tions subsequent to development are very liable to develop still further any sub-microscopic reticulation, and again to coarsen the "grain" of the image. It is hoped to follow this up experimentally when time permits, instruments having been devised for measuring both granularity and minute swellings.

In Fig. XI are given photomicrographs of some of the reticulated preparations described, taken with vertical illumination at 100 diameters.

RESEARCH LABORATORY
EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

LABORATORY AND PLANT

METHODS OF ANALYSIS USED IN THE COAL-TAR INDUSTRY. I—CRUDE TAR

By J. M. WEISS
Received July 20, 1918

INTRODUCTION

In April 1911, S. R. Church¹ published a paper which described in some detail the analytical methods as used by The Barrett Company at that time. This was supplemented by a later paper in 1913,² giving certain revisions and additions which had been made up to that time. These methods, with others, have been in use in the laboratories of The Barrett Company and many other companies for an extended period and have been given the test of continued use. Some of the methods have been the subject of exhaustive investigations to determine the variants which limit the accuracy of the tests. For instance, J. M. Weiss presented a paper³ dealing with the "free carbon" tests on tars and pitches and the factors influencing the results, together with some theoretical consideration of the material known as "free carbