from material ground very finely and thoroughly burned may contain much more lime than the amount usually present, and still be perfectly sound. On the other hand, cements low in lime may, on account of careless preparation of the raw material, be of dangerous character. Furthermore, the composition of the product may be so greatly modified by the ash of the fuel used in burning as to affect in a great degree the significance of the results of analysis.

7. *Methods.*—The methods to be followed, except for determining the loss on ignition, should be those proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, reported in the *Journal of the Society for Chemical Industry,* Vol. 21, p. 12, 1902; and published in *Engineering News,* Vol. 50, p. 60, 1903; and in *Engineering Record,* Vol. 48, p. 49, 1903, and in addition thereto, the following:

(*a*) The insoluble residue may be determined as follows: To a 1-gram sample of the cement are added 30 cubic centimeters of water and 10 cubic centimeters of concentrated hydrochloric acid, and then warmed until effervescence ceases, and digested on a steam bath until dissolved. The residue is filtered, washed with hot water, and the filter paper and contents digested on the steam bath in a 5 per cent. solution of sodium carbonate. This residue is filtered, washed with hot water, then with hot hydrochloric acid, and finally with hot water, and then ignited at a red heat and weighed. The quantity so obtained is the insoluble residue.

(*b*) The loss on ignition shall be determined in the following manner: One-half gram of cement is heated in a weighed platinum crucible, with cover, for 5 minutes with a Bunsen burner (starting with a low flame and gradually increasing to its full height) and then heated for 15 minutes with a blast lamp; the difference between the weight after cooling and the original weight is the loss on ignition. The temperature should not exceed 900° C., or a low red heat; the ignition should preferably be made in a muffle.

SPECIFIC GRAVITY.

8. *Significance.*—The specific gravity of cement is lowered by adulteration and hydration, but the adulteration must be considerable to be detected by tests of specific gravity.

9. Inasmuch as the differences in specific gravity are usually very small, great care must be exercised in making the determination.

10. *Apparatus.*—The determination of specific gravity should be made with a standardized Le Chatelier apparatus. This consists of a flask (*D*), Fig. 62, of about 120 cubic centimeters capacity, the neck of which is about 20 centimeters long; in the middle of this neck is a bulb (*C*), above and below which are two marks (*F*) and (*E*); the volume between these two marks is 20 cubic centimeters. The neck has a diameter of about 9 millimeters, and is graduated into tenths of cubic centimeters above the mark (*F*).

11. Benzine (62° Baumé naphtha) or kerosene free from water should be used in making the determination.

12. *Method.*—The flask is filled with either of these liquids to the lower mark (*E*), and 64 grams of cement, cooled to the temperature of the liquid, is slowly introduced through the funnel (*B*), the stem of

which should be long enough to extend into the flask to the top of the bulb (*C*), taking care that the cement does not adhere to the sides of the flask, and that the funnel does not touch the liquid. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck; this reading, plus 20 cubic centimeters, is the volume displaced by 64 grams of the cement.

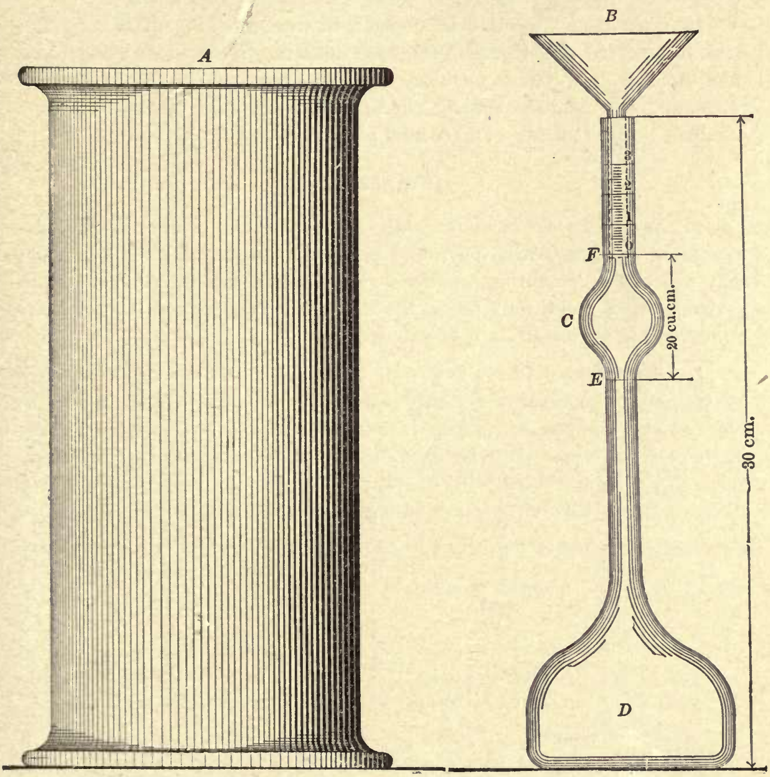

FIG. 62.—Le Chatelier's Specific Gravity Apparatus.

13. The specific gravity is then obtained from the formula,

$$\text{Specific gravity} = \frac{\text{Weight of cement, in grams,}}{\text{Displaced volume, in cubic centimeters.}}$$

14. The flask, during the operation, is kept immersed in water in a jar (*A*), in order to avoid variations in the temperature of the liquid in the flask, which should not exceed ½° C. The results of repeated tests should agree within 0.01. The determination of specific gravity

should be made on the cement as received; if it should fall below 3.10, a second determination should be made after igniting the sample in a covered dish, preferably of platinum, at a low red heat not exceeding 900° C. The sample should be heated for 5 minutes with a Bunsen burner (starting with a low flame and gradually increasing to its full height) and then heated for 15 minutes with a blast lamp; the ignition should preferably be made in a muffle.

15. The apparatus may be cleaned in the following manner: The flask is inverted and shaken vertically until the liquid flows freely, and then held in a vertical position until empty; any traces of cement remaining can be removed by pouring into the flask a small quantity of clean liquid benzine or kerosene and repeating the operation.

FINENESS.

16. *Significance.*—It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses cementing qualities. The more finely cement is pulverized, other conditions being the same, the more sand it will carry and produce a mortar of a given strength.

17. *Apparatus.*—The fineness of a sample of cement is determined by weighing the residue retained on certain sieves. Those known as No. 100 and No. 200, having approximately 100 and 200 wires per linear inch, respectively, should be used. They should be 8 inches in diameter. The frame should be of brass, 8 inches in diameter, and the sieve of brass wire cloth conforming to the following requirements:

No. of sieve	Diameter of wire, inches	Meshes, per linear inch	
		Warp	Woof
100	0.0042 to 0.0048	95 to 101	93 to 103
200	0.0021 to 0.0023	192 to 203	190 to 205

The meshes in any smaller space, down to 0.25 inch, should be proportional in number.

18. *Method.*—The test should be made with 50 grams of cement, dried at a temperature of 100° C (212° F.).

19. The cement is placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward about 200 times per minute, at the same time striking the side gently, on the up stroke, against the palm of the other hand. The operation is continued until not more than 0.05 gram will pass through in 1 minute. The residue is weighed, then placed

on the No. 100 sieve, and the operation repeated. The work may be expedited by placing in the sieve a few large steel shot, which should be removed before the final 1 minute of sieving. The sieves should be thoroughly dry and clean.

NORMAL CONSISTENCY.

20. *Significance.*—The use of a proper percentage of water in making pastes[1] and mortars for the various tests is exceedingly important and affects vitally the results obtained.

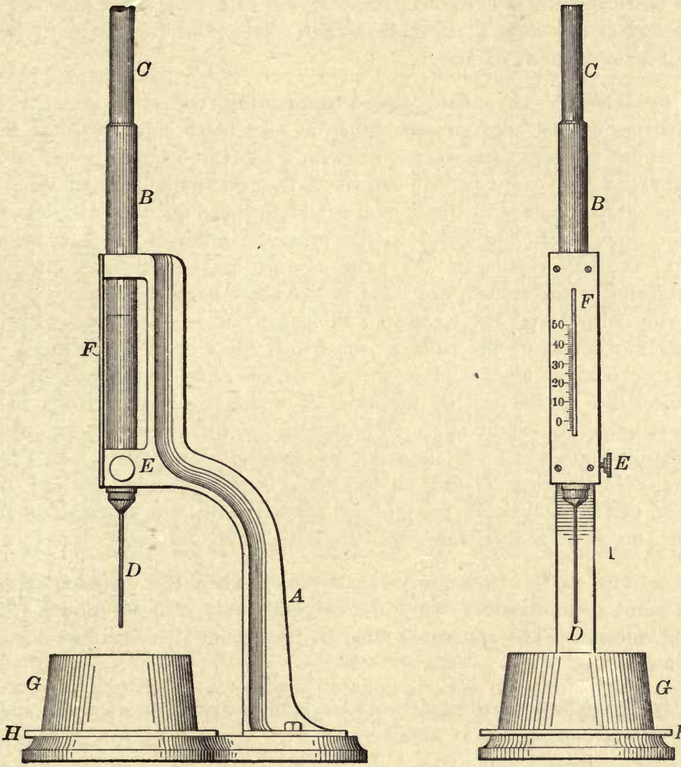

FIG. 63.—Vicat Apparatus.

21. The amount of water, expressed in percentage by weight of the dry cement, required to produce a paste of plasticity desired, termed

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[1] The term "paste" is used in this report to designate a mixture of cement and water and the word "mortar" to designate a mixture of cement, sand and water.

"normal consistency," should be determined with the Vicat apparatus in the following manner:

22. *Apparatus.*—This consists of a frame (*A*), Fig. 63, bearing a movable rod (*B*), weighing 300 grams, one end (*C*) being 1 centimeter in diameter for a distance of 6 centimeters, the other having a removable needle (*D*), 1 millimeter in diameter, 6 millimeters long. The rod is reversible, and can be held in any desired position by a screw (*E*), and has midway between the ends a mark (*F*) which moves under a scale (graduated to millimeters) attached to the frame (*A*). The paste is held in a conical, hard-rubber ring (*G*), 7 centimeters in diameter at the base, 4 centimeters high, resting on a glass plate (*H*) about 10 centimeters square.

23. *Method.*—In making the determination, the same quantity of cement as will be used subsequently for each batch in making the test pieces, but not less than 500 grams, with a measured quantity of water, is kneaded into a paste, as described in paragraph 45, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 inches apart; the ball resting in the palm of one hand is pressed into the larger end of the rubber ring held in the other hand, completely filling the ring with paste; the excess at the larger end is then removed by a single movement of the palm of the hand; the ring is then placed on its larger end on a glass plate and the excess paste at the smaller end is sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations care must be taken not to compress the paste. The paste confined in the ring, resting on the plate, is placed under the rod, the larger end of which is brought in contact with the surface of the paste; the scale is then read, and the rod quickly released.

24. The paste is of normal consistency when the cylinder settles to a point 10 millimeters below the original surface in ½ minute after being released. The apparatus must be free from all vibrations during the test.

25. Trial pastes are made with varying percentages of water until the normal consistency is obtained.

26. Having determined the percentage of water required to produce a paste of normal consistency, the percentage required for a mortar containing, by weight, 1 part of cement to 3 parts of standard Ottawa sand, is obtained from the following table, the amount being a percentage of the combined weight of the cement and sand.

PERCENTAGE OF WATER FOR STANDARD MORTARS.

Neat	One cement, three standard Ottawa sand	Neat	One cement, three standard Ottawa sand	Neat	One cement, three standard Ottawa sand
15	8.0	23	9.3	31	10.7
16	8.2	24	9.5	32	10.8
17	8.3	25	9.7	33	11.0
18	8.5	26	9.8	34	11.2
19	8.7	27	10.0	35	11.3
20	8.8	28	10.2	36	11.5
21	9.0	29	10.3	37	11.7
22	9.2	30	10.5	38	11.8

TIME OF SETTING.

27. *Significance.*—The object of this test is to determine the time which elapses from the moment water is added until the paste ceases to be plastic (called the "initial set"), and also the time until it acquires a certain degree of hardness (called the "final set" or "hard set"). The former is the more important, since, with the commencement of setting, the process of crystallization begins. As a disturbance of this process may produce a loss of strength, it is desirable to complete the operation of mixing or molding or incorporating the mortar into the work before the cement begins to set.

28. *Apparatus.*—The initial and final set should be determined with the Vicat apparatus described in paragraph 22.

29. *Method.*—A paste of normal consistency is molded in the hard rubber ring, as described in paragraph 23, and placed under the rod (*B*), the smaller end of which is then carefully brought in contact with the surface of the paste, and the rod quickly released.

30. The initial set is said to have occurred when the needle ceases to pass a point 5 millimeters above the glass plate; and the final set, when the needle does not sink visibly into the paste.

31. The test pieces should be kept in moist air during the test; this may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth; the cloth to be kept from contact with them by means of a wire screen; or they may be stored in a moist box or closet.

32. Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point may increase the penetration.

33. The time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the paste receives, but by the temperature and humidity of the air, and its determination is, therefore, only approximate.

STANDARD SAND.

34. The sand to be used should be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve, and retained on a No. 30 sieve. The sieves should be at least 8 inches in diameter; the wire cloth should be of brass wire and should conform to the following requirements:

No. of sieve	Diameter of wire, inches	Meshes, per linear inch	
		Warp	Woof
20	0.016 to 0.017	19.5 to 20.5	19 to 21
30	0.011 to 0.012	29.5 to 30.5	28.5 to 31.5

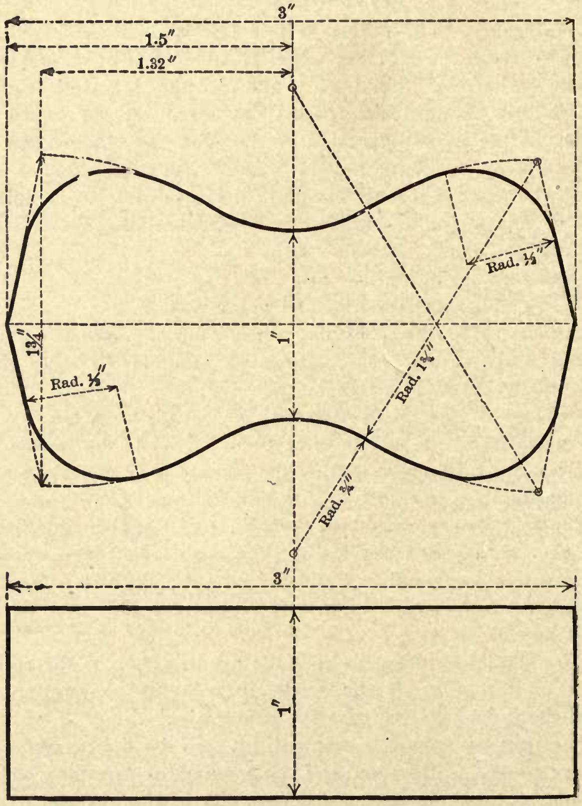

FIG. 64.—Details for Briquet.

Sand which has passed the No. 20 sieve is standard when not more than 5 grams passes the No. 30 sieve in 1 minute of continuous sifting of a 500-gram sample.[1]

FORM OF TEST PIECES.

35. For tensile tests the form of test piece shown in Fig. 55 should be used.

36. For compressive tests, 2-inch cubes should be used.

MOLDS.

37. The molds should be of brass, bronze, or other non-corrodible material, and should have sufficient metal in the sides to prevent spreading during molding.

38. Molds may be either single or gang molds. The latter are preferred by many. If used, the types shown in Figs. 65 and 66 are recommended.

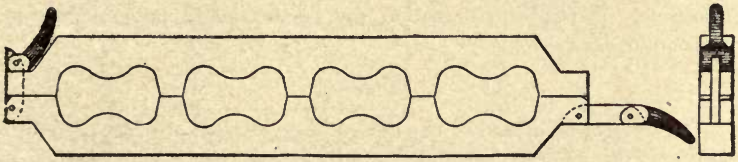

FIG. 65.—Details for Gang Mold.

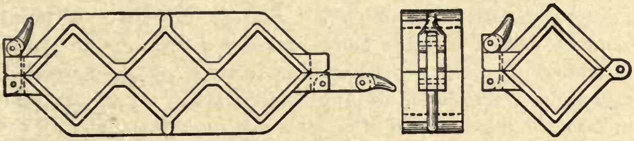

FIG. 66.—Mold for Compression Test Pieces.

39. The molds should be wiped with an oily cloth before using.

MIXING.

40. The proportions of sand and cement should be stated by weight; the quantity of water should be stated as a percentage by weight of the dry material.

41. The metric system is recommended because of the convenient relation of the gram and the cubic centimeter.

42. The temperature of the room and of the mixing water should be maintained as nearly as practicable at 21° C. (70° F.).

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[1] This sand may now (1912) be obtained from the Ottawa Silica Co., at a cost of two cents per pound, f. o. b. cars, Ottawa, Ill.

43. The quantity of material to be mixed at one time depends on the number of test pieces to be made; 1,000 grams is a convenient quantity to mix by hand methods.

44. The Committee has investigated the various mechanical mixing machines thus far devised, but cannot recommend any of them, for the following reasons: (1) the tendency of most cement is to "ball up" in the machine, thereby preventing working it into a homogeneous paste; (2) there are no means of ascertaining when the mixing is complete without stopping the machine; and (3) it is difficult to keep the machine clean.

45. *Method.*—The material is weighed, placed on a non-absorbent surface (preferably plate glass), thoroughly mixed dry if sand be used, and a crater formed in the center, into which the proper percentage of clean water is poured; the material on the outer edge is turned into the center by the aid of a trowel. As soon as the water has been absorbed, which should not require more than 1 minute, the operation is completed by vigorously kneading with the hands for 1 minute. During the operation the hands should be protected by rubber gloves.

MOLDING.

46. The Committee has not been able to secure satisfactory results with existing molding machines; the operation of machine molding is very slow; and is not practicable with pastes or mortars containing as large percentages of water as herein recommended.

47. *Method.*—Immediately after mixing, the paste or mortar is placed in the molds with the hands, pressed in firmly with the fingers, and smoothed off with a trowel without ramming. The material should be heaped above the mold, and, in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the material. The mold should then be turned over and the operation of heaping and smoothing off repeated.

48. A check on the uniformity of mixing and molding may be afforded by weighing the test pieces on removal from the moist closet; test pieces from any sample which vary in weight more than 3 per cent. from the average should not be considered.

STORAGE OF THE TEST PIECES.

49. During the first 24 hours after molding, the test pieces should be kept in moist air to prevent drying.

50. Two methods are in common use to prevent drying: (1) covering the test pieces with a damp cloth, and (2) placing them in a moist closet. The use of the damp cloth, as usually carried out, is objectionable, because the cloth may dry out unequally and in conse-

quence the test pieces will not all be subjected to the same degree of moisture. This defect may be remedied to some extent by immersing the edges of the cloth in water; contact between the cloth and the test pieces should be prevented by means of a wire screen, or some similar arrangement. A moist closet is so much more effective in securing uniformly moist air, and is so easily devised and so inexpensive, that the use of the damp cloth should be abandoned.

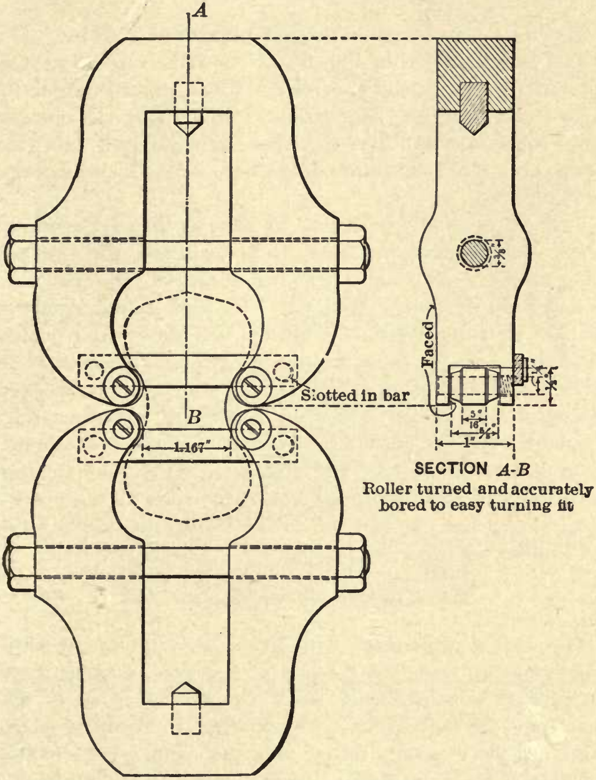

FIG. 67.—Form of Clip.

51. A moist closet consists of a soapstone or slate box, or a wooden box lined with metal, the interior surface being covered with felt or broad wicking kept wet, the bottom of the box being kept covered with water. The interior of the box is provided with glass shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

52. After 24 hours in moist air, the pieces to be tested after longer periods should be immersed in water in storage tanks or pans made of non-corrodible material.

53. The air and water in the moist closet and the water in the storage tanks should be maintained as nearly as practicable at 21° C. (70° F.).

TENSILE STRENGTH.

54. The tests may be made with any standard machine.

55. The clip is shown in Fig. 67. It must be made accurately, the pins and rollers turned, and the rollers bored slightly larger than the pins so as to turn easily. There should be a slight clearance at each end of the roller, and the pins should be kept properly lubricated and free from grit. The clips should be used without cushioning at the points of contact.

56. Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the test pieces in the testing machine, as cross strains, produced by imperfect centering, tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often causes the test pieces to break before the ultimate strength is reached. The bearing surfaces of the clips and test pieces must be kept free from grains of sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 pounds per minute. The average of the results of the test pieces from each sample should be taken as the test of the sample. Test pieces which do not break within ¼ inch of the center, or are otherwise manifestly faulty, should be excluded in determining average results.

COMPRESSIVE STRENGTH.

57. The tests may be made with any machine provided with means for so applying the load that the line of pressure is along the axis of the test piece. A ball-bearing block for this purpose is shown in Fig. 68. Some appliance should be provided to facilitate placing the axis of the test piece exactly in line with the center of the ball-bearing.

58. The test piece should be placed in the testing machine, with a piece of heavy blotting paper on each of the crushing faces, which should be those that were in contact with the mold.

CONSTANCY OF VOLUME.

59. *Significance.*—The object is to detect those qualities which tend to destroy the strength and durability of a cement. Under normal conditions these defects will in some cases develop quickly, and in

other cases may not develop for a considerable time. Since the detection of these destructive qualities before using the cement in construction is essential, tests are made not only under normal conditions but under artificial conditions created to hasten the development of these defects. Tests may, therefore, be divided into two classes: (1) Normal tests, made in either air or water maintained, as nearly as practicable, at 21° C. (70° F.); and (2) Accelerated tests, made in air, steam or water, at temperature of 45° C. (113° F.) and upward. The Committee recommends that these tests be made in the following manner:

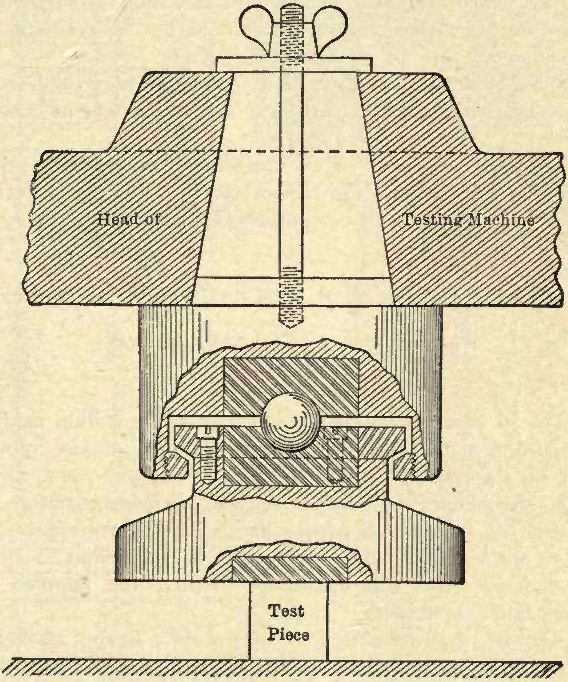

FIG. 68.—Ball-bearing Block for Testing Machine.

60. *Methods.*—Pats, about 3 inches in diameter, ½ inch thick at the center, and tapering to a thin edge, should be made on clean glass plates (about 4 inches square) from cement paste of normal consistency, and stored in a moist closet for 24 hours.

61. *Normal Tests.*—After 24 hours in the moist closet, a pat is immersed in water for 28 days and observed at intervals. A similar

pat, after 24 hours in the moist closet, is exposed to the air for 28 days or more and observed at intervals.

62. *Accelerated Test.*—After 24 hours in the moist closet, a pat is placed in an atmosphere of steam, upon a wire screen 1 inch above boiling water, for 5 hours. The apparatus should be so constructed that the steam will escape freely and atmospheric pressure be maintained. Since the type of apparatus used has a great influence on the results, the arrangement shown in Fig. 69 is recommended.

63. Pats which remain firm and hard and show no signs of cracking distortion, or disintegration are said to be "of constant volume" or "sound."

64. Should the pat leave the plate, distortion may be detected best with a straight-edge applied to the surface which was in contact with the plate.

65. In the present state of our knowledge it cannot be said that a cement which fails to pass the accelerated test will prove defective in the work; nor can a cement be considered entirely safe simply because it has passed these tests.

METHODS FOR TESTING CEMENT.[1]

Condensed for Use in Specifications.

1. Sampling.

Cement in barrels shall be sampled through a hole made in the head, or in one of the staves midway between the heads, by means of an auger or a sampling iron similar to that used by sugar inspectors; if in bags, the sample shall be taken from surface to center. Cement in bins shall be sampled in such a manner as to represent fairly the contents of the bin. The number of samples taken shall be as directed by the engineer, who will determine whether the samples shall be tested separately or mixed.

The samples shall be passed through a sieve having twenty meshes per linear inch, in order to break up lumps and remove foreign material.

2. Chemical Analysis.

The methods to be followed, except for determining the loss on ignition, should be those proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, reported in the *Journal of the Society for Chemical Industry,* Vol. 21, p. 12, 1902, and published in *Engineering News,* Vol. 50, p. 60, 1903, and in *Engineering Record,* Vol. 48, p. 49, 1903, and in addition thereto the following:

[1] Accompanying Final Report of Special Committee on Uniform Tests of Cement of the American Society of Civil Engineers, dated January 17, 1912.

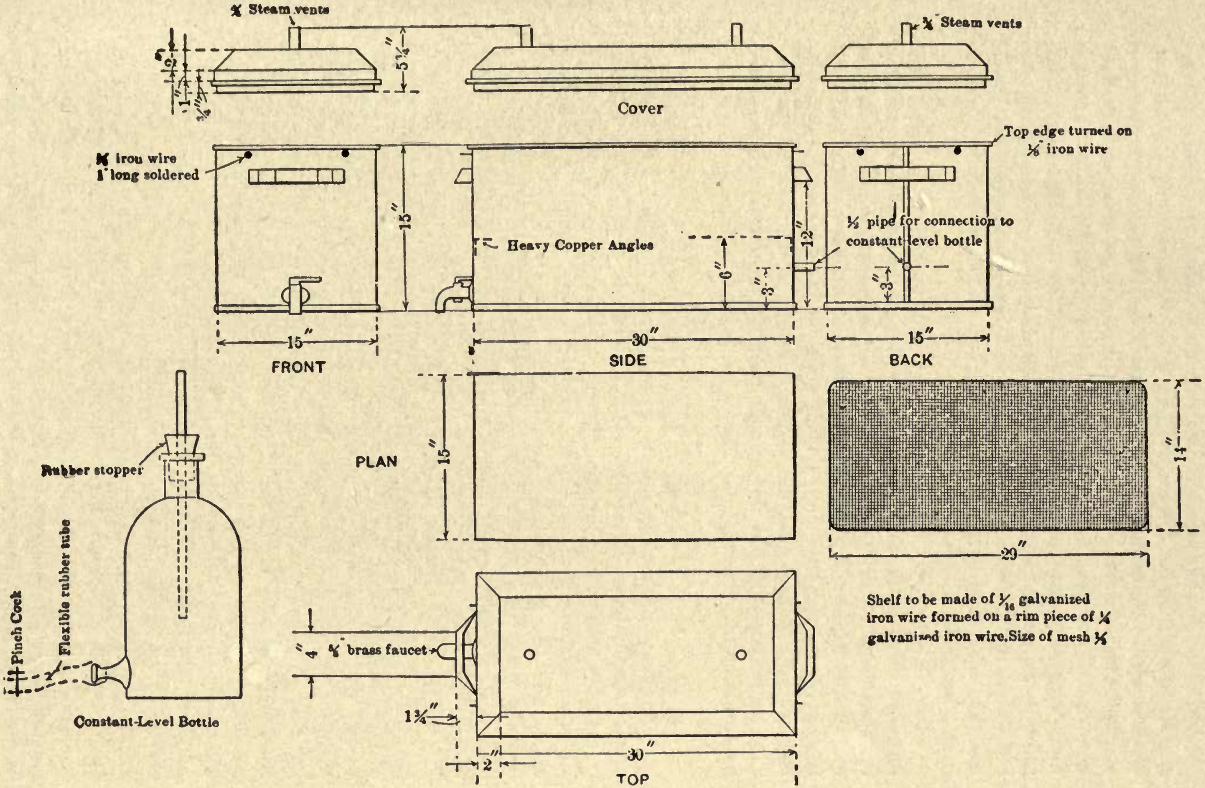

FIG. 69.—Apparatus for Making Accelerated Test for Soundness of Cement.

To be made of sheet copper weighing 22 oz. per sq. ft., tinned inside. All seams to be lapped where possible. Hard solder only to be used.

(*a*) The insoluble residue may be determined as follows: To a 1-gram sample of the cement are added 30 cubic centimeters of water and 10 cubic centimeters of concentrated hydrochloric acid, and then warmed until effervescence ceases, and digested on a steam bath until dissolved. The residue is filtered, washed with hot water, and the filter paper and contents digested on the steam bath in a 5 per cent. solution of sodium carbonate. This residue is filtered, washed with hot water, then with hot hydrochloric acid, and finally with hot water, and then ignited at a red heat and weighed. The quantity so obtained is the insoluble residue.

(*b*) The loss on ignition shall be determined in the following manner: One-half gram of cement is heated in a weighed platinum crucible, with cover, for 5 minutes with a Bunsen burner (starting with a low flame and gradually increasing to its full height) and then heated for 15 minutes with a blast lamp; the difference between the weight after cooling and the original weight is the loss on ignition. The temperature should not exceed 900° C., or a low red heat; the ignition should preferably be made in a muffle.

3. SPECIFIC GRAVITY.

The determination of specific gravity shall be made with a standardized Le Chatelier apparatus. This consists of a flask (*D*), Fig. 62, p. 251, of about 120 cubic centimeters capacity, the neck of which is about 20 centimeters long; in the middle of this neck is a bulb (*C*), above and below which are two marks (*F*) and (*E*); the volume between these two marks is 20 cubic centimeters. The neck has a diameter of 9 millimeters, and is graduated into tenths of cubic centimeters above the mark (*F*).

Benzene (62° Baumé naphtha) or kerosene free from water shall be used in making the determination. The flask is filled with either of these liquids to the lower mark (*E*) and 64 grams of cement, cooled to the temperature of the liquid, is slowly introduced through the funnel (*B*), the stem of which should be long enough to extend into the flask to the top of the bulb (*C*), taking care that the cement does not adhere to the sides of the flask, and that the funnel does not touch the liquid. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck; this reading, plus 20 cubic centimeters, is the volume displaced by 64 grams of the cement. The specific gravity is obtained from the formula,

$$\text{Specific gravity} = \frac{\text{Weight of cement, in grams}}{\text{Displaced volume, in cubic centimeters.}}$$

The flask, during the operation, is kept immersed in water in a jar (*A*) in order to avoid variations in the temperature of the liquid in the flask, which shall not exceed ½° C. The results of repeated tests shall agree within 0.01. The determination of specific gravity shall be made on the cement as received; if it should fall below 3.10, a second determination shall be made after igniting the sample in a covered dish, preferably of platinum, at a low red heat not exceeding 900° C. The sample shall be heated for 5 minutes with a Bunsen burner (starting with a low flame and gradually increasing to its full height) and then heated for 15 minutes with a blast lamp; the ignition should preferably be made in a muffle.

4. FINENESS.

The fineness shall be determined by weighing the residue retained on No. 100 and No. 200 sieves. The sieves, 8 inches in diameter, shall be of brass wire cloth conforming to the following requirements:

No. of sieve	Diameter of wire, inches	Meshes, per linear inch	
		Warp	Woof
100	0.0042 to 0.0048	95 to 101	93 to 103
200	0.0021 to 0.0023	192 to 203	190 to 205

The meshes in any smaller space, down to 0.25 inch, shall be proportional in number.

Fifty grams of cement, dried at a temperature of 100° C. (212° F.), shall be placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward about 200 times per minute, at the same time striking the side gently, on the up stroke, against the palm of the other hand. The operation is continued until not more than 0.05 gram will pass through in 1 minute. The residue is weighed, then placed on the No. 100 sieve, and the operation repeated. The work may be expedited by placing in the sieve a few large steel shot, which should be removed before the final 1 minute of sieving. The sieves should be thoroughly dry and clean.

5. NORMAL CONSISTENCY.

The amount of water, expressed in percentage by weight of the dry cement, required to produce a paste[1] of the plasticity desired, termed "normal consistency," shall be determined with the Vicat apparatus:

[1] The term "paste" is used in these specifications to designate a mixture of cement and water, and the word "mortar" to designate a mixture of cement, sand and water.

This consists of a frame (*A*), Fig. 63, p. 253, bearing a movable rod (*B*), weighing 300 grams, one end (*C*) being 1 centimeter in diameter for a distance of 6 centimeters, the other having a removable needle (*D*), 1 millimeter in diameter, 6 centimeters long. The rod is reversible, and can be held in any desired position by a screw (*E*), and has midway between the ends a mark (*F*) which moves under a scale (graduated to millimeters) attached to the frame (*A*). The paste is held in a conical, hard-rubber ring (*G*), 7 centimeters in diameter at the base, 4 centimeters high, resting on a glass plate (*H*) about 10 centimeters square.

In making the determination of normal consistency, the same quantity of cement as will be used subsequently for each batch in making the test pieces, but not less than 500 grams, together with a measured amount of water, is kneaded into a paste, as described in Section 9, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 inches apart; the ball resting in the palm of one hand is pressed into the larger end of the rubber ring held in the other hand, completely filling the ring with paste; the excess at the larger end is then removed by a single movement of the palm of the hand; the ring is then placed on its larger end on a glass plate and the excess paste at the smaller end is sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations care must be taken not to compress the paste. The paste confined in the ring, resting on the plate, is placed under the rod, the larger end of which is carefully brought in contact with the surface of the paste; the scale is then read, and the rod quickly released.

The paste is of normal consistency when the cylinder settles to a point 10 millimeters below the original surface in ½ minute after being released. The apparatus must be free from all vibrations during the test.

Trial pastes are made with varying percentages of water until the normal consistency is attained.

Having determined the percentage of water required to produce a paste of normal consistency, the percentage required for a mortar containing, by weight, 1 part of cement to 3 parts of standard Ottawa sand, shall be obtained from the following table, the amount being a percentage of the combined weight of the cement and sand.

PERCENTAGE OF WATER FOR STANDARD MORTARS.

Neat	One cement, three standard Ottawa sand	Neat	One cement, three standard Ottawa sand	Neat	One cement, three standard Ottawa sand
15	8.0	23	9.3	31	10.7
16	8.2	24	9.5	32	10.8
17	8.3	25	9.7	33	11.0
18	8.5	26	9.8	34	11.2
19	8.7	27	10.0	35	11.3
20	8.8	28	10.2	36	11.5
21	9.0	29	10.3	37	11.7
22	9.2	30	10.5	38	11.8

6. TIME OF SETTING.

The time of setting shall be determined with the Vicat apparatus in the following manner:

A paste of normal consistency is molded in the hard-rubber ring, as described in Section 5, and placed under the rod (*B*), the smaller end of which is then carefully brought in contact with the surface of the paste, and the rod quickly released.

The cement is considered to have acquired its initial set when the needle ceases to pass a point 5 millimeters above the glass plate; and the final set, when the needle does not sink visibly into the paste.

The test pieces must be kept in moist air during the test.

7. STANDARD SAND.

The sand shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve, and retained on a No. 30 sieve.

The sieves shall be at least 8 inches in diameter, and the wire cloth shall be of brass wire and shall conform to the following requirements:

No. of sieve	Diameter of wire, inches	Meshes, per linear inch	
		Warp	Woof
20	0.016 to 0.017	19.5 to 20.5	19 to 21
30	0.011 to 0.012	29.5 to 30.5	28.5 to 31.5

Sand which has passed the No. 20 sieve is standard when not more than 5 grams pass the No. 30 sieve in 1 minute of continuous sifting of a 500-gram sample.[1]

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[1] This sand may now (1912) be obtained from the Ottawa Silica Co., at a cost of two cents per pound, f. o. b. cars, Ottawa, Ill.

8. FORM OF TEST PIECES.

For tensile tests, the form of test pieces shown in Fig. 64, p. 256, shall be used.

For compressive tests, 2-inch cubes shall be used.

9. MIXING AND MOLDING.

The material shall be weighed, placed on a non-absorbent surface, thoroughly mixed dry if sand be used, and a crater formed in the center, into which the proper percentage of clean water shall be poured; the material on the outer edge shall be turned into the center by the aid of a trowel. As soon as the water has been absorbed, the operation of mixing shall be completed by vigorously kneading with the hands for 1 minute.

Immediately after mixing, the paste or mortar shall be placed in the mold (Figs. 65 and 66, p. 257) with the hands, pressed in firmly with the fingers, and smoothed off with a trowel without ramming. The material shall be heaped above the mold, and, in smoothing off, the trowel shall be drawn over the mold in such a manner as to exert a moderate pressure on the material; the mold shall then be turned over and the operation of heaping and smoothing off repeated.

The temperature of the room and of the mixing water shall be maintained as nearly as practicable at 21° C. (70° F.).

10. STORAGE OF THE TEST PIECES.

During the first 24 hours after molding, the test pieces shall be stored in a moist closet. This consists of a box of soapstone or slate, or of wood lined with metal, the interior surface being covered with felt or broad wicking kept wet, the bottom of the box being kept covered with water. The interior of the box is provided with glass shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

Test pieces from any sample which vary more than 3 per cent. in weight from the average, after removal from the moist closet, shall not be considered in determining strength.

After 24 hours in the moist closet, the pieces to be tested after longer periods shall be immersed in water in storage tanks or pans made of non-corrodible material.

The air and water in the moist closet and the water in the storage tanks shall be maintained, as nearly as practicable, at 21° C. (70° F.).

11. TESTS OF TENSILE STRENGTH.

The tests may be made with any standard machine.

The clip is shown in Fig. 67, p. 259. It must be made accurately, the pins and rollers turned, and the rollers bored slightly larger than the pins so as to turn easily. There should be a slight clearance at each end of the roller, and the pins should be kept properly lubricated and free from grit. The clips shall be used without cushioning at the points of contact.

The test pieces shall be broken as soon as they are removed from the water. The load shall be applied at the rate of 600 pounds per minute.

Test pieces which do not break within ¼ inch of the center, or are otherwise manifestly faulty, shall be excluded in determining average results.

12. TESTS OF COMPRESSIVE STRENGTH.

The tests may be made with any machine provided with means for so applying the load that the line of pressure is along the axis of the test piece. A ball-bearing block for this purpose is shown in Fig. 68, p. 261.

The test pieces as soon as they are removed from the water shall be placed in the testing machine, with a piece of heavy blotting paper on each of the crushing faces, which should be those that were in contact with the mold.

13. CONSTANCY OF VOLUME.

Tests for constancy of volume comprise "normal tests" which are made in air or water, maintained as nearly as practicable, at 21° C. (70° F.), and the "accelerated test," which is made in steam. These tests shall be made in the following manner:

Pats about 3 inches in diameter, ½ inch thick at the center, and tapering to a thin edge, shall be made on clean glass plates (about 4 inches square) from cement paste of normal consistency, and stored in a moist closet for 24 hours.

Normal Tests.—After 24 hours in the moist closet, a pat is immersed in water and observed at intervals. A similar pat, after 24 hours in the moist closet, is exposed to the air for 28 days or more and observed at intervals. The air and water are maintained, as nearly as practicable, at 21° C. (70° F.).

Accelerated Test.—After 24 hours in the moist closet, a pat is placed in an atmosphere of steam, upon a wire screen 1 inch above boiling water, for 5 hours, the apparatus being such that the steam will escape freely and atmospheric pressure be maintained. The apparatus is shown in Fig. 69, p. 263.

The cement passes these tests when the pats remain firm and hard, with no signs of cracking, distortion, or disintegration.

APPENDIX.

METHODS FOR THE CHEMICAL ANALYSIS OF LIMESTONES, RAW MIXTURES AND PORTLAND CEMENTS.

Recommended by the Committee on Uniformity in Technical Analysis of the New York Section of the Society for Chemical Industry.

Solution.—One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for 15 minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cubic centimeters of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.[1] The solution is then evaporated to dryness, as far as this may be possible on the bath.

Silica (*SiO_2*).—The residue without further heating is treated at first with 5 to 10 cubic centimeters of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum, crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 15 minutes and checked by a further blasting for 10 minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cubic centimeters of HFl and four drops of H_2SO_4 and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.[2]

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[1] If anything remains undecomposed it should be separated, fused with a little Na_2CO_2, dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

[2] For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

Alumina and Iron (*Al_2O_3 and Fe_2O_3*).—The filtrate, about 250 cubic centimeters, from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 cubic centimeters strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitate iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted 5 minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3 + Fe_2O_3$.[1]

Iron (*Fe_2O_3*).—The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed and corrected by HFl and H_2SO_4.[2] The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing CO_2 through the flask, and titrated with permanganate.[3] The strength of the permanganate solution should not be greater than 0.0040 gram Fe_2O_3 per cubic centimeter.

Lime (*CaO*).—To the combined filtrate from the $Al_2O_3 + Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cubic centimeters of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for 20 minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 cubic centimeters with water.

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[1] This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

[2] This correction of Al_2O_3 Fe_2O_3 for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 mg. of SiO are still to be found with the Al_2O_3 Fe_2O_3.

[3] In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al_2O_3 separates this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered and washed,[1] weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.[2]

Magnesia (*MgO*).—The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 cubic centimeters, 10 cubic centimeters of saturated solution of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium orthophosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 cubic centimeters, 1 cubic centimeter of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about 2 hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$.

Alkalies (K_2O *and* Na_2O).—For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of $CaCO_3$ with NH_4Cl.

Anhydrous Sulphuric Acid (SO_3).—One gram of the substance is dissolved in 15 cubic centimeters of HCl, filtered and residue washed thoroughly.[3]

The solution is made up to 250 cubic centimeters in a beaker and boiled. To the boiling solution 10 cubic centimeters of a saturated solution of $BaCl_2$ is added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as $BaSO_4$.

Total Sulphur.—One gram of the material is weighed out in a large platinum crucible and fused with Na_2CO_3 and a little KNO_3, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in

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[1] The volume of wash-water should not be too large; *vide* Hillebrand.

[2] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

[3] Evaporation to dryness is unnecessary, unless gelatinous silica should have separated and should never be performed on a bath heated by gas; *vide* Hillebrand.

an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with HCl and made up to 250 cubic centimeters with distilled water, boiled, the sulphur precipitated as $BaSO_4$ and allowed to stand over night or for a few hours.

Loss on Ignition.—Half a gram of cement is to be weighed out in a platinum crucible, placed in a hole in an asbestos board so that about three-fifths of the crucible projects below, and blasted 15 minutes, preferably with an inclined flame. The loss by weight, which is checked by a second blasting of 5 minutes, is the loss on ignition.

May, 1903: Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should, therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

STEEL.

METHODS OF CHEMICAL ANALYSIS FOR PLAIN CARBON STEEL, AS PUBLISHED BY THE AMERICAN SOCIETY FOR TESTING MATERIAL.

ADOPTED, 1914.

DETERMINATION OF CARBON BY THE DIRECT-COMBUSTION METHOD.

The method of direct combustion of the metal in oxygen is recommended, the carbon dioxide obtained being absorbed in barium-hydroxide solution, the precipitated barium carbonate filtered off, washed, dissolved in a measured excess of hydrochloric acid and the excess titrated against standard alkali.

The use of potassium-hydroxide solution or soda lime for the absorption of carbon dioxide, with suitable purifying train following the furnace, is recognized as being capable of very satisfactory refinement and as possessing merit where the time element is of prime significance.

Owing to the diversity of apparatus by which correct results may be obtained in the determination of carbon, the recommendations are intended more to indicate what is acceptable than to prescribe definitely what shall be used.

Apparatus.

Purifying Train.—The method employed eliminates the necessity of a purifying train following the furnace, inasmuch as no precautions are necessary to prevent access of water vapor, or sulphur trioxide—the impurities usually guarded against—from the absorbing apparatus. All that is needed is a calcium-chloride tower filled with stick sodium hydroxide placed before the furnace, or between the furnace and catalyzer, if, as recommended, the latter is used for the purpose of oxidizing organic matter in the oxygen.

Material for Lining Boats.—Alundum, "RR Alundum, alkali-free, specially prepared for carbon determination," as supplied by dealers is suitable, and is recommended. The 90-mesh or finer grades are used. Chromite, properly sized and freed from materials causing a blank, may also be employed. No substance containing alkali or alkaline earth metals, or carbon as carbonates or in other form, should be used as a lining material. Quartz sand, owing to its liability to fuse or to slag with the oxides of iron, causing bubbles of gas to be enclosed, is objectionable. Aluminum oxide, made by calcining alum or otherwise, often contains sulphate not easily destroyed, or may contain objectionable substances of an alkaline nature.

Catalyzers.—Suitable catalyzers are copper oxide, platinized quartz or asbestos, or platinum gauze. One of these should be used in the forward part of the combustion apparatus, as well as in the purifying train preceding the combustion tube (see above). Platinized materials sometimes give off volatile substances on heating, and whatever material is used should not be subject to this defect.

Combustion Apparatus.—Any apparatus heated by gas or electricity which will bring the sample to a temperature of 950 to 1,100° C. may be used. Combustion tubes may be porcelain, glazed on one or both sides, quartz or platinum. Quartz is liable to devitrification when used continuously at temperatures above 1,000° C., and may then become porous. Combustion crucibles of platinum may be heated by blast or by Meker burners.

Boats or Other Containers of Samples being Burned.—These may be of porcelain, quartz, alundum, clay, platinum, or nickel, and should always receive a lining of granular alundum.

Purifying Train before Combustion Apparatus.—This consists of a tower filled with stick sodium hydroxide, preceded by a catalyzer.

The Train after the Combustion Apparatus.—This consists merely of the Meyer tube for absorption of the carbon dioxide, protected by a soda-lime tube at the far end. Meyer tubes with 7 to 10 bulbs of 10 to 15 cubic centimeter capacity each, and large bulbs at the ends, having volumes equal to the combined capacity of the small bulbs, have been used and found satisfactory.

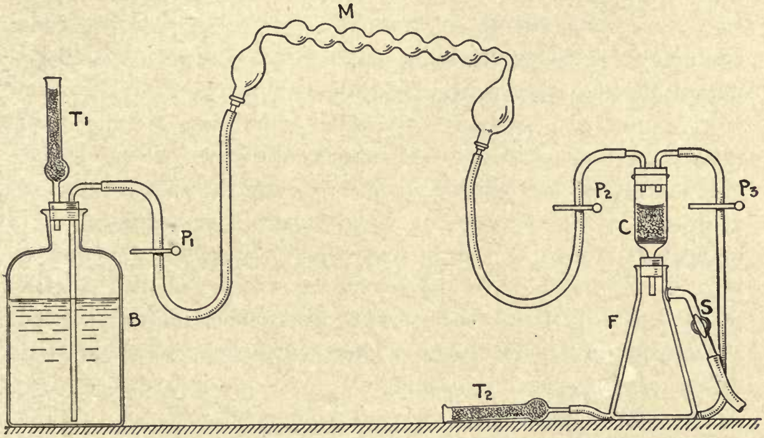

FIG. 70.—Apparatus for Filtration in Determination of Carbon by the Direct-Combustion Method.

Filtering Apparatus.—In filtration for accurate work, care should be taken to protect the solution from access of extraneous carbon dioxide. This is accomplished in the apparatus shown in Fig. 70. For work requiring less accuracy, the barium carbonate may be filtered off on a filter made by fitting a carbon funnel with a perforated porcelain disk and filtering by suction. The precipitate is then washed with distilled water from which the carbon dioxide has been removed by boiling.

Reagents.

Oxygen.—Oxygen of not less than 97 per cent. purity is recommended. Endeavor should be made to obtain oxygen which gives no blank, since the correction for or elimination of this is troublesome and uncertain. For the most accurate work, particularly with low-carbon products, such as ingot iron, etc., the blank should be completely eliminated by the use of a catalyzer before the furnace, with a carbon-dioxide absorbent interposed between furnace and catalyzer.

Tenth-normal Hydrochloric Acid.—This may be standardized by any of the accepted methods, or as follows: Twenty cubic centimeters of the approximately N/10 acid is measured out with a pipette, and the silver chloride precipitated by an excess of silver-nitrate solution in a volume of 50 to 60 cubic centimeters. After digesting at 70 to 80° C., until the supernatant liquid is clear, the chloride is filtered off on a tared Gooch filter and washed with water containing 2 cubic centimeters of nitric acid per 100 cubic centimeters of water until freed from silver nitrate. After drying to constant weight at 130° C., the increase of weight over the original tare is noted and from this weight, corresponding to the silver chloride, the strength of the hydrochloric acid is calculated, after which it is adjusted to the strength prescribed. The standardization should be based upon several concordant determinations using varying amounts of acid.

1 cc. N/10 HCl = 0.0006 g. carbon.

Methyl Orange.—Dissolve 0.02 gram in 100 cubic centimeters of hot distilled water and filter.

Tenth-normal Sodium-Hydroxide Solution.—This is standardized against the hydrochloric acid. Methyl orange is used as the indicator. The sodium-hydroxide solution should be stored in a large bottle from which it may be driven out by air pressure, protecting against carbon dioxide by soda-lime tubes.

Barium-Hydroxide Solution.—A saturated solution is filtered and stored in a large reservoir from which it is delivered by air pressure, protecting from carbon dioxide by a soda-lime tube. Three or four small bulbs of the Meyer tube are filled, and CO_2-free water is added until the remaining small bulbs are filled.

Factors Influencing Rapid Combustion.

Size of Particles of Sample.—The finer the chips the better, except with samples which burn too vigorously (see under "Rate of Admitting Oxygen"). Particles too coarse to pass a 20-mesh sieve are not recommended, nor long curly drillings which will not pack closely. A ½-inch flat drill may be used for taking the sample and the pressure and speed of the drill-press regulated to secure the desired result; or, better still, the sample may be obtained with a small milling machine suitable for sampling, or by a shaping machine. Oil, dust, and other foreign matter should be carefully excluded.

Manner of Distributing Sample in Boat.—This is of considerable importance. With all samples, close packing in a small space is conducive to rapid combustion. In the case of samples which burn too vigorously, a satisfactory regulation may sometimes be attained by spreading the sample loosely over the lining in the boat.

Rate of Admitting Oxygen.—The rate at which oxygen is admitted is also a factor in the velocity of combustion. Assuming the combustion apparatus to be heated to the temperature range recommended above (950 to 1,100° C.), it is possible, if the material is closely packed and if oxygen is admitted at too rapid a rate, that the combustion may be so violent as to cause excessive spattering of fused oxides, and such fluidity of the molten slag that the boat or other container may be injured or destroyed; therefore a moderate rate of burning is to be sought. This is desirable also from the standpoint of the complete absorption of the carbon dioxide by the barium-hydroxide solution. The factors, temperature of combustion apparatus, manner of distribution of sample, and rate of admission of oxygen, can be governed so as to burn successfully steels of a very wide range of compositions, in either fine or coarse particles.

Method.

After having properly set up and tested the apparatus, place 2 grams of steel (see note No. 1) in the form recommended above, in a moderately packed condition on the bed material and introduce the boat into the combustion apparatus, already heated to the proper temperature. After about a minute (to allow the sample and container to reach the temperature of the furnace), admit oxygen somewhat more rapidly than it is consumed, as shown by the rate of bubbling in the Meyer tube (see note No. 2). The sample burns completely in 1 or 2 minutes, and all that is now necessary is to sweep all the carbon dioxide into the absorption apparatus. This can be accomplished in 6 to 8 minutes by passing about 1 or 2 liters of oxygen. Detach the Meyer tube (see note No. 2) and filter and wash the barium carbonate, using the special filtering apparatus shown. After solution in a measured excess of hydrochloric acid (the Meyer tube being washed out with a portion of the acid, to remove adhering barium carbonate), titrate the excess of acid against alkali and from the data thus obtained calculate the percentage of carbon.

NOTES.

1. When working with steels high in carbon (above 1 per cent.) it is advisable not to use more than 1 gram in order that filtration may be sufficiently rapid.

2. As a precaution against error resulting from too rapid passage of the gases, it is well to attach a second barium-hydroxide tube to retain any carbon dioxide that may pass the first.

3. For the most accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished the tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4. The flask containing the carbonate should be thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

Apparatus and Procedure for. Filtration.

The apparatus is shown to approximately one-tenth size in Fig. 70, which is self-explanatory. The stop-cock is a three-way cock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of best-grade black rubber, and the lengths used should be so chosen as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon tube *C* is fitted with a perforated porcelain plate sliding easily.

The funnel is prepared for filtration by making on the porcelain disk a felt of asbestos about $^1/_{16}$ to $^1/_8$ inch in thickness, using amphibole (not serpentine) asbestos which has been carefully digested with strong hydrochloric acid for several hours and washed with water until it gives no acid reaction. On top of the asbestos pad is placed a layer of similarly treated quartz, mixed with asbestos, of the height shown. A mixture of quartz grains of various sizes (approximately 50 per cent. passing a 20-mesh sieve and 50 per cent. passing a 10-mesh and remaining on a 20-mesh sieve) is suitable. The mixture of quartz and asbestos may be obtained by filling the funnel from a beaker (directing against it a stream from a wash-bottle) while maintaining a gentle suction. In this way the asbestos is properly mixed with the quartz. A little experience and attention to these details will enable one to prepare the quartz-bed in a manner that will greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown and the liquid and precipitate sucked into the funnel. Only a gentle suction should be used. When necessary P_3 is opened to admit air back of the column of liquid in the Meyer tube. When the contents of the Meyer tube have been transferred, the large bulb nearest *B* is half filled with water by opening P_1; the stop-cock *S* is operated during this and subsequent operations so as to maintain a gentle suction all the time. *M* is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked through *C*; P_2 is left open during this and subsequent washings. After eight washings as directed, allowing the wash water to drain off thoroughly each time before adding more, *M* may be detached, the stopper removed from the funnel and the washings completed by filling *C* to the top with CO_2-free water, sucking off completely and repeating the operation once. With care the washing may be done with 150 cubic centimeters of water. Air is now admitted through the side opening of *S*, *C* is removed and the porcelain disk carrying the asbestos, quartz and barium carbonate is thrust, by means of a long glass rod, into a flask, removing any adhering particles from the sides of *C*, by a stream of water from a wash bottle. An excess of the standard acid is now added from a burette or pipette, using a portion to wash out *M*, and after the contents of the flask have been thoroughly agitated by shaking, the excess of acid is titrated against the standard alkali, using 3 drops of the methyl-orange indicator.

NOTES.

The operation of filtering can be carried out very rapidly after a little practice.

Glass wool should on no account be used as a substitute for the quartz, on account of the probability of errors arising from its attack by the alkali or acid.

It is well to wash out the rubber tubes connected to the Meyer tube with a little water each day before beginning work.

DETERMINATION OF CARBON BY THE COLORIMETRIC METHOD.

(*Routine.*)

Solution Required.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Method.

In a small Erlenmeyer flask or test tube, dissolve 0.2 to 0.5 gram of steel, depending on the carbon content of the sample, in 5 to 20 cubic centimeters of the nitric acid. Boil gently until the solution is complete and the liquid is clear. Cool and compare with a solution of a standard steel treated under like conditions.

NOTE.

In order to obtain reliable results by this method the standard steel should be of the same kind, of approximately the same chemical composition, and in the same physical condition as the sample steel. The carbon content of the standard steel is determined by the direct combustion method.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD.

Solutions Required.

Nitric Acid.—Mix 500 cubic centimeters of nitric acid, specific gravity 1.42, and 1,500 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 30 cubic centimeters of nitric acid, specific gravity 1.42, and 970 cubic centimeters of distilled water.

Stock Sodium Arsenite.—To 15 grams of arsenious acid (As_2O_3) in a 300 cubic centimeter Erlenmeyer flask, add 45 grams of sodium carbonate and 150 cubic centimeters of distilled water. Heat the flask and contents on a water bath until the arsenious acid is dissolved, cool the solution and make up to 1,000 cubic centimeters with distilled water.

Standard Sodium Arsenite.—Dilute 300 cubic centimeters of stock-sodium-arsenite solution to 1,000 cubic centimeters with distilled water and titrate against potassium permanganate solution (about N/10), which has been standardized by using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.10 per cent. of manganese, when a 1-gram sample is taken.

[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

The factor $Na_2C_2O_4 \rightarrow Mn = 0.16397$ (using the 1913 atomic weights).

Method.

In a 300 cubic centimeter Erlenmeyer flask dissolve 1 gram of steel in 50 cubic centimeters of the nitric acid, and boil to expel the oxides of nitrogen. Cool, and add about ½ gram of sodium bismuthate and heat for a few minutes, or until the pink color has disappeared, with or without precipitation of manganese dioxide. Add small portions of ferrous sulphate (or any suitable reducing agent) in sufficient quantity to clear the solution, and boil to expel the oxides of nitrogen. Cool to 15° C., add an excess of sodium bismuthate and agitate for a few minutes. Add 50 cubic centimeters of 3 per cent. nitric acid and filter through an alundum filter or asbestos pad, washing with 3 per cent. nitric acid. Titrate immediately with standard-sodium-arsenite solution to the disappearance of the pink color, each cubic centimeter required representing 0.10 per cent. manganese.

NOTES.

In the method, the preliminary treatment with sodium bismuthate has been found by a number of investigators to be apparently unnecessary; however, the available data to confirm this position are not considered sufficient to warrant its omission.

In making the asbestos filter pad it is advisable to have a thin bed, and as much surface as possible. This insures rapid filtration, and the filter may be used until it becomes clogged with bismuthate.

The filtrate must be perfectly clear, since the least particle of bismuthate carried through the filter will vitiate the results.

DETERMINATION OF MANGANESE BY THE PERSULPHATE METHOD.

(*Routine.*)

Solutions Required.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Silver Nitrate.—Dissolve 1.33 grams of silver nitrate in 1,000 cubic centimeters of distilled water.

Stock Sodium Arsenite.—To 15 grams of arsenious acid (As_2O_3) in a 300 cubic centimeter Erlenmeyer flask, add 45 grams of sodium carbonate and 150 cubic centimeters of distilled water. Heat the flask and contents on a water bath until the arsenious acid is dissolved, cool the solution and make up to 1,000 cubic centimeters with distilled water.

Standard Sodium Arsenite.—Dilute a sufficient quantity of stock-sodium-arsenite solution with distilled water, and standardize against a steel of known manganese content, as determined by the bismuthate method. This solution should be of such strength that each cubic centimeter will be equivalent to 0.10 per cent. of manganese on the basis of the weight of sample taken.

Method.

In a small Erlenmeyer flask or large test tube, dissolve 0.1 to 0.3 gram of steel, depending on the manganese content of the sample, in 15 cubic centimeters of the nitric acid. Boil gently until the solution is complete and the liquid is clear. Add 15 cubic centimeters silver nitrate solution and 1 gram of ammonium persulphate, and continue heating the solution for ½ minute after the oxidation begins and bubbles rise freely. Cool in running water and complete the determination by either of the following procedures:

(*a*) *Colorimetric.*—Compare the color of the solution with that of a standard steel treated under like conditions.

(*b*) *Titration.*—Titrate with standard-sodium-arsenite solution to the disappearance of the pink color, each cubic centimeter required representing 0.10 per cent. of manganese.

NOTES.

In order to obtain reliable results by the colorimetric procedure, the standard should be of the same kind and of approximately the same chemical composition as the sample steel. The manganese content of the standard steel is determined by the bismuthate method.

The ammonium persulphate should be kept in moistened condition by small additions of distilled water at required intervals.

DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE-MAGNESIA METHOD.

Solutions Required.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 20 cubic centimeters nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Ammonium Bisulphite.—Dissolve 30 grams of ammonium bisulphite in 1,000 cubic centimeters of distilled water.

Ammonium Hydroxide, approximately 10 per cent.—Mix 1,000 cubic centimeters of ammonium hydroxide, specific gravity 0.90, and 2,000 cubic centimeters of distilled water.

Ammonium Molybdate—Solution No. 1.—Place in a beaker 100 grams of 85 per cent. molybdic acid, mix it thoroughly with 240 cubic centimeters of distilled water, add 140 cubic centimeters of ammonium hydroxide, specific gravity 0.90, filter, and add 60 cubic centimeters of nitric acid, specific gravity 1.42.

Solution No. 2.—Mix 400 cubic centimeters of nitric acid, specific gravity 1.42, and 960 cubic centimeters of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cubic centimeters of distilled water, and let stand at least 24 hours before using.

Magnesia Mixture.—Dissolve 50 grams of magnesium chloride and 125 grams of ammonium chloride in 750 cubic centimeters of distilled water, and then add 150 cubic centimeters of ammonium hydroxide, specific gravity 0.90.

Method.

In a 300 cubic centimeter Erlenmeyer flask dissolve 5 grams of steel in 75 cubic centimeters of the nitric acid. Heat to boiling; while boiling add about 12 cubic centimeters of the potassium-permanganate solution, and continue boiling until manganese dioxide precipitates. Dissolve this precipitate by additions of the ammonium bisulphite solution, boil until clear and free from brown fumes, cool to 35° C., add 100 cubic centimeters of the ammonium-molybdate solution at room temperature, let stand 1 minute, shake or agitate for 3 minutes, filter on a 9-centimeter paper and wash the precipitate at least 3 times with the 2 per cent. nitric-acid solution to free it from iron.

Treat the precipitate on the filter with the 10 per cent. ammonium-hydroxide soluion, letting the solution run into a 100-cubic centimeter beaker containing 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 0.5 gram of citric acid; add 30 cubic centimeters of ammonium hydroxide, specific gravity 0.90, cool, and then add 10 cubic centimeters of the magnesia mixture very slowly, while stirring the solution vigorously. Set aside in a cool place for 2 hours, filter and wash with the 10 per cent. ammonium hydroxide solution. Ignite and weigh. Dissolve the precipitate of magnesium pyrophosphate with 5 cubic centimeters of nitric acid, specific gravity 1.20, and 20 cubic centimeters of distilled water, filter and wash with hot water. Ignite and weigh. The difference in weights represents pure magnesium pyrophosphate containing 27.84 per cent. of phosphorus.

NOTE.

The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD.

(Routine.)

Solutions Required.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 20 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Ammonium Bisulphite.—Dissolve 30 grams of ammonium bisulphite in 1,000 cubic centimeters of distilled water.

Ammonium Molybdate.—Solution No. 1.—Place in a beaker 100 grams of 85 per cent. molybdic acid, mix it thoroughly with 240 cubic centimeters of distilled water, add 140 cubic centimeters of ammonium hydroxide, specific gravity 0.90, filter and add 60 cubic centimeters of nitric acid, specific gravity 1.42.

Solution No. 2.—Mix 400 cubic centimeters of nitric acid, specific gravity 1.42, and 960 cubic centimeters of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cubic centimeters of distilled water and let stand at least 24 hours before using.

Potassium Nitrate, 1 per cent.—Dissolve 10 grams of potassium nitrate in 1,000 cubic centimeters of distilled water.

Phenolphthalein Indicator.—Dissolve 0.2 gram in 50 cubic centimeters of 95 per cent. ethyl alcohol and 50 cubic centimeters of distilled water.

Standard Sodium Hydroxide.—Dissolve 6.5 grams of purified sodium hydroxide in 1,000 cubic centimeters of distilled water, add a slight excess of 1 per cent. solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content, as determined by the molybdate magnesia method, so that 1 cubic centimeter will be equivalent to 0.01 per cent. of phosphorus on the basis of a 2-gram sample (see notes). Protect the solution from carbon dioxide with a soda lime tube.

Standard Nitric Acid.—Mix 10 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water. Titrate the solution against standardized sodium hydroxide, using phenolphthalein as indicator, and make it equivalent to the sodium hydroxide by adding distilled water.

Method.

In a 300 cubic centimeter Erlenmeyer flask dissolve 2 grams of steel in 50 cubic centimeters of the nitric acid. Heat the solution to boiling and while boiling add about 6 cubic centimeters of the potassium permanganate solution and continue boiling until manganese dioxide precipitates. Dissolve this precipitate by addition of the ammonium bisulphite solution, boil until clear and free from brown fumes, cool to 80° C., add 50 cubic centimeters of the ammonium molybdate solution at room temperature, let stand 1 minute, shake or agitate for 3 minutes, and filter on a 9 centimeter paper. Wash the precipitate three times with the 2 per cent. nitric acid solution to free it from iron, and continue the washing with the 1 per cent potassium nitrate solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cubic centimeters of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard sodium hydroxide solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of sodium hydroxide solution by titrating with standard nitric acid solution. Each cubic centimeter of standard sodium hydroxide solution represents 0.01 per cent. of phosphorus.

NOTES.

The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titration should be freed from carbon dioxide by boiling or otherwise.

Bureau of Standards Standard Steel No. 19(*a*) is recommended as a suitable steel for standardization of the sodium hydroxide solution.

DETERMINATION OF SULPHUR BY THE OXIDATION METHOD.

Solution Required.

Barium Chloride.—Dissolve 100 grams of barium chloride in 1,000 cubic centimeters of distilled water.

Method.

In a 400 cubic centimeter beaker dissolve 5 grams of the steel in a mixture of 40 cubic centimeters of nitric acid, specific gravity 1.42, and 5 cubic centimeters of hydrochloric acid, specific gravity 1.20, add 0.5 gram of sodium carbonate and evaporate the solution to dryness. Add 40 cubic centimeters of hydrochloric acid, specific gravity 1.20, evaporate to dryness and bake at a moderate heat. After solution of the residue in 30 cubic centimeters of hydrochloric acid, specific gravity 1.20, and evaporation to sirupy consistency, add 2 to 4 cubic centimeters of hydrochloric acid, specific gravity 1.20, and then 30 to 40 cubic centimeters of hot water. Filter and wash with cold water, the final volume not exceeding 100 cubic centimeters. To the cold filtrate add 10 cubic centimeters of the barium chloride solution. Let stand at least 24 hours, filter on a 9 centimeter paper, wash the precipitate first with a hot solution containing 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 1 gram barium chloride to the liter, until free from iron; and then with hot water till free from chloride. Ignite and weigh as barium sulphate.

Keep the washings separate from the main filtrate and evaporate them to recover any dissolved barium sulphate.

NOTE.

A blank determination on all reagents used should be made and the results corrected accordingly.

DETERMINATION OF SULPHUR BY THE EVOLUTION-TITRATION METHOD.

(Routine.)

Apparatus.

Use a 480 cubic centimeter flask with a delivery tube and a 300 cubic centimeter tumbler of tall form (Fig. 71).

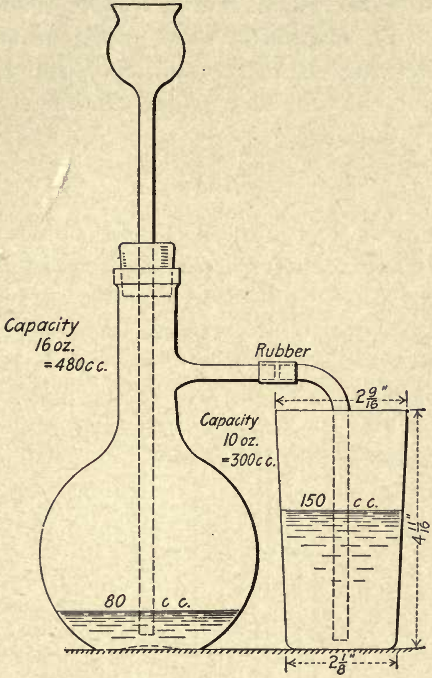

FIG. 71.—Apparatus for Determination of Sulphur by the Evolution Method.

Solutions Required.

Dilute Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 500 cubic centimeters of distilled water.

Ammoniacal Cadmium Chloride.—Dissolve 10 grams of cadmium chloride in 400 cubic centimeters of distilled water and add 600 cubic centimeters of ammonium hydroxide, specific gravity 0.90.

Potassium Iodate.—Dissolve 1.116 grams of potassium iodate and 12 grams of potassium iodide in 1,000 cubic centimeters of distilled water. Standardize with a steel of known sulphur content. Each cubic centimeter should be equivalent to 0.01 per cent. of sulphur, when a 5 gram sample is used (see notes).

Starch.—To 1,000 cubic centimeters of boiling distilled water, add a cold suspension of 6 grams of starch in 100 cubic centimeters of distilled water; cool, add a solution of 6 grams of zinc chloride in 50 cubic centimeters of distilled water, and mix thoroughly.

Method.

Place 5 grams of steel in the flask and connect the latter as shown in Fig. 62. Place 10 cubic centimeters of the ammoniacal cadmium chloride solution and 150 cubic centimeters of distilled water in the tumbler. Add 80 cubic centimeters of the dilute hydrochloric acid to the flask through the thistle tube, heat the flask with its contents gently until the solution of the steel is complete, then boil the solution for ½ minute. Re-

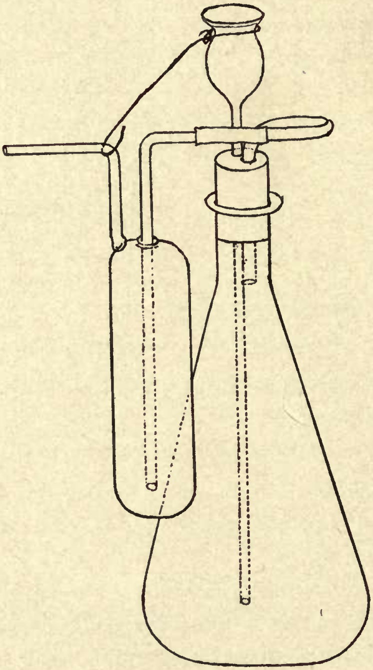

FIG. 72.

move the tumbler which contains all the sulphur as cadmium sulphide, and to it add 5 cubic centimeters of starch solution and 40 cubic centimeters of the dilute hydrochloric acid, titrating immediately with potassium iodate solution to a permanent blue color.

NOTES.

Extremely slow or rapid evolution of hydrogen sulphide is to be avoided.

Bureau of Standards Standard Steel No. 8(*a*) is recommended for standardizing the potassium iodiate solution.

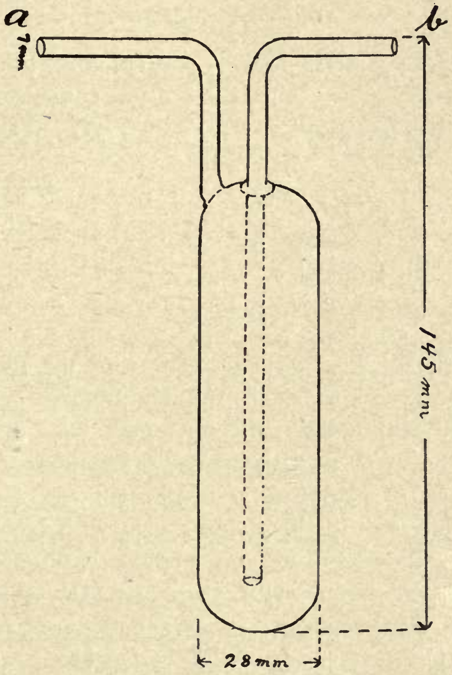

FIG. 73.

Editor's Note.—Another very convenient apparatus is shown in Figs. 72 and 73. It can be heated without getting the cadmium chloride solution hot while heating the flask containing the steel. In using this form, 10 cubic centimeters of the cadmium solution are drawn into the tube, Fig. 73, without diluting.

After all the H_2S has been driven over, the tube is disconnected and emptied into a 600 cubic centimeter beaker by pouring it out through *a*. The tube is then washed by filling it up first with water, then with dilute hydrochloric acid, and again with water. This is best accomplished by holding the nozzle of a wash bottle against *b* and blowing until the water or acid reaches the top of the tube. Remove wash bottle and empty the tube into beaker as above.

DETERMINATION OF SILICON BY THE NITRO-SULPHURIC METHOD.

Solutions Required.

Nitro-Sulphuric Acid.—Mix 1,000 cubic centimeters of sulphuric acid, specific gravity 1.84, 1,500 cubic centimeters of nitric acid, specific gravity 1.42, and 5,500 cubic centimeters of distilled water.

Dilute Hydrochloric Acid.—Mix 100 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 900 cubic centimeters of distilled water.

Method.

Add cautiously 80 cubic centimeters of the nitro-sulphuric acid to 4.702 grams of steel, in a platinum or porcelain dish of 300 cubic centimeters capacity, cover with a watch glass, heat until the steel is dissolved and evaporate slowly until copious fumes of sulphuric acid are evolved. Cool, add 125 cubic centimeters of distilled water, heat with frequent stirring until all salts are dissolved, add 5 cubic centimeters of hydrochloric acid, specific gravity 1.20, heat for 2 minutes, and filter on a 9 centimeter paper. Wash the precipitate several times with hot water, then with hydrochloric acid and hot water alternately to complete the removal of iron salts, and finally with hot water until free from acid. Transfer the filter to a platinum crucible, burn off the paper carefully with the crucible covered, finally igniting over a blast lamp or in a muffle furnace at 1,000° C. for at least 20 minutes; cool in a desiccator and weigh. Add sufficient sulphuric acid, specific gravity 1.84, to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights in milligrams divided by 100 equals the percentage of silicon.

NOTE.

A blank determination on all reagents used should be made and the results corrected accordingly.

DETERMINATION OF SILICON BY THE SULPHURIC ACID METHOD.

(Optional.)

Solution Required.

Dilute Hydrochloric Acid.—Mix 100 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 900 cubic centimeters of distilled water.

Method.

To 2.351 grams of steel, in a beaker of low form of 500 cubic centimeters capacity, add 60 cubic centimeters of distilled water, and then cautiously 15 cubic centimeters of sulphuric acid, specific gravity 1.84. Cover with a watch glass, heat until the steel is dissolved and evaporate until copious fumes of sulphuric acid are evolved. Cool, add 100 cubic centimeters of distilled water and heat with frequent stirring until the salts are in solution. Filter on a 9 centimeter paper, wash the precipitate several times with cold water, then with cold dilute hydrochloric acid until free from iron, and finally with cold water until free from acid. Ignite and weigh. Add sufficient sulphuric acid, specific gravity 1.84, to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights in milligrams divided by 50 equals the percentage of silicon.

NOTE.

A blank determination on all reagents used should be made and the results corrected accordingly.

DETERMINATION OF COPPER.

Solutions Required.

Sulphuric Acid.—Mix 200 cubic centimeters of sulphuric acid specific gravity × 1.84, and 800 cubic centimeters of distilled water.

Potassium Ferrocyanide.—Dissolve 10 grams of potassium ferrocyanide in 100 cubic centimeters of distilled water.

Standard Copper Nitrate.—Dissolve 2 grams of purest electrolytic copper in 20 cubic centimeters of nitric acid (1 : 1), and dilute to 1,000 cubic centimeters with distilled water. Each cubic centimeter is equivalent to 0.02 per cent. of copper on the basis of a 10 gram sample.

Method.

In a 300 cubic centimeter beaker dissolve 10 grams of the steel in 75 cubic centimeters of the sulphuric acid, and then add 150 cubic centimeters of distilled water. Heat the solution and saturate with hydrogen sulphide, filter and wash the precipitate free from iron with 1 per cent. sulphuric acid containing hydrogen sulphide. Incinerate the paper with its contents in a porcelain crucible and fuse with 0.5 gram of acid sodium sulphate. Extract with hot water, filter, and complete the determination colorimetrically as under 1(*a*) or 1(*b*), or electrolytically as under 2, as follows:

1. Evaporate the filtrate to about 25 cubic centimeters, make faintly ammoniacal, filter into a 100 cubic centimeter Nessler tube and wash with hot water.

(*a*) If the solution is a strong blue, to another 100 cubic centimeter Nessler tube add 50 cubic centimeters of distilled water, 5 cubic centimeters of ammonium hydroxide, specific gravity 0.90, and from a burette the standard copper nitrate solution until the blue colors match.

(*b*) If the solution is a faint blue, to the filtrate in a Nessler tube add the dilute sulphuric acid to faint acidity and then a few drops of the potassium ferrocyanide solution. To another 100 cubic centimeter Nessler tube add 50 cubic centimeters of distilled water, a few drops of the potassium ferrocyanide solution, and from a burette the standard copper nitrate solution until the reddish brown colors match.

2. Make the filtrate slightly acid with sulphuric acid, dilute with distilled water to a suitable volume, and determine the copper electrolytically.

DETERMINATION OF NICKEL BY THE GRAVIMETRIC DIMETHYLGLYOXIME METHOD.

Solutions Required.

Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity, 1.20, and 500 cubic centimeters of distilled water.

Dimethylglyoxime.—Dissolve 1 gram of dimethylglyoxime in 100 cubic centimeters of 95 per cent. ethyl alcohol.

Method.

In a 150 cubic centimeter beaker dissolve 1 gram of the steel in 20 cubic centimeters of the hydrochloric acid, and add about 2 cubic centimeters of nitric acid, specific gravity 1.42, to oxidize the iron. Filter the solution and add to the filtrate 6 grams of tartaric acid, and water till the volume is 300 cubic centimeters. Make the solution faintly ammoniacal, then faintly acid with the hydrochloric acid and heat nearly to boiling; add 20 cubic centimeters of the dimethylglyoxime solution and then ammonium hydroxide, specific gravity 0.90, drop by drop till faintly alkaline, stirring vigorously. After standing 1 hour, filter on a weighed Gooch crucible, wash with hot water, dry at 110° to 120° C. and weigh. The precipitate contains 20.31 per cent. of nickel.

NOTES.

In making dimethylglyoxime solution, methyl alcohol may be substituted for ethyl alcohol.

The weight of sample taken should be varied according to the nickel content.

DETERMINATION OF NICKEL BY THE VOLUMETRIC DIMETHYLGLYOXIME METHOD.

(Routine.)

Solutions Required.

Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 500 cubic centimeters of distilled water.

Dimethylglyoxime.—Dissolve 1 gram of dimethylglyoxime in 100 cubic centimeters of 95 per cent. ethyl alcohol.

Silver Nitrate.—Dissolve 0.5 gram of silver nitrate in 1,000 cubic centimeters of distilled water.

Potassium Iodide.—Dissolve 20 grams of potassium iodide in 100 cubic centimeters of distilled water.

Standard Potassium Cyanide.—Dissolve 2.29 grams of potassium cyanide in 1,000 cubic centimeters of distilled water. Standardize this solution by the procedure described below, against a steel of known nickel content as determined by the gravimetric dimethylglyoxime method, so that each cubic centimeter is equivalent to 0.05 per cent. of nickel on the basis of a 1-gram sample (see notes).

Method.

In a 150 cubic centimeter beaker dissolve 1 gram of the steel in 20 cubic centimeters of the hydrochloric acid, and add about 2 cubic centimeters of nitric acid, specific gravity 1.42, to oxidize the iron. Filter the solution and add to the filtrate 6 grams of tartaric acid, and water until the volume is 300 cubic centimeters. Make the solution faintly ammoniacal, then faintly acid with the hydrochloric acid, and cool thoroughly. Add 20 cubic centimeters of the dimethylglyoxime solution and then ammonium hydroxide, specific gravity 0.90, drop by drop, till faintly alkaline, stirring vigorously. After standing for a few minutes, filter on a Gooch crucible and wash with hot water. Dissolve the precipitate on the filter with 10 to 20 cubic centimeters of nitric acid (hot), specific gravity 1.42, added drop by drop, and then wash 5 times with hot water, using suction. To the solution in a 500 cubic centimeter beaker add 3 grams of ammonium persulphate and boil for 5 minutes. Cool, make distinctly ammoniacal, add 10 cubic centimeters each of the silver nitrate and potassium iodide solutions, and titrate with the standard potassium cyanide solution to a faint turbidity.

NOTES.

In making dimethylglyoxime solution, methyl alcohol may be substituted for ethyl alcohol.

Bureau of Standards Standard Steel No. 33 is recommended for standardizing the potassium cyanide solution.

The weight of sample taken should be varied according to the nickel content.

DETERMINATION OF CHROMIUM.

Solutions Required.

Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 500 cubic centimeters of distilled water.

Sodium Carbonate.—A saturated solution; approximately 60 grams of sodium carbonate and 100 cubic centimeters of distilled water.

Barium Carbonate.—Ten grams of finely divided barium carbonate suspended in 100 cubic centimeters of distilled water.

Standard Sodium Chromate.—Dissolve 2.6322 grams of sodium chromate in 1,000 cubic centimeters of distilled water. Each cubic centimeter is equivalent to 0.02 per cent. chromium, when a 5-gram sample is used.

Standard Potassium Permanganate.—Dissolve 2 grams of potassium permanganate in 1,000 cubic centimeters of distilled water. Standardize by using Bureau of Standards sodium oxalate,[1] and dilute the solution with distilled water so that 1 cubic centimeter is equivalent to 0.02 per cent. chromium, when a 5-gram sample is taken.

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

The factor $Na_2C_2O_4 \rightarrow Cr = 0.2584$ (using the 1913 atomic weights).

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1:1).

Method.

In a 300 cubic centimeter Erlenmeyer flask, covered, dissolve 5 grams of steel in 50 cubic centimeters of the hydrochloric acid. When completely dissolved, and gradually the saturated solution of sodium carbonate until practically all the free acid is neutralized; finish the neutralization with the barium carbonate suspension, using an excess of about 1 gram of the carbonate. Boil the solution in the flask for 10 or 15 minutes, with the cover on. Filter the precipitate rapidly on paper and wash twice with hot water. Transfer the filter to a platinum crucible and after burning off the paper, fuse the residue for 10 minutes with a mixture of 5 grams of sodium carbonate and 0.25 gram of potassium nitrate. Dissolve the fusion in water, transfer to a beaker, add 2 cubic centimeters of 3 per cent. hydrogen peroxide, boil a few minutes and filter. Complete the determination of chromium in the filtrate by either of the following procedures:

1. If the solution is a strong yellow, add 10 cubic centimeters of sulphuric acid (1:1), and then the ferrous sulphate solution in measured excess. Cool thoroughly and titrate with the standard potassium permanganate solution. The number of cubic centimeters of the potassium permanganate solution obtained, subtracted from the number corresponding to the volume of the ferrous sulphate solution used, will give the volume of the potassium permanganate solution equivalent to the chromium in the sample.

2. If the solution is a light yellow, cool the solution and transfer to a 100 cubic centimeter Nessler tube. To another Nessler tube add distilled water, and from a burette add the standard sodium chromate solution until the yellow colors match.

NOTE.

If procedure No. 1 is used, all hydrogen peroxide must be destroyed by boiling before acidifying, otherwise chromic acid will be reduced at this stage.

CHEMICAL ANALYSIS OF ALLOY STEELS AS PUBLISHED BY THE AMERICAN SOCIETY FOR TESTING MATERIALS.

ADOPTED, 1915.

NICKEL STEEL.

Determination of Carbon.

See the Determination of Carbon in Plain Carbon Steel by the Direct-Combustion Method.[1]

Determination of Manganese.

See the Determination of Manganese in Plain Carbon Steel by the Bismuthate Method.[1]

See the Determination of Manganese in Plain Carbon Steel by the Persulphate Method (Routine).

Determination of Phosphorus.

See the Determination of Phosphorus in Plain Carbon Steel by the Molybdate Magnesia Method.[1]

See the Determination of Phosphorus in Plain Carbon Steel by the Alkalimetric Method (Routine).[1]

Determination of Sulphur.

See the Determination of Sulphur in Plain Carbon Steel by the Oxidation Method.[1]

See the Determination of Sulphur in Plain Carbon Steel by the Evolution-Titration Method (Routine).[1]

NOTES.

The Evolution-Titration Method should not be used with steels containing appreciable amounts of tungsten, or of copper or other metals precipitated by hydrogen sulphide from acid solutions.

The annealing of the steel drillings has been found by a number of investigators to increase the degree of refinement of the method.

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

Determination of Silicon.

See the Determination of Silicon in Plain Carbon Steel by the Nitro-Sulphuric Method.[1]

See the Determination of Silicon in Plain Carbon Steel by the Sulphuric Acid Method (Optional).[1]

Determination of Nickel.

See the Determination of Nickel in Plain Carbon Steel by the Gravimetric Dimethylglyoxime Method.[1]

See the Determination of Nickel in Plain Carbon Steel by the Volumetric Dimethylglyoxime Method (Routine).[1]

Determination of Nickel by the Ether Extraction-Cyanide Titration Method.

(Optional Routine.)

SOLUTIONS REQUIRED.

Hydrochloric Acid.—Mix 600 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 400 cubic centimeters of distilled water.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium Iodide.—Dissolve 20 grams of potassium iodide in 1,000 cubic centimeters of distilled water.

Silver Nitrate.—Dissolve 0.5 gram of silver nitrate in 1,000 cubic centimeters of distilled water.

Standard Potassium Cyanide.—Dissolve 4.589 grams of potassium cyanide in 1,000 cubic centimeters of distilled water. Standardize the solution by the procedure described below, against a steel of known nickel content as determined by the gravimetric-dimethylglyoxime method, so that 1 cubic centimeter is equivalent to 0.10 per cent. nickel on the basis of a 1-gram sample (see note).

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

METHOD.

In a 150 cubic centimeter beaker dissolve 1 gram of the steel in 20 cubic centimeters of the hydrochloric acid, add about 2 cubic centimeters of nitric acid, specific gravity 1.42, to oxidize the iron, and boil to expel the oxides of nitrogen. Cool, and transfer the solution into an 8-ounce separatory funnel, rinsing the beaker with small portions of the hydrochloric acid. Add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off lower clear solution into another 8-ounce separatory funnel. Add 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, to the solution in the first separatory funnel, cool, shake thoroughly, allow to settle for 1 minute, and then draw off the lower clear solution into the second separatory funnel. To the combined solutions in the second separatory funnel add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the clear layer into a 150 cubic centimeter beaker. Heat the aqueous solution gently to expel the ether, add 0.2 gram of potassium chlorate, boil until chlorate is decomposed, dilute to 100 cubic centimeters with hot water, make faintly ammoniacal, and boil for 5 minutes. Filter and wash with hot water. To the filtrate add 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, heat just short of boiling and precipitate the copper with hydrogen sulphide. Filter and wash with hot water. Boil the filtrate to expel hydrogen sulphide, reducing the volume by evaporation to approximately 100 cubic centimeters, cool, and make solution distinctly ammoniacal, add 10 cubic centimeters each of the silver-nitrate and potassium-iodide solutions, and titrate with the standard potassium-cyanide solution to a clear solution.

NOTE.

Bureau of Standards Standard Steel No. 33 is recommended for standardizing the potassium cyanide solution.

CHROME-NICKEL STEEL.

Determination of Carbon.

See the Determination of Carbon by the Direct-Combustion Method.[1]

Determination of Manganese by the Zinc Oxide-Bismuthate Method.

SOLUTIONS REQUIRED.

Sulphuric Acid.—Mix 200 cubic centimeters of sulphuric acid, specific gravity 1.84, and 800 cubic centimeters of distilled water.

Nitric Acid.—Mix 500 cubic centimeters of nitric acid, specific gravity 1.42 and 1,500 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 30 cubic centimeters of nitric acid, specific gravity 1.42, and 970 cubic centimeters of distilled water.

Sodium Carbonate.—A saturated solution; approximately 60 grams of sodium carbonate and 100 cubic centimeters of distilled water.

Zinc Oxide.—Twenty grams of zinc oxide (dry process) suspended in 100 cubic centimeters of distilled water (see notes).

Stock Sodium Arsenite.—To 15 grams of arsenious oxide (As_2O_3) in a 300 cubic centimeter Erlenmeyer flask, add 45 grams of sodium carbonate and 150 cubic centimeters of distilled water. Heat the flask and contents on a water bath until the arsenious oxide is dissolved, cool the solution and make up to 1,000 cubic centimeters with distilled water.

Standard Sodium-Arsenite.—Dilute 300 cubic centimeters of the stock-sodium-arsenite solution to 1,000 cubic centimeters with distilled water and titrate against potassium-permanganate solution (about N/10) which has been standardized by

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.10 per cent. of manganese on the basis of a 1-gram sample.

The factor $Na_2C_2O_4 \longrightarrow Mn = 0.16397$ (using the 1913 atomic weights).

METHOD.

In a platinum or porcelain dish of 300 cubic centimeters capacity, to 2.5 grams of the steel add 40 cubic centimeters of the sulphuric acid, cover with a watch glass, and heat until the steel is dissolved. Add about 4 cubic centimeters of nitric acid, specific gravity 1.42, to oxidize the iron and evaporate slowly until copious fumes of sulphuric acid are evolved. Cool, add 100 cubic centimeters of hot water, heat with frequent stirring until all salts are dissolved, then transfer the solution into a volumetric 500 cubic centimeter flask. Add the sodium-carbonate solution until near neutrality, and the precipitate formed dissolves with difficulty, then add small portions of the zinc-oxide suspension, shaking vigorously after each addition, until after settling of the coagulated precipitate, the supernatant liquid is practically clear. Cool, and make up to the mark with water. Mix thoroughly by pouring the entire contents of the flask into a large, dry beaker, and back again to the flask, repeating several times. Allow the precipitate to settle, filter off 200 cubic centimeters of the solution into a 300 cubic centimeter Erlenmeyer flask, add 25 cubic centimeters of the nitric acid solution, and boil to expel the oxides of nitrogen. Cool, add 0.5 gram of sodium bismuthate and heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add small portions of ferrous sulphate (or other suitable reducing agent) in sufficient quantity to clear the solution, and boil to expel the oxides of nitrogen. Cool to 15° C., add an excess of sodium bismuthate and agitate for a few minutes. Let settle and filter through an alundum filter or asbestos pad, washing with the 3 per cent. nitric acid. Titrate immediately

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

with the standard sodium-arsenite solution to the disappearance of the pink color.

NOTES.

In the method, the preliminary treatment with sodium bismuthate has been found by a number of investigators to be apparently unnecessary; however, the available data to confirm this position are not considered sufficient to warrant its omission.

In making the asbestos filter pad it is advisable to have a thin bed and as much surface as possible. This insures rapid filtration and the filter may be used until it becomes clogged with bismuthate.

The filtrate must be perfectly clear since the least particle of bismuthate carried through the filter will vitiate the results.

The zinc-oxide reagent should be free from manganese, or a correction applied if it is present.

Determination of Manganese by the Modified Bismuthate Method.

(Routine.)

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 500 cubic centimeters of nitric acid, specific gravity 1.42, and 1,500 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 30 cubic centimeters of nitric acid, specific gravity 1.42, and 970 cubic centimeters of distilled water.

Stock Sodium Arsenite.—To 15 grams of arsenious oxide (As_2O_3) in a 300 cubic centimeter Erlenmeyer flask, add 45 grams of sodium carbonate and 150 cubic centimeters of distilled water. Heat the flask and contents on a water bath until the arsenious oxide is dissolved, cool the solution and make up to 1,000 cubic centimeters with distilled water.

Standard Sodium Arsenite.—Dilute 300 cubic centimeters of the stock-sodium-arsenite solution to 1,000 cubic centimeters with distilled water and titrate against potassium-permanganate solution (about N/10) which has been standardized by using Bureau of Standards sodium oxalate.[1] Adjust the solu-

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1 1912.

tion so that 1 cubic centimeter is equivalent to 0.10 per cent. of manganese on the basis of a 1-gram sample.

The factor $Na_2C_2O_4 \longrightarrow Mn = 0.16397$ (using the 1913 atomic weights).

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 1 gram of the steel in 50 cubic centimeters of the nitric acid, and boil to expel the oxides of nitrogen. Cool to 60-70° C., add about 0.5 gram of sodium bismuthate, and heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add sufficient sulphurous acid or sodium sulphite to clear the solution and to reduce all of the chromic acid. Cool to approximately 0° C. in ice water, add an excess of sodium bismuthate and agitate. After 30 seconds standing, filter rapidly through an alundum filter or asbestos pad, washing with 3 per cent. nitric acid previously cooled in ice water to approximately 0° C. Titrate immediately with the standard sodium-arsenite solution to the disappearance of the pink color.

NOTES.

In the method, the preliminary treatment with sodium bismuthate has been found by a number of investigators to be apparently unnecessary; however, the available data to confirm this position are not sufficient to warrant its omission.

In making the asbestos filter pad it is advisable to have a thin bed, and as much surface as possible. This insures rapid filtration, and the filter may be used until it becomes clogged with bismuthate.

The filtrate must be ice cold and perfectly clear, since any appreciable rise of temperature above 0° C., or the least particle of bismuthate carried through the filter will vitiate the results.

See the Determination of Manganese in Plain Carbon Steel by the Persulphate Method.[1]

NOTE.

In making the titration special care should be given to standardizing the end-point reading, and the reading should be corrected by a blank, which varies with the amount of chromium present.

[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

Determination of Phosphorus.

See the Determination of Phosphorus in Plain Carbon Steel by the Molybdate-Magnesia Method.[1]

See the Determination of Phosphorus in Plain Carbon Steel by the Alkalimetric Method.[1]

Determination of Sulphur.

See the Determination of Sulphur in Plain Carbon Steel by the Oxidation Method.[1]

See the Determination of Sulphur in Plain Carbon Steel by the Evolution-Titration Method (Routine).[1]

NOTES.

The Evolution-Titration Method should not be used with steels containing appreciable amounts of tungsten, or of copper or other metals precipitated by hydrogen sulphide from acid solutions.

The annealing of the steel drillings has been found by a number of investigators to increase the degree of refinement of the method.

Determination of Silicon.

See the Determination of Silicon in Plain Carbon Steel by the Nitro-Sulphuric Method.[1]

See the Determination of Silicon in Plain Carbon Steel by the Sulphuric Acid Method (Optional).[1]

Determination of Chromium by the Fusion Method.

SOLUTIONS REQUIRED.

Sulphuric Acid.—Mix 1,000 cubic centimeters of sulphuric acid, specific gravity 1.84, and 3,000 cubic centimeters of distilled water.

Sodium Carbonate.—A saturated solution; approximately 60 grams of sodium carbonate and 100 cubic centimeters of distilled water.

Magnesium Carbonate.—Ten grams of finely divided magnesium carbonate suspended in 100 cubic centimeters of distilled water.

Barium Carbonate.—Ten grams of finely divided barium carbonate suspended in 100 cubic centimeters of distilled water.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium-Ferricyanide Indicator.—Dissolve 0.1 gram of potassium ferricyanide in 50 cubic centimeters of distilled water (see notes).

Standard Potassium Bichromate.—Dissolve 5 grams of potassium bichromate in 1,000 cubic centimeters of distilled water, standardize against pure ferrous ammonium sulphate, and adjust to tenth-normal.

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1 : 1).

METHOD.

In a 300 cubic centimeter Erlenmeyer flask, covered, dissolve 1 gram of the steel in 50 cubic centimeters of the sulphuric acid (see notes). When completely dissolved, add 50 to 75 cubic centimeters of hot water, then gradually the sodium-carbonate solution until near neutrality, then add an excess of the magnesium-carbonate suspension (see notes), and boil vigorously for 15 minutes, with the cover on, adding fresh portions of the carbonate suspension during this time, so that there is present in the solution at the end of the operation an excess of 2 to 3 grams of the carbonate. Let settle and pour the supernatant liquid on a rapid filter, washing by decantation twice with cold water, pouring the washings through the filter. Transfer the filter to a platinum crucible and after burning off the paper, fuse the residue for 10 minutes with a mixture of 5 grams of sodium carbonate and 0.25 gram of potassium nitrate. Dissolve the fusion in water, transfer to a beaker, add 2 cubic centimeters of 3 per cent. hydrogen peroxide, boil a few minutes and filter. Add 20 cubic centimeters of the sulphuric acid, stir vigorously, cool and titrate against the standardized ferrous-sulphate solution, using the potassium-ferricyanide solution as outside indicator, or add at once a measured amount (in excess) of the ferrous-sulphate solution, and titrate back against the potassium-bichromate solution, using the same indicator.

NOTES.

The solution of the steel may be in hydrochloric acid, specific gravity 1.20 or any other desired strength, adjusting the amount of acid used to avoid a large excess being present.

Barium carbonate suspension may be substituted for the magnesium carbonate suspension when hydrochloric acid is used as solvent.

All hydrogen peroxide must be destroyed by boiling before acidifying, otherwise chromic acid will be reduced at this stage.

The insoluble residue remaining after extraction of the fusion should be examined for chromium.

The potassium ferricyanide indicator should be prepared fresh on the day it is used.

The ferrous sulphate solution should be standardized on the day it is used.

In titrating with the ferrous sulphate solution it is convenient to divide the solution, roughly titrate one portion, add the other and finish carefully.

Determination of Chromium by the Chlorate Method.

(Routine.)

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium-Ferricyanide Indicator.—Dissolve 0.1 gram of potassium ferricyanide in 50 cubic centimeters of distilled water (see notes).

Standard Potassium Bichromate.—Dissolve 5 grams of potassium bichromate in 1,000 cubic centimeters of distilled water, and standardize against pure ferrous ammonium sulphate, and adjust to tenth-normal.

Standard Potassium Permanganate.—Dissolve 2 grams of potassium permanganate in 1,000 cubic centimeters of distilled water. Standardize by using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.10 per cent. chromium on the basis of a 1-gram

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

sample. The factor $Na_2C_2O_4 > Cr = 0.2584$ (using the 1913 atomic weights).

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1 : 1).

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 1 gram of the steel in 30 cubic centimeters of the nitric acid, and evaporate rapidly to approximately one-half volume. Add 50 cubic centimeters of nitric acid, specific gravity 1.42, and add 1 gram of sodium chlorate (see notes). Evaporate to boiling to approximately one-half volume and complete the determination by either of the following procedures:

1. Dilute the solution with 100 cubic centimeters of distilled water and filter off the manganese dioxide, using suction, washing with hot water. Cool the filtrate, dilute with cold water to 600 cubic centimeter volume, and titrate against the standard ferrous-sulphate solution, using the potassium-ferricyanide solution as outside indicator, or add at once a measured amount (in excess) of the ferrous-sulphate solution and titrate back against the standard potassium-bichromate solution, using the same indicator.

2. Add 10 cubic centimeters of hydrochloric acid (1 : 1) and boil until the solution is clear and all manganese dioxide dissolved. Cool, dilute the solution with water to 300 cubic centimeter volume, add the ferrous-sulphate solution in measured amount (in excess), and titrate back with the standard potassium-permanganate solution to a permanent pink color.

NOTES.

The potassium-ferricyanide indicator should be prepared fresh on the day it is used.

The ferrous-sulphate solution should be compared on the day it is used, with the standard potassium-permanganete or standard potassium-bichromate solutions.

Potassium chlorate may be used as oxidizing agent in the place of sodium chlorate.

In titrating with the ferrous-sulphate solution it is convenient to divide the solution, roughly titrate one portion, add the other and finish carefully.

Determination of Chromium by the Permanganate Oxidation Method.

(*Optional Routine.*)

SOLUTIONS REQUIRED.

Sulphuric Acid.—Mix 1,000 cubic centimeters of sulphuric acid, specific gravity 1.84, and 3,000 cubic centimeters of distilled water.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Standard Potassium Permanganate.—Dissolve 2 grams of potassium permanganate in 1,000 cubic centimeters of distilled water. Standardize by using Bureau of Standard sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.10 per cent. chromium on the basis of a 1-gram sample.

The factor $Na_2C_2O_4 \longrightarrow Cr = 0.2584$ (using the 1913 atomic weights).

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1:1).

METHOD.

In a 300 cubic centimeter Erlenmeyer flask, dissolve 1.25 grams (procedure No. 1) or 1 gram (procedure No. 2) of the steel in 50 cubic centimeters of the sulphuric acid. When completely dissolved, add 5 cubic centimeters of the nitric acid, and boil until clear and free from oxides of nitrogen. Dilute with hot water to approximately 150 cubic centimeter volume, heat, and while boiling add the potassium-permanganate solution slowly until a permanent brown precipitate appears (see notes). Complete the determination by either of the following procedures:

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

1. Add 25 cubic centimeters of ammonium hydroxide, specific gravity 0.90, shake well, place on the cooler part of the hot plate to avoid bumping. Shake occasionally and digest for about 15 minutes, or until the permanganate is all decomposed, then add cautiously 20 cubic centimeters of the sulphuric acid and bring gently to a boil. Cool the solution and pour into a volumetric 250 cubic centimeter flask. Make up to mark with cold water and mix thoroughly. Allow precipitate to settle, filter off 200 cubic centimeters of the clear solution (equal to 1 gram), add the ferrous-sulphate solution in measured amount (in excess) and titrate back with the standard potassium-permanganate solution to a permanent pink color. The number of cubic centimeters of the standard potassium-permanganate solution obtained, subtracted from the number corresponding to the volume of the ferrous-sulphate solution used, will give the volume of the standard potassium-permanganate solution equivalent to the chromium in the sample.

2. Add 10 cubic centimeters of hydrochloric acid (1 : 1), and boil until the solution is clear and all manganese dioxide dissolved. Cool, dilute the solution with water to 300 cubic centimeter volume, add the ferrous-sulphate solution in measured amount (in excess), and titrate back with the standard potassium-permanganate solution to a permanent pink color.

NOTES.

In oxidizing with the potassium-permanganate solution care should be taken to avoid a large excess, since the manganese-dioxide precipitate tends to hold the chromic acid.

In the solution of the manganese dioxide under procedure No. 2, the boiling should be continued until all chlorine fumes are expelled.

The ferrous-sulphate solution should be compared on the day it is used with the standard potassium-permanganate solution.

Determination of Nickel.

See the Determination of Nickel in Plain Carbon Steel by the Gravimetric-Dimethylglyoxime Method.[1]

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915, Year-Book, p. 201.

See the Determination of Nickel in Plain Carbon Steel by the Volumetric Dimethylglyoxime Method (Routine).

VANADIUM STEEL.

Determination of Carbon.

See the Determination of Carbon in Plain Carbon Steel by the Direct-Combustion Method.

Determination of Manganese.

See the Determination of Manganese in Chrome-Nickel Steel by the Zinc Oxide-Bismuthate Method.

For the Routine Determination of Manganese, see the Determination of Manganese in Plain Carbon Steel by the Bismuthate Method.

Determination of Phosphorus by the Modified Molybdate-Magnesia Method.

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 20 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Sodium Bisulphite.—Dissolve 30 grams of sodium bisulphite in 1,000 cubic centimeters of distilled water.

Ammonium Molybdate.—Solution No. 1.—Place in a beaker 100 grams of 85 per cent. molybdic acid, mix it thoroughly with 240 cubic centimeters of distilled water, add 140 cubic centimeters of ammonium hydroxide, specific gravity 0.90, filter, and add 60 cubic centimeters of nitric acid, specific gravity 1.42.

Solution No. 2.—Mix 400 cubic centimeters of nitric acid, specific gravity 1.42, and 960 cubic centimeters of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cubic centimeters of distilled water, and let stand at least 24 hours before using.

Magnesia Mixture.—Dissolve 50 grams of magnesium chloride and 125 grams of ammonium chloride in 750 cubic centimeters of distilled water and then add 150 cubic centimeters of ammonium hydroxide, specific gravity 0.90.

Ammonium Hydroxide, Approximately 10 per cent.—Mix 1,000 cubic centimeters of ammonium hydroxide, specific gravity 0.90, and 2,000 cubic centimeters of distilled water.

Ferrous Sulphate.—A saturated solution; approximately 40 grams of ferrous sulphate and 100 cubic centimeters of distilled water.

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 5 grams of steel in 75 cubic centimeters of the nitric acid. Heat, and while boiling add about 12 cubic centimeters of the potassium-permanganate solution, and continue boiling until manganese dioxide precipitates. Dissolve the precipitate by additions of the sodium-bisulphite solution, boil until clear and free from oxides of nitrogen. Cool to 15-20° C., add 5 cubic centimeters of the ferrous-sulphate solution, and 2 or 3 drops of concentrated sulphurous acid, and then 100 cubic centimeters of the ammonium-molybdate solution. Let stand 1 minute, shake or agitate thoroughly for 5 minutes, filter on a 9-centimeter paper and wash at least 3 times with the 2 per cent. nitric acid solution to free from iron.

Treat the precipitate on the filter with the 10 per cent. ammonium-hydroxide solution, letting the solution run into a 100 cubic centimeter beaker containing 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 0.5 gram of citric acid; add 30 cubic centimeters of ammonium hydroxide, specific gravity 0.90, cool, and then add 10 cubic centimeters of the magnesia mixture very slowly, while stirring the solution vigorously. Set aside in a cool place for 2 hours, filter and wash with the 10 per cent. ammonium-hydroxide solution. Ignite and weigh. Dissolve the precipitate of magnesium pyrophosphate with 5 cubic centimeters of nitric acid, specific gravity 1.20, and 20 cubic centimeters of water, filter and wash with hot water. Ignite and weigh. The difference in weights represents pure magnesium pyrophosphate containing 27.84 per cent. of phosphorus.

NOTE.

The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

Determination of Phosphorus by the Modified Alkalimetric Method.

(Routine.)

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 20 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Sodium Bisulphite.—Dissolve 30 grams of sodium bisulphite in 1,000 cubic centimeters of distilled water.

Ammonium Molybdate.—Solution No. 1.—Place in a beaker 100 grams of 85 per cent. molybdic acid, mix it thoroughly with 240 cubic centimeters of distilled water, add 140 cubic centimeters of ammonium hydroxide, specific gravity 0.90, filter, and add 60 cubic centimeters of nitric acid, specific gravity 1.42.

Solution No. 2.—Mix 400 cubic centimeters of nitric acid, specific gravity 1.42, and 960 cubic centimeters of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cubic centimeters of distilled water, and let stand at least 24 hours before using.

Ferrous Sulphate.—A saturated solution; approximately 40 grams of ferrous sulphate and 100 cubic centimeters of distilled water.

Potassium Nitrate, 1 per cent.—Dissolve 10 grams of potassium nitrate in 1,000 cubic centimeters of distilled water.

Phenolphthalein Indicator.—Dissolve 0.2 gram of phenolphthalein in 50 cubic centimeters of 95 per cent. ethyl alcohol and 50 cubic centimeters of distilled water.

Standard Sodium Hydroxide.—Dissolve 6.5 grams of purified sodium hydroxide in 1,000 cubic centimeters of distilled water, add a slight excess of 1 per cent. solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content, as determined by the molybdate magnesia method, so that 1 cubic centimeter will be equivalent to 0.01 per cent. of phosphorus on the basis of a 2-gram sample (see notes). Protect the solution from carbon dioxide with a soda-lime tube.

Standard Nitric Acid.—Mix 10 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water. Titrate the solution against the standardized sodium hydroxide, using phenolphthalein as indicator, and make it equivalent to the sodium hydroxide by adding distilled water.

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 2 grams of steel in 50 cubic centimeters of the nitric acid. Heat, and while boiling add 6 cubic centimeters of the potassium permanganate solution and continue boiling until manganese dioxide precipitates. Dissolve this precipitate by additions of the sodium bisulphite solution, boil until clear and free from oxides of nitrogen, cool to 15°-20° C., add 5 cubic centimeters of the ferrous sulphate solution and 2 or 3 drops of concentrated sulphurous acid, and then 50 cubic centimeters of the ammonium molybdate solution. Let stand for 1 minute, shake or agitate for 5 minutes, filter on a 9 centimeter paper, wash the precipitate three times with the 2 per cent. nitric acid solution to free it from iron, and continue the washing with the 1 per cent. potassium nitrate solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to the solution flask, add 20 cubic centimeters of distilled water (see notes), 5 drops of phenolphthalein solution as indicator, and an excess of the standard sodium hydroxide solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of standard sodium hydroxide solution by titrating with standard nitric acid solution. Each cubic centimeter of standard sodium hydroxide solution represents 0.01 per cent. of phosphorus.

NOTES.

The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titration should be freed from carbon dioxide by boiling or otherwise.

Bureau of Standards Standard Steel No. 24 is recommended as a suitable steel for standardizing the sodium-hydroxide solution.

Determination of Sulphur.

See the Determination of Sulphur in Plain Carbon Steel by the Oxidation Method.

See the Determination of Sulphur in Plain Carbon Steel by the Evolution-Titration Method (Routine).

NOTES.

The Evolution-Titration Method should not be used with steels containing appreciable amounts of tungsten, or of copper or other metals precipitated by hydrogen sulphide from acid solutions.

The annealing of the steel drillings has been found by a number of investigators to increase the degree of refinement of the method.

Determination of Silicon.

See the Determination of Silicon in Plain Carbon Steel by the Nitro-Sulphuric Method.[1]

See the Determination of Silicon in Plain Carbon Steel by the Sulphuric Acid Method (Optional).[1]

Determination of Vanadium by the Phosphomolybdate-Precipitation Method.

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Nitric Acid for Washing.—Mix 20 cubic centimeters of nitric acid, specific gravity 1.42, and 1,000 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Sodium Bisulphite.—Dissolve 30 grams of sodium bisulphite in 1,000 cubic centimeters of distilled water.

Ammonium Phosphate.—Dissolve 50 grams of ammonium phosphate in 1,000 cubic centimeters of distilled water.

Ammonium Molybdate.—Solution No. 1.—Place in a beaker 100 grams of 85 per cent. molybdic acid, mix it thoroughly with 240 cubic centimeters of distilled water, add 140 cubic centimeters of ammonium hydroxide, specific gravity 0.90, filter, and add 60 cubic centimeters of nitric acid, specific gravity 1.42.

Solution No. 2.—Mix 400 cubic centimeters of nitric acid, specific gravity 1.42, and 960 cubic centimeters of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cubic centimeters of distilled water, and let stand at least 24 hours before using.

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

Acid Ammonium Sulphate.—Mix 50 cubic centimeters of sulphuric acid, specific gravity 1.84, and 950 cubic centimeters of distilled water, and when cold add 15 cubic centimeters of ammonium hydroxide, specific gravity 0.90. Use at a temperature of 80° C.

Standard Potassium Permanganate.—Dissolve 0.35 gram of potassium permanganate in 1,000 cubic centimeters of distilled water, and standardize by using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.02 per cent. vanadium on the basis of a 2.5 gram sample.

The factor $Na_2C_2O_4 \longrightarrow V = 0.7612$ (using the 1913 atomic weights).

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 2.5 grams of steel in 50 cubic centimeters of the nitric acid. Heat, and while boiling add 6 cubic centimeters of the potassium permanganate solution and continue boiling until manganese dioxide precipitates. Dissolve the precipitate by additions of the sodium bisulphite solution and boil until clear and free from oxides of nitrogen. Add 5 cubic centimeters of the ammonium phosphate solution and 10 grams of ammonium nitrate, heat to boiling, remove from the plate and add immediately 50 cubic centimeters of the ammonium molybdate solution. Let stand 1 minute, shake or agitate for 3 minutes, filter the supernatant liquid by suction through an asbestos filter, and wash three times with the hot acid ammonium sulphate solution. The flask containing the bulk of the precipitate is then set under the funnel fitted into a bell-jar filter and the asbestos pad is treated with successive small portions of hot sulphuric acid, specific gravity 1.84. The solution is then heated until the precipitate is completely dissolved, a few drops of the nitric acid added, and the heating continued until copious fumes of sulphuric acid are evolved. Cool the solution, add hydrogen peroxide in small quantities, with vig-

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

orous shaking after each addition, until the solution takes on a deep brown color. Replace flask on the hot plate, fume for 4 or 5 minutes, cover the flask, cool, add 100 cubic centimeters of distilled water, heat to 80° C. and titrate with the standard potassium permanganate solution to a permanent pink color.

NOTE.

If, after the addition of hydrogen peroxide and subsequent heating, the solution does not take on a clear green or blue color, it should be heated until fumes of sulphuric acid are evolved to rid of any traces of nitric acid which interferes with the reduction, then cooled and the treatment with hydrogen peroxide repeated.

Determination of Vanadium by the Ether Extraction Hydrochloric Acid Reduction Method.

(*Routine.*)

SOLUTIONS REQUIRED.

Hydrochloric Acid.—Mix 600 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 400 cubic centimeters of distilled water.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Sulphuric Acid.—Mix 500 cubic centimeters of sulphuric acid, specific gravity, 1.84, and 500 cubic centimeters of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cubic centimeters of distilled water.

Standard Potassium Permanganate.—Dissolve 0.35 gram of potassium permanganate in 1,000 cubic centimeters of distilled water, and standardize by using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.02 per cent. vanadium on the basis of a 2.5-gram sample.

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

The factor $Na_2C_2O_4 \longrightarrow V = 0.7612$ (using the 1913 atomic weights).

METHOD.

In a 150 cubic centimeter beaker dissolve 2.5 grams of the steel in 50 cubic centimeters of the hydrochloric acid, add small portions of the nitric acid to oxidize the iron, and heat to expel the oxides of nitrogen. Cool, and transfer the solution into an 8-ounce separatory funnel, rinsing the beaker with small portions of the hydrochloric acid. Add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off lower clear solution into another 8-ounce separatory funnel. Add 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, to the solution in the first separatory funnel, shake thoroughly, allow to settle for 1 minute, and then draw off the lower clear solution into the second separatory funnel. To the combined solutions in the second separatory funnel add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the clear layer into a 150 cubic centimeter beaker. Heat the aqueous solution gently to expel the ether, add 25 cubic centimeters of the sulphuric acid, and heat until copious fumes are evolved. Cool, dilute with 25 cubic centimeters of water, add a slight excess of the potassium permanganate solution, and boil. Add 15 cubic centimeters of hydrochloric acid, specific gravity 1.20, and heat to fuming for 10 minutes. Cool, add 100 cubic centimeters of water, heat to 80° C., and titrate with the standard potassium permanganate solution to a permanent pink color.

NOTE.

In heating the solution to expel oxides of nitrogen care should be taken not to boil.

CHROME-VANADIUM STEEL.

Determination of Carbon.

See the Determination of Carbon in Plain Carbon Steel by the Direct Combustion Method.[1]

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

Determination of Manganese.

See the Determination of Manganese in Chrome-Nickel Steel by the Zinc Oxide Bismuthate Method.

See the Determination of Manganese in Chrome-Nickel Steel by the Modified Bismuthate Method.

Determination of Phosphorus.

See the Determination of Phosphorus in Vanadium Steel by the Modified Molybdate Magnesia Method.

See the Determination of Phosphorus in Vanadium Steel by the Modified Alkalimetric Method (Routine).

Determination of Sulphur.

See the Determination of Sulphur in Plain Carbon Steel by the Oxidation Method.[1]

See the Determination of Sulphur in Plain Carbon Steel by the Evolution-Titration Method (Routine).

NOTES.

The Evolution-Titration Method should not be used with steels containing appreciable amounts of tungsten, or of copper or other metals precipitated by hydrogen sulphide from acid solutions.

The annealing of the steel drillings has been found by a number of investigators to increase the degree of refinement of the method.

Determination of Silicon.

See the Determination of Silicon in Plain Carbon Steel by the Nitro-Sulphuric Method.

See the Determination of Silicon in Plain Carbon Steel by the Sulphuric Acid Method (Optional).

Determination of Chromium by the Fusion Method.

SOLUTIONS REQUIRED.

Sulphuric Acid.—Mix 1,000 cubic centimeters of sulphuric acid, specific gravity 1.84, and 3,000 cubic centimeters of distilled water.

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

Sodium Carbonate.—A saturated solution; approximately 60 grams of sodium carbonate and 100 cubic centimeters of distilled water.

Magnesium Carbonate.—Ten grams of finely divided magnesium carbonate suspended in 100 cubic centimeter of distilled water.

Barium Carbonate.—Ten grams of finely divided barium carbonate suspended in 100 cubic centimeters of distilled water.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium Ferricyanide Indicator.—Dissolve 0.1 gram of potassium ferricyanide in 50 cubic centimeters of distilled water (see notes).

Standard Potassium Bichromate.—Dissolve 5 grams of potassium bichromate in 1,000 cubic centimeters of distilled water, standardize against pure ferrous ammonium sulphate, and adjust to tenth-normal.

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1 : 1). The strength of this solution should be expressed in terms of chromium and vanadium.

METHOD.

In a 300 cubic centimeter Erlenmeyer flask, covered, dissolve 1 gram of steel in 50 cubic centimeters of the sulphuric acid (see notes). When completely dissolved, add 50 to 75 cubic centimeters of hot water, then gradually the sodium carbonate solution until near neutrality, and then add an excess of the magnesium carbonate suspension (see notes), and boil vigorously for 15 minutes, with the cover on, adding fresh portions of the carbonate suspension during this time, so that there is present in the solution at the end of the operation an excess of 2 to 3 grams of the carbonate. Let settle and pour the supernatant liquid on a rapid filter, washing by decantation twice with cold water, pouring the washings through the filter. Transfer the filter to a platinum crucible and after burning off the paper, fuse the residue for 10 minutes with a mixture of 5 grams of sodium carbonate and 0.25 gram of potassium nitrate. Dissolve the fusion in water, transfer to a beaker, add 2 cubic centimeters of 3 per cent. hydrogen peroxide, boil a few minutes and filter. Add 20 cubic centimeters of the sulphuric acid, stir vigorously, cool and titrate against the standardized ferrous sulphate solution, using the potassium ferricyanide as outside indicator, or add at once a measured amount (in excess) of the ferrous sulphate solution and titrate back against the standard potassium bichromate solution, using the same indicator.

From the number of cubic centimeters of the standard ferrous sulphate solution required deduct the number of cubic centimeters of the standard ferrous sulphate solution equivalent to the vanadium in the steel, as determined by the Phosphomolybdate Precipitation Method for Vanadium Steel, and the result will be the number of cubic centimeters of the standard ferrous sulphate solution equivalent to the chromium in the steel.

NOTES.

The solution of the steel may be in hydrochloric acid, specific gravity 1.20 or any other desired strength, adjusting the amount of acid used to avoid a large excess being present.

Barium-carbonate suspension may be substituted for the magnesium-carbonate suspension when hydrochloric acid is used as solvent.

All hydrogen peroxide must be destroyed by boiling before acidifying, otherwise chromic acid will be reduced at this stage.

The insoluble residue remaining after extraction of the fusion should be examined for chromium.

The potassium ferricyanide indicator should be prepared fresh on the day it is used.

The ferrous sulphate solution should be standardized on the day it is used.

In titrating with the ferrous sulphate solution it is convenient to divide the solution, roughly titrate one portion, add the other and finish carefully.

Determination of Chromium by the Chlorate Method.

(*Routine.*)

SOLUTIONS REQUIRED.

Nitric Acid.—Mix 1,000 cubic centimeters of nitric acid, specific gravity 1.42, and 1,200 cubic centimeters of distilled water.

Potassium Ferricyanide Indicator.—Dissolve 0.1 gram of potassium ferricyanide in 50 cubic centimeters of distilled water (see notes).

Standard Potassium Bichromate.—Dissolve 5 grams of potassium bichromate in 1,000 cubic centimeters of distilled water, standardize against pure ferrous ammonium sulphate, and adjust to tenth-normal.

Standard Potassium Permanganate.—Dissolve 0.5 gram of potassium permanganate in 1,000 cubic centimeters of distilled water. Standardize by using Bureau of Standards sodium oxalate.[1] Adjust the solution so that 1 cubic centimeter is equivalent to 0.05 per cent. vanadium on the basis of a 1 gram sample.

The factor $Na_2C_2O_4 \longrightarrow V = 0.7612$ (using the 1913 atomic weights).

Ferrous Sulphate.—Dissolve 25 grams of ferrous ammonium sulphate in 900 cubic centimeters of distilled water and 100 cubic centimeters of sulphuric acid (1:1). The strength of this solution should be expressed in terms of chromium and vanadium.

METHOD.

In a 300 cubic centimeter Erlenmeyer flask dissolve 1 gram of the steel in 30 cubic centimeters of the nitric acid, and evaporate rapidly to approximately one-half volume. Add 50 cubic centimeters of nitric acid, specific gravity 1.42, and 1 gram of sodium chlorate (see notes). Evaporate by boiling to one-half volume, dilute with 100 cubic centimeters of water and filter off the manganese dioxide, using suction,

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[1] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

washing with hot water. Cool the solution to room temperature and complete the determination by either of the following procedures:

1. Titrate against the ferrous sulphate solution, using the potassium ferricyanide solution as outside indicator (see notes). From the number of cubic centimeters of the ferrous sulphate solution required deduct the number of cubic centimeters of the ferrous sulphate solution equivalent to the vanadium in the steel, as determined by the Phosphomolybdate Precipitation Method for Vanadium Steel, and the result will be the number of cubic centimeters of the ferrous sulphate solution equivalent to the chromium in the steel.

2. Titrate against the ferrous sulphate solution, using the potassium ferricyanide solution as outside indicator (see notes). Cool to 15° C. and titrate against the standard potassium permanganate solution to a pink color permanent for 10 seconds. Deduct the number of cubic centimeters of the standard potassium permanganate solution consumed, which gives a direct measure of the vanadium content of the steel, from the first titration; the remainder will represent the chromium content of the steel.

NOTES.

The potassium-ferricyanide indicator should be prepared fresh on the day it is used.

The ferrous-sulphate solution should be compared on the day it is used with the standard potassium-permanganate or potassium-bichromate solutions.

Potassium chlorate may be used as oxidizing agent in the place of sodium chlorate.

In titrating with the ferrous-sulphate solution it is convenient to divide the solution, roughly titrate one portion, add the other and finish carefully.

Determination of Vanadium.

See the Determination of Vanadium in Vanadium Steel by the Phosphomolybdate Precipitation Method.

Determination of Vanadium by the Ether Extraction Hydrochloric Acid Reduction Method.

(Routine.)

SOLUTIONS REQUIRED.

Hydrochloric Acid.—Mix 500 cubic centimeters of hydrochloric acid, specific gravity 1.20, and 500 cubic centimeters of distilled water.

Standard Potassium Permanganate.—Dissolve 2 grams of potassium permanganate in 1,000 cubic centimeters of distilled water, and standardize by using Bureau of Standards sodium oxalate.[2] Adjust the solution so that 1 cubic centimeter is equivalent to 0.10 per cent. vanadium on the basis of when a 5-gram sample.

The factor $Na_2C_2O_4 \longrightarrow V = 0.7612$ (using the 1913 atomic weights).

METHOD.

In a 150 cubic centimeter beaker, dissolve 5 grams of the steel in 60 cubic centimeters of the hydrochloric acid, add small portions of nitric acid, specific gravity 1.42, to oxidize the iron, avoiding an excess, and heat to expel the oxides of nitrogen. Cool, and transfer the solution into an 8-ounce separatory funnel, rinsing the beaker with small portions of the hydrochloric acid. Add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off lower clear solution into another separatory funnel. Add 10 cubic centimeters of hydrochloric acid, specific gravity 1.20, to the solution in the first separatory funnel, shake thoroughly, allow to settle for 1 minute, and then draw off the lower clear solution into the second separatory funnel. To the combined solution in the second separatory funnel add 50 cubic centimeters of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the clear layer into a 150 cubic centimeter beaker. Heat the aqueous solution gently to expel the ether, evaporate to approximately one-fourth original volume, add

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[2] *Circular No. 40*, Bureau of Standards, Oct. 1, 1912.

0.5 gram of potassium chlorate and boil down to a volume of 10 cubic centimeters. Add 25 cubic centimeters of hydrochloric acid, specific gravity 1.20, and again evaporate to 10 cubic centimeters. Add 20 cubic centimeters of sulphuric acid, specific gravity 1.84, and evaporate until copious fumes of sulphuric acid are evolved. Cool, dilute with water to 100 cubic centimeters volume, and titrate against the standard potassium permanganate to a pink color permanent for 10 seconds. Deduct the chromium blank and the remainder is equivalent to the vanadium content of the steel.

NOTE.

If much chromium relative to the vanadium is present the result will be high due to the oxidation of a portion of the chromium by the permanganate, and should be corrected by a blank which varies with the amount of the chromium present. This blank is conveniently made by putting a suitable amount of a chrome or chrome-nickel steel, free from vanadium, through the above process. By using varying amounts of this steel, so as to vary the chromium correspondingly, a curve may be constructed showing the relation between amount of chromium present and the amount of blank, and this curve can then be used in all subsequent work.

SILICO-MANGANESE STEEL.

Determination of Carbon.

See the Determination of Carbon in Plain Carbon Steel by the Direct Combustion Method.[1]

Determination of Manganese.

See the Determination of Manganese in Plain Carbon Steel by the Bismuthate Method.

See the Determination of Manganese in Plain Carbon Steel by the Persulphate Method (Routine).

Determination of Phosphorus.

See the Determination of Phosphorus in Plain Carbon Steel by the Molybdate Magnesia Method.

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[1] Standard Methods for Chemical Analysis of Plain Carbon Steel (Serial Designation: A 33), 1915 Year-Book, p. 201.

See the Determination of Phosphorus in Plain Carbon Steel by the Alkalimetric Method (Routine).

Determination of Sulphur.

See the Determination of Sulphur in Plain Carbon Steel by the Oxidation Method.

See the Determination of Sulphur in Plain Carbon Steel by the Evolution-Titration Method (Routine).

NOTES.

The Evolution-Titration Method should not be used with steels containing appreciable amounts of tungsten, or of copper or other metals precipitated by hydrogen sulphide from acid solutions.

The annealing of the steel drillings has been found by a number of investigators to increase the degree of refinement of the method.

Determination of Silicon.

See the Determination of Silicon in Plain Carbon Steel by the Nitro-Sulphuric Method.

See the Determination of Silicon in Plain Carbon Steel by the Sulphuric Acid Method (Optional).

CONVERSION TABLE USED IN WATER ANALYSIS.

		Factor			Factor
Na_2O	to Na_2SO_4	2.29	AgCl	to Cl	0.247
SO_3	“ “	1.775	$CaCO_3$	“ CO_2	0.439
Cl	“ NaCl	1.6486	$MgCO_3$	“ CO_2	0.521
NaCl	“ Na_2O	0.53028	Na_2SO_4	“ Na_2O	0.4366
Na_2O	“ NaCl	1.8858	CaO	“ $CaCl_2$	1.9777
Na_2O	“ Na_2CO_3	1.71	CaO	“ $CaSO_4$	2.4
CaO	“ $CaCO_3$	1.7844	$CaSO_4$	“ CaO	0.412
MgO	“ $MgCO_3$	2.1	Na_2CO_3	“ CO_2	0.415
SO_3	“ $CaSO_4$	1.7	SO_3	“ $CaSO_4$	1.7005
SO_3	“ $MgSO_4$	1.5	CaO	“ $CaCO_3$	1.7844
Cl	“ $CaCl_2$	1.563	NgO	“ $NgCO_3$	2.0912
MgO	“ $MgCl_2$	2.4	Na_2O	“ NaCl	1.8858
Cl	“ $MgCl_2$	1.34	Cl	“ NaCl	1.6486
MgO	“ Mg	0.6	$CaCO_3$	“ CO_2	0.4396
MgO	“ $MgSO_4$	3.0	$MgCO_3$	“ CO_2	0.5218
$CaSO_4$	“ $CaCO_3$	0.736	NaCl	“ Na	0.3934
$Mg_2P_2O_7$	“ MgO	0.36	Na	“ Na_2O	1.3478
$BaSO_4$	“ S	0.137	Na_2O	“ Na	0.7419
$BaSO_4$	“ SO_3	0.343	MgO	“ Mg	0.603
			Mg	“ MgO	1.657

TABLES FOR CALCULATING ANALYSIS.

Sought	Found	Factor	Log
Ag	AgBr	0.5744	.75924
	AgCl	0.7527	.87665
	Ag_2S	0.8707	.93986
Al	Al_2O_3	0.5303	.72455
As	As_2S_3	0.6093	.78480
	As_2S_5	0.4834	.68431
	$(NH_4MgAsO_4)_2.H_2O$	0.3938	.59528
	$Mg_2As_2O_7$	0.4828	.68375
	$Mg_2P_2O_7$	0.6736	.82837
	$BaSO_4$	0.2141	.33070
As_2O_3	As_2S_3	0.8042	.90538
	As_2S_5	0.6381	.80489
	$(NH_4MgAsO_4)_2.H_2O$	0.5198	.71586
	$Mg_2As_2O_7$	0.6373	.80433
	$Mg_2P_2O_7$	0.8891	.94895
	$BaSO_4$	0.2827	.45128
As_2O_5	As_2S_3	0.9342	.97044
	As_2S_5	0.7412	.86995
	$(NH_4MgAsO_4)_2.H_2O$	0.6038	.78092
	$Mg_2As_2O_7$	0.7403	.86939
	$Mg_2P_2O_7$	1.0328	.01401
	$BaSO_4$	0.3284	.51634
AsO_3	As_2S_3	0.9992	.99965
	As_2S_5	0.7928	.89916
	$(NH_4MgAsO_4)_2.H_2O$	0.6458	.81013
	$Mg_2As_2O_7$	0.7918	.89860
	$Mg_2P_2O_7$	1.1046	.04322
	$BaSO_4$	0.3512	.54555
AsO_4	As_2S_3	1.1291	.05275
	As_2S_5	0.8959	.95226
	$(NH_4MgAsO_4)_2.H_2O$	0.7298	.86323
	$Mg_2As_2O_7$	0.8947	.95170
	$Mg_2P_2O_7$	1.2483	.09632
	$BaSO_4$	0.3969	.59865
Ba	$BaCO_3$	0.6961	.84266
	$BaCrO_4$	0.5420	.73401
	$BaSO_4$	0.5886	.76981
	$BaSiF_6$	0.4906	.69077
$BaCO_3$	$BaCrO_4$	0.7787	.89135
$Ba(NO_3)_2$	$BaCrO_4$	1.0314	.01342
BaO	$BaCO_3$	0.7771	.89049
	$BaCrO_4$	0.6051	.78184
	$BaSO_4$	0.6571	.81764
	$BaSiF_6$	0.5478	.73860
Be	BeO	0.3626	.55937
Bi	Bi_2O_3	0.8968	.95269
	BiOCl	0.8019	.90414
	Bi_2S_3	0.8125	.90985
Br	AgBr	0.4255	.62895

TABLES FOR CALCULATING ANALYSIS.—(*Continued*)

Sought	Found	Factor	Log
C	CO_2	0.2727	.43573
CN	AgCN	0.1944	.28860
CO_2	$CaCO_3$	0.4394	.64289
	CaO	0.7839	.89425
	MgO	1.0902	.03750
CO_3	CO_2	1.3636	.13470
Ca	$CaCO_3$	0.4008	.60291
	CaO	0.7149	.85427
	$CaSO_4$	0.2947	.46932
$CaCO_3$	$CaSO_4$	0.7352	.86641
CaO	CO_2	1.2757	.10575
	$CaCO_3$	0.5606	.74864
	$CaSO_4$	0.4121	.61505
	$CaSO_4.2H_2O$	0.3259	.51312
$CaSO_4$	$BaSO_4$	0.5833	.76588
Cd	CdO	0.8754	.94220
	CdS	0.7779	.89090
	$CdSO_4$	0.5391	.73166
CdO	CdS	0.8886	.94870
Ce	Ce_2O_3	0.8539	.93139
	CeO_2	0.8140	.91064
Cl	Ag	0.3285	.51650
	AgCl	0.2473	.39315
Co	Co_3O_4	0.7344	.86595
	$CoSO_4$	0.3804	.58024
CoO	Co	1.2712	.10421
	$CoSO_4$	0.4837	.68456
Cr	Cr_2O_3	0.6847	.83550
	$PbCrO_4$	0.1613	.20776
Cr_2O_3	$PbCrO_4$	0.2356	.37226
CrO_3	Cr_2O_3	1.3153	.11902
	$PbCrO_4$	0.3099	.49128
CrO_4	Cr_2O_3	1.5255	.18341
	$PbCrO_4$	0.3595	.55567
Cs	Cs_2SO_4	0.7344	.86596
Cu	CuO	0.7990	.90255
	Cu_2S	0.7987	.90238
$CuFeS_2$	Cu_2S	2.3056	.36279
Cu_2O	CuO	0.8995	.95400
CuO	Cu	1.2516	.09745
	Cu_2S	0.9996	.99983
$CuSO_4.5H_2O$	Cu	3.9267	.59403
	Cu_2S	3.1362	.49641
Er	Er_2O_3	0.9737	.94136
F	CaF_2	0.4870	.68756

TABLES FOR CALCULATING ANALYSIS.—(*Continued*)

Sought	Found	Factor	Log
Fe	Fe_2O_6	0.6996	.84482
FeO	Fe	1.2863	.10935
	Fe_2O_6	0.8999	.95417
Fe_2O_3	Fe	1.4295	.15518
	$FePO_4$	0.5294	.72375
FeS_2	Fe_2O_6	1.5022	.17674
H	H_2O	0.119	.04869
HBr	AgBr	0.4309	.63439
HCl	AgCl	0.2543	.40532
HJ	AgJ	0.5448	.73626
HNO_3	NH_4Cl	1.1781	.07117
	$(NH_4)_2PtCl_6$	0.2842	.45363
	NO	2.0989	.32199
	Pt	0.6473	.81113
H_2SO_4	$BaSO_4$	0.4201	.62331
Hg	HgCl	0.8493	.92904
	HgS	0.8617	.93535
J	AgJ	0.5405	.73282
	PdJ_2	0.7046	.84795
K	KCl	0.5248	.71999
	$KClO_4$	0.2825	.45097
	K_2PtCl_6	0.1612	.20730
	K_2SO_4	0.4491	.65231
	Pt	0.4019	.60417
K_2O	KCl	0.6320	.80074
	$KClO_4$	0.3402	.53172
	K_2PtCl_6	0.1941	.28805
	K_2SO_4	0.5408	.73306
	Pt	0.4841	.68492
K_2SO_4	$BaSO_4$	0.7468	.87318
La	La_2O_3	0.8527	.93078
Mg	MgO	0.6036	.78073
	$Mg_2P_2O_7$	0.2188	.33999
$MgCO_3$	$Mg_2P_2O_7$	0.7576	.87945
MgO	$Mg_2P_2O_7$	0.3625	.55926
Mn	Mn_3O_4	0.7205	.85764
	$Mn_2P_2O_7$	0.3873	.58807
	MnS	0.6315	.80034
$MnCO_3$	Mn_3O_4	1.5066	.17798
MnO	Mn_3O_4	0.9301	.96854
	MnS	0.8152	.91124
Mo	MoO_3	0.6667	.82391
	MoS_2	0.5996	.77788
N	NH_4Cl	0.2623	.41885
	$(NH_4)_2PtCl_6$	0.06329	.80131
	Pt	0.1441	.15881
	NH_3	0.8235	.91566

TABLES FOR CALCULATING ANALYSIS.—(*Continued*)

Sought	Found	Factor	Log
NH_3	NH_4Cl	0.3177	.50346
	$(NH_4)_2PtCl_6$	0.07690	.88592
	Pt	0.1752	.24342
NH_4	NH_4Cl	0.3376	.52844
	$(NH_4)_2PtCl_6$	0.08145	.91090
	Pt	0.1855	.26840
NO_3	NH_4Cl	1.1592	.06415
	$(NH_4)_2PtCl_6$	0.2796	.44661
	NO	2.0652	.31497
	Pt	0.6370	.80411
N_2O_5	NH_4Cl	1.0097	.00430
	$(NH_4)_2PtCl_6$	0.2436	.38666
	NO	1.7990	.25502
	Pt	0.5548	.74416
Na	NaCl	0.3940	.59551
	Na_2SO_4	0.3243	.51092
Na_2O	NaCl	0.5308	.72490
	Na_2SO_4	0.4368	.64031
Ni	NiO	0.7858	.89532
NiO	Ni	1.2726	.10468
P	$Mg_2P_2O_7$	0.2784	.44467
	$(NH_4)_3PO_4.12MoO_3$	0.01639	.21448
	$P_2O_5.24MoO_2$	0.01723	.23633
P_2O_5	$Mg_2P_2O_7$	0.6376	.80457
	$(NH_4)_3PO_4.12MoO_3$	0.03753	.57438
	$P_2O_5.24MoO_3$	0.03947	.59623
PO_4	$Mg_2P_2O_7$	0.8532	.93103
	$(NH_4)_3PO_4.12MoO_3$	0.05022	.70084
	$P_2O_5.24MoO_3$	0.05281	.72269
P_2O_5	P	2.3	.36172
Pb	$PbCrO_4$	0.6405	.80654
	PbO	0.9282	.96765
	PbO_2	0.8660	.93754
	PbS	0.8658	.93743
	$PbSO_4$	0.6829	.83438
PbO	$PbCrO_4$	0.6901	.83889
	PbO_2	0.9330	.96989
	PbS	0.9328	.96978
	$PbSO_4$	0.7357	.86673
PbS	$PbSO_4$	0.7888	.89695
Rb	Rb_2SO_4	0.6402	.80633
S	$BaSO_4$	0.1373	.13769
SO_3	$BaSO_4$	0.3429	.53515
SO_4	$BaSO_4$	0.4114	.61427
Sb	Sb_2O_4	0.7898	.89749
	Sb_2S_3	0.7142	.85382
	Sb_2S_5	0.5999	.77811

TABLES FOR CALCULATING ANALYSIS.—(*Continued*)

Sought	Found	Factor	Log
Sb_2O_3	Sb_2O_4	0.9475	.97656
	Sb_2S_3	0.8568	.93289
	Sb_2S_5	0.7198	.85718
Sb_2S_3	Sb_2O_4	1.1058	.04367
SeO_2	Se	1.4040	.14737
SeO_3	Se	1.6061	.20576
Si	SiO_2	0.4702	.67228
SiO_3	SiO_2	1.2649	.10205
Si_2O_7	SiO_2	1.3973	.14530
SiO_4	SiO_2	1.5298	.18463
Sn	SnO_2	0.7881	.89657
Sr	$SrCO_3$	0.5936	.77350
	$SrCO_4$	0.4771	.67859
$SrCO_3$	$Sr(NO_3)_2$	0.6973	.84344
	$Sr(OH)_2.8H_2O$	0.5555	.74468
	SrS	1.2334	.09111
	SrS_2O_3	0.7391	.86869
$Sr(OH)_2.8H_2O$	$Sr(NO_3)_2$	1.2553	.09876
	$Sr(SH)_2$	1.7283	.23762
	SrS_2O_3	1.3305	.12401
$SrSO_4$	$BaSO_4$	0.7868	.89584
TeO_2	Te	1.2508	.09718
TeO_3	Te	1.3762	.13867
Th	$Th(NO_3)_4 4H_2O$	0.4207	.62393
	ThO_2	0.8790	.94399
Ti	TiO_2	0.6007	.77866
U	$Na_2U_2O_7$	0.7511	.87568
	UO_2	0.8817	.94532
	U_3O_8	0.8482	.92852
W	WO_3	0.7931	.89933
Y	Y_2O_3	0.7876	.89631
Zn	ZnO	0.8035	.90496
	ZnS	0.6710	.82675
ZnO	ZnS	0.8352	.92179
ZnS	ZnO	1.1973	.07821
$ZnSO_4.7H_2O$	ZnO	3.5329	.54813
	ZnS	2.9507	.46992
Zr	ZrO_2	0.7390	.86864

GAS FACTORS.

Grams per M3 × 43.7 = grains per 100 cubic feet.

Grams per M3 × 0.437 = grains per cubic foot.

Grains per cubic foot × 2.288 = grams per M3.

Grains per 100 cubic feet × 0.02288 = grams per M3.

Grams per cubic foot × 35.31 = grams per M3.

Grams benzine per M3 × 0.0088 = gallons per 1,000 cubic feet.

1 M3 of gas at 0° C. and 760 millimeters = 1.05505 M3 at 15° C. and 760 millimeters.

1 M3 of gas at 0° C. and 760 millimeters = 1.0734 M3 at 20° C. and 760 millimeters.

1 M3 of gas at 15° C. and 760 millimeters = 0.94782 M3 at 0° C. and 760 millimeters.

1 M3 of gas at 20° C. and 760 millimeters = 0.93162 M3 at 0° C. and 760 millimeters.

Vapor tension divided by total pressure = percentage by volume of vapor in saturated gas.

22.37 liters of any true gas or vapor, at 0° C. and 760 millimeters pressure, has a weight in grams equal to its molecular weight. Hence it follows that the molecular weight of any gas or vapor divided by 22.37 gives the weight in kilos of a cubic meter of that gas.

Gas at 0° C. × 1.367 = volume at 100° C.

LINEAR EQUIVALENTS.

Mm.	Cm.	Meter	Inch	Foot	Yard	Mile
1.	0.1	0.001	0.03937	0.00328	0.00109	
10.	1.	0.01	0.393700	0.03280	0.01093	
1,000.	100.	1.	39.3700	3.28083	1.093611	
25.4001	2.5400	0.02540	1.	0.08333	0.02778	
304.801	30.4801	0.304801	12.	1.	0.33333	
914.402	91.4402	0.914402	36.	3.	1.	0.0005681
1,609,344.	160,934.	1,609.3	63,360.	5,280.	1,760.	1.
		1,000.				0.62137

VOLUME EQUIVALENTS.

Meter	Liter	Cu. cm.	Cu. yd.	Cu. ft.	Cu. in.	Gal.	Lbs. H_2O @ 15° C.
1.	1,000.	1,000,000.	1.308	35.314	61,022.	264.17	2,202.
0.001	1.	1,000.	0.0013	0.03531	61.022	0.2642	2.202
0.000001	0.001	1.	0.0000013	0.000035	0.06102	0.00026	0.00022
0.7645	764.5	764,500.	1.	27.	46,656.	201.97	1,684.
0.02832	28.317	28,317.	0.03704	1.	1,728.	7.4805	62.37
0.000016	0.0164	16.388	0.0000215	0.00058	1.	0.00433	0.03608
0.003785	3.785	3,785.	0.00495	0.13368	231.	1.	8.331
0.000457	0.4569	456.92	0.000594	0.016038	27.716	0.1200	1.

1 liquid ounce = 29.57 cubic centimeters.
1 liquid quart = 0.9463 liter. 1 liter = 1.0567 liquid quarts.
1 dry quart = 1.101 liters. 1 liter = 0.908 dry quart.
1 peck = 8.81 liters. 1 liter = 1.135 pecks.
1 bushel = 35.24 liters. 1 hectoliter = 2.8375 bushels.
1 cubic centimeter H_2O at 4° C. weighs 1 gram.
1 liter H_2O at 4° C. weighs 1 kilogram.
Grams per liter × 58.4 = grains per gallon.

SURFACE EQUIVALENTS.

Sq. Mm.	Sq. Cm.	Sq. Meter	Sq. inch	Sq. Foot	Sq. yard	Sq. Mile	Acre
1.	0.01	0.000001	0.00155	0.0000108			
100.	1.	0.0001	0.15500	0.00108	0.000119		
1,000,000.	10,000.	1.	1,550.00	10.7638	1.1960		
645.16	6.4516	0.000645	1.	0.00694	0.00077		
92,903.6	929.036	0.09290	144.	1.	0.11111		
	8,361.27	0.83613	1,296.	9.	1.		0.000206
		2,588,881.			3,097,600.	1.	640.
		4,046.869		43,560.	4,840.	0.00156	1.

GRAVIMETRIC EQUIVALENTS.

Gram.	Kg.	Oz.	Lbs.	Tons
1.	0.001	0.03527	0.0022046	0.0000011
1,000.	1.	35.2736	2.2746	0.0011023
28.350	0.028350	1.	0.0625	0.00003125
453.60	.453600	16.	1.	0.0005
907,180.	907.18	32,000.	2,000.	1.
	1,000.			1.1023 = .9842 gross ton.

1 grain T. or A. = 0.0648 grams. 1 gram = 15.432 grains Troy.
1 oz. T. = 31.1035 grams. 1 gram = 0.03215 oz. Troy.
1 lb. Troy = 0.3732 kilograms. 1 kilogram = 2.679 lbs. Troy.

PRESSURE EQUIVALENTS.

Pounds per square inch	Ounces per inch	Square feet water	Inches water	Centimeters water	Inches Kerosene	Centimeter Kerosene	Inches mercury	Centimeters mercury
1.	16.	2.309	27.71	70.48	35.08	89.20	2.04	5.19
0.063	1.	0.144	1.732	4.405	2.19	5.575	0.127	0.325
0.433	6.928	1.	12.	30.36	15.12	38.56	0.888	2.259
0.036	0.576	0.083	1.	2.53	1.26	3.188	0.074	0.187
0.014	0.224	0.033	0.393	1.	0.496	1.26	0.029	0.074
0.028	0.448	0.064	0.79	2.03	1.	2.53	0.058	0.147
0.011	0.17	0.026	0.311	0.79	0.393	1.	0.023	0.058
0.490	7.84	1.13	13.59	34.38	17.20	43.41	1.	2.53
0.190	3.04	0.441	5.299	13.59	6.742	17.20	0.392	1.

1 pound per square inch = 0.0703 kilos per square centimeter. 1 kilo per square centimeter = 14.2232 pounds per square inch.

1 pound per square foot = 4.8825 kilos per square meter. 1 kilo per square meter = 0.2048 pound per square foot.

1 gross ton per square foot = 10.937 metric tons per square meter. 1 metric ton per square meter = 0.091 gross ton per square foot.

1 atmosphere = 14.72 pounds per square inch = 1.0333 kilos per square centimeter.

Kerosene = specific gravity 0.79 (approx. 0.8).

760 millimeters mercury = 14.71 pounds pressure per square inch = 29.94 inches mercury = 33.52 feet water.

30 inches mercury = 761.9 millimeters mercury.

A TABLE OF CONSTANTS FOR CERTAIN GASES AND VAPORS
The United Gas Improvement Company

All volumes of gases and vapors are given at 60° F. and 30″ pressure. The temperature of products of combustion is reduced to 18° C. = 64.4° F.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Name of gas or vapor	Formula	Molecular weight	Sp. Gravity gas or vapor at 60° F air = 1.0	Boiling point ° Fahr.	Sp. gravity liquid at 60° F. w'ter = 1.0	Sp. heat eq. wts. at const. pt. w'ter = 1.0	Cubic feet per pound	Weight 1 cubic foot in pounds	Heat of combustion		
									Calories per molecular wt. in grams	British thermal units	
										Per cu. ft.	Per lb.
Carbon to CO	* C_2	24	0.8292	. . . . .	. . . . .	. . . . .	15.749	0.06350	29,000	276.2	4,350
Carbon to CO_2	* C_2	24	0.8292	. . . . .	. . . . .	. . . . .	15.749	0.06350	96,960	923.5	14,544
Carbonic Oxide	CO	28	0.9671	. . . . .	. . . . .	0.2450	13.503	0.07407	67,960	323.5	4,368
Hydrogen	H_2	2	0.0692	. . . . .	. . . . .	3.4090	188.620	0.00530	68,360	326.2	61,523
Methane	Paraffine series C_nH_{2n+2} CH_4	16	0.5529	. . . . .	. . . . .	0.5929	23.626	0.04234	211,930	1,009.0	23,838
Ethane	C_2H_6	30	1.0368	. . . . .	. . . . .	. . . . .	12.594	0.07940	370,440	1,764.4	22,226
Propane	C_8H_{80}	44	1.5206	—13°	. . . . .	. . . . .	8.587	0.11645	529,210	2,521.0	21,651
Butane	C_4H_{12}	58	2.0045	+33°	. . . . .	. . . . .	6.514	0.15350	687,190	3,274.0	21,326
Pentane	C_5H_{14}	72	2.4883	+100°	0.6273	. . . . .	5.248	0.19055	847,110	4,035.6	21,177
Hexane	C_6H_1	86	2.9721	+156°	0.6640	. . . . .	4.393	0.22760	959,200	4,759.8	20,914
Ethylene	Olefin series C_nH_{2n} C_2H_4	28	0.9676	. . . .	. . . .	0.4040	13.495	0.07410	333,350	1,588.0	21,430
Propylene	C_8H_6	42	1.4514	. . . . .	. . . . .	. . . . .	8.997	0.11115	492,740	2,347.2	21,120
Butylene	C_4H_8	56	1.9353	+23°	. . . . .	. . . . .	6.747	0.14820	650,620	3,099.2	20,913
Amylene	C_5H_{10}	70	2.4191	+102°	0.6511	. . . . .	5.398	0.18525	807,630	3,847.2	20,767
Acetylene	Acetylene series C_nH_{2n-2} C_2H_2	26	0.8984	. . . . .	. . . . .	. . . . .	14.534	0.06880	310,050	1,476.7	21,465
Allylene	C_8H_4	40	1.3823	. . . . .	. . . . .	. . . . .	9.447	0.10585	467,550	2,227.1	21,040
Crotonylene	C_4H_6	54	1.8661	+64°	. . . . .	. . . . .	6.998	0.14290	. . . . . .	. . . . .	. . . . .
Benzene	Aromatic Series C_nH_{2n-6} C_6H_6	78	2.6953	+177°	0.8846	0.3754	4.845	0.20640	799,350	3,807.5	18,447
Toluene	C_7H_8	92	3.1792	+230°	0.8720	. . . . .	4.107	0.24345	955,680	4,552.0	18,699
Xylene	C_8H_{10}	106	3.6630	+287°	0.8692	. . . . .	3.565	0.28050	. . . . . .	. . . . .	. . . . .
Mesitylene	C_9H_{12}	120	4.1468	+326°	. . . . .	. . . . .	3.149	0.31755	1,282,310	6,108.0	19,235
Naphthalene	$C_{10}H_8$	128	4.4230	+424.4°	1.1517	. . . . .	2.952	0.33870	. . . . . .	. . . . .	. . . . .
Hydrogen Sulphide	H_2S	34	1.1769	. . . . .	. . . . .	0.2423	11.096	0.09012	140,900	672.2	7,459
Ammonia	NH_3	17	0.5888	. . . . .	. . . . .	0.5083	22.178	0.04509	90,650	432.8	9,598
Hydrocyanic acid	HCN	27	0.9348	. . . . .	. . . . .	. . . . .	13.968	0.07159	158,620	757.0	10,575
Cyanogen	C_2N_2	52	1.8000	. . .	. . . . .	. . . . .	7.258	0.13779	259,620	1,238.2	8,986
Carbon Bi-Sulphide	CS_2	76	2.6298	+114.8°	. . . . .	. . . . .	4.965	0.20139	265,130	1,264.6	6,279
Methyl Alcohol	CH_4O	32	1.1121	+131.2°	0.8027	. . . . .	11.742	0.08516	182,230	872.9	10,250
Ethyl Alcohol	C_2H_6O	46	1.5894	+172.9°	0.7946	1.4534	8.216	0.12172	340,530	1,622.0	13,325
Carbonic Acid	CO_2	44	1.5195	. . . . .	. . . . .	0.2163	8.593	0.11637	. . . . . .	. . . . .	. . . . .
Water	H_2O	18	0.6217	+212°	1.0000	0.4805	21.004	0.04761	. . . . . .	. . . . .	. . . . .
Sulphur Dioxide	SO_2	64	2.2128	. . . . .	. . . . .	0.1553	5.901	0.16945	. . . . . .	. . . . .	. . . . .
Oxygen	O_2	32	1.1052	. . . . .	. . . . .	0.2174	11.816	0.08463	. . . . . .	. . . . .	. . . . .
Nitrogen	N_2	28	0.9701	. . . . .	. . . . .	0.2438	13.460	0.07429	. . . . . .	. . . . .	. . . . .
Air	. . . .	. . . .	1.0000	. . . . .	. . . . .	0.2374	13.059	0.07658	. . . . . .	. . . . .	. . . . .

*Calculated for C_2 as a gas.

A TABLE FOR CONSTANTS OF CERTAIN GASES AND VAPORS.—(*Continued.*)

The United Gas Improvement Company

All volumes of gases and vapors are given at 60° F. and 30″ pressure. The temperature of products of combustion is reduced to 18° C. = 64.4 F.

XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXVII	XXIII	XXIV	XXV	XXVI
Cu. ft. per cu. ft. of combustible					Pounds per pound of combustible					Heat of formation at const. pres.			Name of gas or vapor
Req. for combust'n		Products of combustion			Req. for combust'n		Products of combustion			Calories per molecular wt. in grams	B. T. U.		
Air	Oxygen	CO_2	H_2O		Air	Oxygen	CO_2	H_2O			Per cu. ft.	Per pound	
4.785	1.0	....	....	CO—2.0	5.771	1.333+	....	...	CO—2.333+	......	......	......	Carbon, to CO
9.570	2.0	2.0	....	.....	11.541	2.666+	3.666+	...	......	......	......	......	Carbon, to CO_2
2.393	0.5	1.0	....	.....	2.471	0.571	1.571	...	......	......	+138.4	+1869.2	Carbonic Oxide
2.393	0.5	....	1.0	.....	34.624	8.000	....	9,000	......	......	......	......	Hydrogen
9.570	2.0	1.0	2.0	.....	17.312	4.000	2.750	2.250	......	+21,750	+103.1	+2435.6	Methane
16.748	3.5	2.0	3.0	.....	16.156	3.733	2.933	1.800	......	+28,560	+136.0	+1713.6	Ethane
23.925	5.0	3.0	4.0	.....	15.737	3.636	3.000	1.636	......	+35,110	+167.2	+1436.3	Propane
31.103	6.5	4.0	5.0	.....	15.520	3.586	3.034	1.552	......	+42,450	+202.2	+1317.3	Butane
38.280	8.0	5.0	6.0	.....	15.386	3.555	3.055	1.500	......	+47,850	+227.9	+1196,2	Pentane
45.458	9.5	6.0	7.0	.....	15.295	3.534	3.069	1.465	......	+61,080	+290.9	+1278.4	Hexane
14.355	3.0	2.0	2.0	.....	14.836	3.428	3.142	1.286	......	—2,710	—12.9	—174.2	Ethylene
21.533	4.5	3.0	3.0	.....	14.836	3.428	3.142	1.286	......	+3,220	+15.3	+138.0	Propylene
28.710	6.0	4.0	4.0	.....	14.836	3.428	3.142	1.286	......	+10,660	+50.7	+342.6	Butylene
35.888	7.5	5.0	5.0	.....	14.836	3.428	3.142	1.286	......	+18,970	+113.7	+614.1	Amylene
11.963	2.5	2.0	1.0	.....	13.313	3.076	3.384	0.692	......	—47,770	—227.5	—3300.7	Acetylene
19.140	4.0	3.0	2.0	.....	13.850	3.200	3.300	0.900	......	—39,650	—188.8	—1784.2	Allylene
26.318	5.5	4.0	3.0	.....	14.105	3.259	3.259	1.300	......	......	......	......	Crotonylene
35.888	7.5	6.0	3.0	.....	13.313	3.076	3.384	0.692	......	—12,510	—47.3	—229.3	Benzene
43.065	9.0	7.0	4.0	.....	13.547	3.130	3.348	0.782	......	—3,520	—16.7	—68.8	Toluene
53.240	10.5	8.0	5.0	.....	13.720	3.170	3.311	0.849	......	......	......	......	Xylene
57.420	12.0	9.0	6.0	.....	13.850	3.200	3.300	0.900	......	+490	+2.3	+7.3	Mesitylene
57.420	12.0	10.0	4.0	.....	12.984	3.000	3.437	0.563	......	......	......	......	Naphthalene
7.178	1.5	....	1.0	SO_2—1.0	6.111	1.412	....	0.529	SO_2—1.883	+4,740	+22.6	+250.9	Hydrogen Sulphide
3.589	0.75	...	1.5	N—0.5	6.111	1.412	....	1.588	N—0.823	+11,890	+56.7	+1259.0	Ammonia
5.981	1.25	1.0	0.5	N—0.5	6.410	1.481	1.630	0.333	N—0.518	—27,480	—131.1	—1832.0	Hydrocyanic Acid
9.570	2.0	2.0	....	N—1.0	5.323	1.230	1.692	...	N—0.538	—65,700	—313.2	—2273.9	Cyanogen
14.355	3.0	1.0	....	SO_2—2.0	5.466	1.263	0.579	...	SO_2—1.684	—26,010	—124.0	—616.0	Carbon Bi-Sulphide
7.178	1.5	1.0	2.0	.....	6.492	1.500	1.375	1.125	......	+51,450	+246.4	+2894.0	Methyl Alcohol
14.355	3.0	2.0	3.0	.....	9.033	2.087	1.913	1.174	......	+58,470	+278.5	+2288.0	Ethyl Alcohol
.....	.....	....	....	.....	.....	.....	....	...	......	......	+463.1	+3979.1	Carbonic Acid
.....	.....	....	....	.....	.....	.....	....	...	......	......	+327.1	+6870.4	Water
.....	.....	....	....	.....	.....	.....	....	...	......	......	+337.3	+1999.1	Sulphur Dioxide
.....	.....	....	....	.....	.....	.....	....	...	......	......	......	......	Oxygen
.....	.....	....	....	.....	.....	.....	....	...	......	......	......	......	Nitrogen
.....	.....	....	....	.....	.....	.....	....	...	......	......	......	......	Air

AUTHORITIES AND METHODS OF CALCULATION

In column IX the figures given in Hempel's "Gas Analysis," p. 375, were selected for the fundamental weight of oxygen, nitrogen, hydrogen, carbonic oxide and air.

The formula used for the conversion to English units is,—grams per liter at 0° C. and 760 mm. + 0.05922 = pounds per cu. ft. at 60° F. and 30″ pressure. The derivation of the factor employed is

$$0.05922 = \frac{28.316 \times 0.0022046 \times 30.00 \times 492}{29.92 \times 520}$$

The weights of the compound gases are calculated from these data by Avogadro's law.

Column IV is calculated by the formula: $\text{sp. gr.} = \dfrac{\text{wt. 1 cu. ft. gas}}{\text{wt. 1 cu. ft. air}}$, and the figures thus obtained agree with the theoretical formula,

$$\text{sp. gr.} = \frac{\text{mol. wt.}}{28.94}$$

Columns V and VI are taken chiefly from Lunge's "Coal Tar and Ammonia."

Column VII is from Ganot's "Physics," edition 1896, page 445.

Columns X and XXIII are from Julius Thomsen's "Thermochemical Investigations," and his results are translated into English units in columns XI–XII and XXIV–XXV.

Columns XIII and XVIII are calculated on the assumption that

air = 20.9% oxygen + 79.1% nitrogen *by volume.*
air = 23.13% oxygen + 76.87% nitrogen *by weight.*

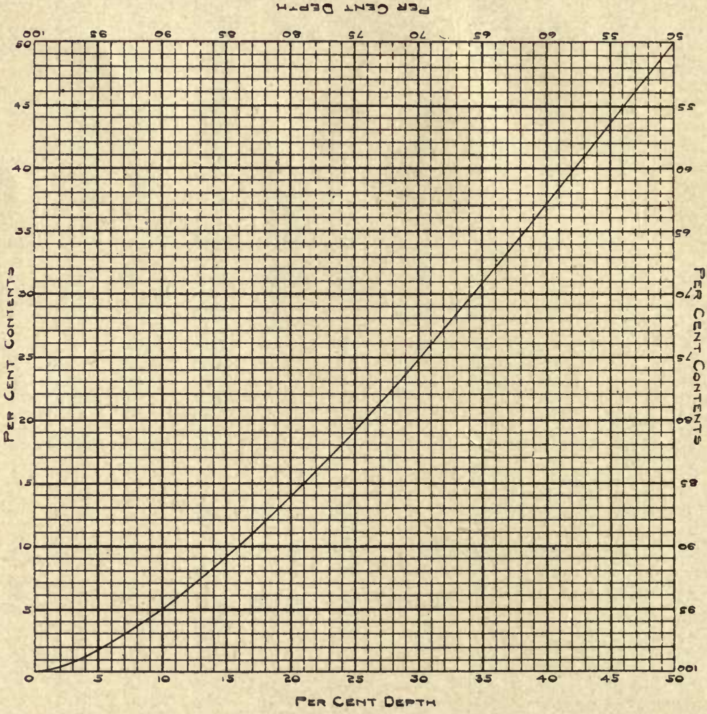
Comparison of Degrees Baumé with Specific Gravity, American Standard, for Liquids Lighter than Water. Sp. gr. ± $\frac{140}{1.30 + B°}$ at 60° F.

Deg. Baumé	Specific gravity									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
10	1.0000	0.9993	0.9986	0.9979	0.9972	0.9964	0.9957	0.9950	0.9943	0.9936
11	0.9929	0.9922	0.9915	0.9908	0.9901	0.9894	0.9887	0.9880	0.9873	0.9886
12	0.9859	0.9852	0.9845	0.9838	0.9831	0.9825	0.9818	0.9811	0.9804	0.9997
13	0.9790	0.9783	0.9777	0.9770	0.9763	0.9756	0.9749	0.9743	0.9736	0.9729
14	0.9722	0.9715	0.9709	0.9702	0.9695	0.9689	0.9682	0.9675	0.9669	0.9662
15	0.9655	0.9649	0.9642	0.9635	0.9629	0.9622	0.9615	0.9609	0.9602	0.9596
16	0.9589	0.9582	0.9576	0.9569	0.9563	0.9556	0.9550	0.9543	0.9537	0.9530
17	0.9524	0.9517	0.9511	0.9505	0.9498	0.9492	0.9485	0.9479	0.9472	0.9466
18	0.9459	0.9453	0.9447	0.9440	0.9434	0.9428	0.9421	0.9415	0.9409	0.9402
19	0.9396	0,9390	0.9383	0.9377	0.9371	0.9365	0.9358	0.9352	0.9346	0.9340
20	0.9333	0.9327	0.9321	0.9315	0.9309	0.9302	0.9296	0.9290	0.9284	0.9278
21	0.9272	0.9265	0.9259	0.9253	0.9247	0.9241	0.9235	0.9229	0.9223	0.9217
22	0.9211	0.9204	0.9198	0.9192	0.9186	0.9180	0.9174	0.9168	0.9162	0.9156
23	0.9150	0.9144	0.9138	0.9132	0.9126	0.9121	0.9115	0.9109	0.9103	0.9097
24	0.9091	0.9085	0.9079	0.9073	0.9067	0.9061	0.9056	0.9050	0.9044	0.9038
25	0.9032	0.9026	0.9021	0.9015	0.9009	0.9003	0.8997	0.8992	0.8986	0.8980
26	0.8974	0.8969	0.8963	0.8957	0.8951	0.8946	0.8940	0.8934	0.8929	0.8923
27	0.8917	0.8912	0.8906	0.8900	0.8895	0.8889	0.8883	0.8878	0.8872	0.8866
28	0.8861	0.8855	0.8850	0.8844	0.8838	0.8833	0.8827	0.8822	0.8816	0.8811
29	0.8805	0.8799	0.8794	0.8788	0.8783	0.8777	0.8772	0.8766	0.8761	0.8755
30	0.8750	0.8745	0.8739	0.8734	0.8728	0.8723	0.8717	0.8712	0.8706	0.8701
31	0.8696	0.8690	0.8685	0.8679	0.8674	0.8669	0.8663	0.8658	0.8653	0.8647
32	0.8642	0.8637	0.8631	0.8626	0.8621	0.8615	0.8610	0.8605	0.8600	0.8594
33	0.8589	0.8584	0.8578	0.8573	0.8568	0.8563	0.8557	0.8552	0.8547	0.8542
34	0.8537	0.8531	0.8526	0.8521	0.8516	0.8511	0.8505	0.8500	0.8495	0.8490
35	0.8485	0.8480	0.8475	0.8469	0.8464	0.8459	0.8454	0.8449	0.8444	0.8439
36	0.8434	0.8429	0.8424	0.8418	0.8413	0.8408	0.8403	0.8398	0.8393	0.8388
37	0.8383	0.8378	0.8373	0.8368	0.8363	0.8358	0.8353	0.8348	0.8343	0.8338
38	0.8333	0.8328	0.8323	0.8318	0.8314	0.8309	0.8304	0.8299	0.8294	0.8289
39	0.8284	0.8279	0.8274	0.8269	0.8264	0.8260	0.8255	0.8250	8.8245	0.8240
40	0.8235	0.8230	0.8226	0.8221	0.8216	0.8211	0.8206	0.8202	0.8197	0.8192
41	0.8187	0.8182	0.8178	0.8173	0.8168	0.8163	0.8159	0.8154	0.8149	0.8144
42	0.8140	0.8135	0.8130	0.8125	0.8121	0.8116	0.8111	0.8107	0.8102	0.8097
43	0.8092	5.8088	0.8083	0.8078	0.8074	0.8069	0.8065	0.8060	0.8055	0.8051
44	0.8046	0.8041	0.8037	0.8032	0.8028	0.8023	0.8018	0.8014	0.8009	0.8005
45	0.8000	0.7995	0.7991	0.7986	0.7982	0.7977	0.7973	0.7968	0.7964	0.7959
46	0.7955	0.7950	0.7946	0.7941	0.7937	0.7832	0.7928	0.7923	0.7919	0.7914
47	0.7910	0.7905	0.7901	0.7896	0.7892	0.7887	0.7883	0.7878	0.7874	0.7870
48	0.7865	0.7861	0.7856	0.7852	0.7848	0.7843	0.7839	0.7834	0.7830	0.7826
49	0.7821	0.7817	0.7812	0.7808	0.7804	0.7799	0.7795	0.7791	0.7786	0.7782
50	0.7778	0.7773	0.7769	0.7765	0.7761	0.7756	0.7752	0.7748	0.7743	0.7739
51	0.7735	0.7731	0.7726	0.7722	0.7718	0.7713	0.7709	0.7705	0.7701	0.7697
52	0.7692	0.7688	0.7684	0.7680	0.7675	0.7671	0.7667	0.7663	0.7659	0.7654
53	0.7650	0.7646	0.7642	0.7638	0.7634	0.7629	0.7625	0.7621	0.7617	0.7613
54	0.7609	0.7605	0.7600	0.7596	0.7592	0.7588	0.7584	0.7580	0.7576	0.7572
55	0.7568	0.7563	0.7559	0.7555	0.7551	0.7547	0.7543	0.7539	0.7535	0.7531
56	0.7527	0.7523	0.7519	0.7515	0.7511	0.7507	0.7503	0.7500	0.7495	0.7491
57	0.7487	0.7483	0.7479	0.7475	0.7471	0.7467	0.7463	0.7459	0.7455	0.7451
58	0.7447	0.7443	0.7439	0.7435	0.7431	0.7427	0.7423	0.7419	0.7415	0.7411
59	0.7407	0.7403	0.7400	0.7396	0.7392	0.7388	0.7384	0.7380	0.7376	0.7372
60	0.7368	0.7365	0.7361	0.7357	0.7353	0.7349	0.7345	0.7341	0.7338	0.7334
61	0.7330	0.7326	0.7322	0.7318	0.7315	0.7311	0.7307	0.7303	0.7299	0.7295
62	0.7292	0.7288	0.7284	0.7280	0.7277	0.7273	0.7269	0.7265	0.7261	0.7258
63	0.7254	0.7250	0.7246	0.7243	0.7239	0.7235	0.7231	0.7228	0.7224	0.7220
64	0.7216	0.7213	0.7209	0.7205	0.7202	0.7198	0.7194	0.7191	0.7187	0.7183
65	0.7179	0.7176	0.7172	0.7168	0.7165	0.7161	0.7157	0.7154	0.7150	0.7147
66	0.7143	0.7139	0.7136	0.7132	0.7128	0.7125	0.7121	0.7117	0.7114	0.7110
67	0.7107	0.7103	0.7099	0.7096	0.7092	0.7089	0.7085	0.7081	0.7078	0.7074
68	0.7071	0.7067	0.7064	0.7060	0.7056	0.7053	0.7049	0.7046	0.7042	0.7039
69	0.7035	0.7032	0.7028	0.7025	0.7021	0.7018	0.7014	0.7011	0.7007	0.7004
70	0.7000	0.6997	0.6995	0.6990	0.6986	0.6983	0.6979	0.6976	0.6972	0.6969
71	0.6965	0.6962	0.6958	0.6955	0.6951	0.6948	0.6944	0.6941	0.6938	0.6934
72	0.6931	0.6927	0.6924	0.6920	0.6917	0.6914	0.6910	0.6907	0.6903	0.6900
73	0.6897	0.6893	0.6890	0.6886	0.6883	0.6880	0.6876	0.6873	0.6869	0.6866
74	0.6863	0.6859	0.6856	0.6853	0.6849	0.6846	0.6843	0.6839	0.6836	0.6833
75	0.6829	0.6826	0.6823	0.6819	0.6816	0.6813	0.6809	0.6806	0.6803	0.6799
76	0.6796	0.6793	0.6790	0.6786	0.6783	0.6780	0.6776	0.6773	0.6770	0.6767
77	0.6763	0.6760	0.6757	0.6753	0.6750	0.6747	0.6744	0.6740	0.6737	0.6734
78	0.6731	0.6728	0.6724	0.6721	0.6718	0.6715	0.6711	0.6708	0.6705	0.6702
79	0.6699	0.6695	0.6692	0.6689	0.6686	0.6683	0.6679	0.6676	0.6673	0.6670
80	0.6667									

CONVERSION TABLE FOR CONVERTING $BaSO_4$ TO SULPHUR.

Mgs. of $BaSO_4$	Milligrams of Sulphur									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0 8	0.9
0	0.00	0.01	0.02	0.03	0.04	0.06	0.08	0.010	0.011	0.012
1	0.14	0.15	0.17	0.18	0.19	0.21	0.22	0.23	0.25	0.26
2	0.28	0.29	0.30	0.32	0.33	0.34	0.36	0.37	0.39	0.40
3	0.41	0.43	0.44	0.45	0.47	0.48	0.49	0.51	0.52	0.53
4	0.55	0.56	0.58	0.59	0.60	0.62	0.63	0.65	0.66	0.67
5	0.68	0.70	0.72	0.73	0.74	0.76	0.77	0.78	0.80	0.81
6	0.82	0.84	0.85	0.86	0.88	0.89	0.91	0.92	0.93	0.95
7	0.96	0.98	0.99	1.00	1.02	1.03	1.04	1.06	1.07	1.09
8	1.10	1.11	1.13	1.14	1.16	1.17	1.18	1.20	1.21	1.23
9	1.24	1.25	1.27	1.28	1.29	1.31	1.32	1.33	1.35	1.36
10	1.37	1.39	1.40	1.42	1.43	1.44	1.46	1.47	1.49	1.50
11	1.51	1.53	1.54	1.55	1.57	1.58	1.59	1.61	1.62	1.64
12	1.65	1.66	1.68	1.69	1.70	1.72	1.73	1.75	1.76	1.77
13	1.79	1.80	1.81	1.83	1.84	1.86	1.87	1.88	1.90	1.91
14	1.92	1.94	1.95	1.97	1.98	1.99	2.01	2.02	2.03	2.05
15	2.06	2.08	2.09	2.10	2.12	2.13	2.15	2.16	2.17	2.19
16	2.20	2.21	2.23	2.24	2.26	2.27	2.28	2.30	2.31	2.32
17	2.34	2.35	2.37	2.38	2.39	2.41	2.42	2.44	2.45	2.46
18	2.48	2.49	2.51	2.52	2.53	2.55	2.56	2.57	2.59	2.60
19	2.61	2.63	2.64	2.66	2.67	2.68	2.70	2.71	2.73	2.74
20	2.75	2.77	2.78	2.79	2.81	2.82	2.84	2.85	2.86	2.88
21	2.89	2.90	2.92	2.93	2.95	2.96	2.97	2.99	3.00	3.01
22	3.03	3.04	3.06	3.07	3.08	3.10	3.11	3.12	3.14	3.15
23	3.16	3.18	3,19	3.21	3.22	3.23	3.25	3.26	3.27	3.29
24	3.30	3.32	3.33	3.34	3.36	3.37	3.39	3.40	3.41	3.43
25	3.44	3.45	3.47	3.48	3.49	3.51	3.52	3.54	3.55	3.56
26	3.58	3.59	3.61	3.62	3.63	3.65	3.66	3.67	3.69	3.70
27	3.71	3.73	3.74	3.76	3.77	3.78	3.80	3.81	3.82	3.84
28	3.85	3.87	3.88	3.89	3.91	3.92	3.94	3.95	3.96	3.98
29	3.99	4.00	4.02	4.03	4.05	4.06	4.07	4.09	4.10	4.11
30	4.13	4.14	4.15	4.17	4.18	4.19	4.21	4.22	4.24	4.25
31	4.26	4.28	4.29	4.30	4.32	4.33	4.35	4.36	4.37	4.39
32	4.40	4.41	4.43	4.44	4.46	4.47	4.48	4.50	4.51	4.52
33	4.54	4.55	4.57	4.58	4.59	4.61	4.62	4.63	4.65	4.66
34	4.68	4.69	4.70	4.72	4.73	4.75	4.76	4.77	4.79	4.80
35	4.81	4.83	4.84	4.86	4.87	4.88	4.90	4.91	4.92	4.94
36	4.93	4.97	4.98	4.99	5.01	5.02	5.03	5.05	5.06	5.08
37	5.09	5.10	5.12	5.13	5.15	5.16	5.17	5.19	5.20	5.22
38	5.23	5.24	5.26	5.27	5.28	5.30	5.31	5.33	5.34	5.35
39	5.37	5.38	5.39	5.41	5.42	5.44	5.45	5.46	5.48	5.49
40	5.50	5.52	5.53	5.55	5.56	5.57	5 59	5.60	5.61	5.63
41	5.64	5.66	5 67	5.68	5.70	5.71	5.72	5.74	5.75	5.77
42	5.78	5.79	5.81	5.82	5.83	5.85	5.86	5.87	5.89	5.90
43	5.92	5.93	5.94	5.96	5.97	5.98	6.00	6.01	6.03	6.04
44	6.05	6.07	6.08	6.09	6.11	6.12	6.14	6.15	6.16	6.18
45	6.19	6.20	6.22	6.23	6.26	6.26	6.27	6.29	6.30	6.31
46	6.33	6.34	6.36	6.37	6.38	6.40	6.41	6.42	6.44	6.45
47	6.47	6.48	6.49	6.51	6.52	6.53	6.55	6.56	6.58	6.59
48	6.60	6.62	6.63	6.64	6.66	6.67	6.69	6.70	6.71	6.73
49	6.74	6.75	6.77	6.78	6.80	6.81	6.82	6.84	6.85	6.86
50	6.88	6.89	6.90	6.92	6.93	6.94	6.96	6.97	6.99	7.00
51	7.01	7.03	7.04	7.05	7.07	7.08	7.10	7.11	7.12	7.14
52	7.15	7.16	7.18	7.19	7.20	7.22	7.23	7.25	7.26	7.27
53	7.29	7.30	7.31	7.33	7.34	7.36	7.37	7.38	7.40	7.41
54	7.43	7.44	7.45	7.47	7.48	7.49	7.51	7.52	7.54	7.55
55	7.56	7.58	7.59	7.60	7.62	7.63	7.64	7.66	7.67	7.69
56	7.70	7.71	7.73	7.74	7.76	7.77	7.78	7.80	7.81	7 82
57	7.84	7.85	7.87	7.88	7.89	7.91	7.92	7.94	7.95	7.96
58	7 98	7.99	8.01	8.02	8.03	8.05	8.06	8.08	8.09	8.10
59	8.12	8.13	8.14	8.15	8.17	8.19	8.20	8.21	8.23	8.24
60	8.26	8.27	8.28	8.30	8.31	8.32	8.34	8.35	8.37	8.38
61	8.39	8.41	8.42	8.43	8.45	8.46	8.48	8.49	8,50	8.51
62	8.53	8.55	8.56	8.57	8.59	8.60	8.61	8.63	8.64	8.66
63	8.67	8.68	8.70	8.71	8.73	8.74	8.75	8.77	8.78	8.79
64	8.81	8.82	8.84	8.85	8.86	8.88	8.89	8.90	8.92	8.93
65	8.95	8.96	8.97	8.99	9.00	9.02	9.03	9.04	9.06	9.07
66	9.09	9.10	9.11	9.13	9.14	9.15	9.17	9.18	9.20	9.21
67	9.22	9.24	9.25	9.27	9.28	9.29	9.31	9.32	9.33	9.35
68	9.36	9.38	9.39	9.40	9.42	9.43	9.45	9.46	9 47	9.49
69	9.50	9.52	9.53	9.54	9.57	9.57	9.59	6.60	9.61	9.62
70	9.63	9.64	9.66	9.67	9.68	9.70	9.71	9.73	9.74	9.75
71	9.77	9.78	9.80	9.81	9.82	9.84	9.85	9.86	9.88	9.89
72	9.91	9.92	9.93	9.95	9.96	9.98	9.99	10.00	10.02	10.03

CURVE FOR CALCULATING ULLAGES OF CYLINDRICAL TANKS WITH CURVED HEADS IN HORIZONTAL POSITION.



INTERNATIONAL ATOMIC WEIGHTS.

Revision of 1915

As Published by the American Chemical Society.

Name of element	Symbol	Atomic Weight	Name of element	Symbol	Atomic Weight
Aluminum	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	102.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (Radium emanation	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Calcium	Cs	40.07	Platinum	Pt	195.2
Caesium	Ca	132.81	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140 25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysrosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulfur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Holmium	Ho	163.5	Thorium	Th	232.4
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	119.0
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.5
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.10	Ytterbium (Neoytterbium	Yb	172.0
Lithium	Li	6.94	Yttrium	Yt	89.0
Lutecium	Lu	174.0	Zinc	Zn	65.37
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Maganese	Mn	54.93			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

INDEX.

SH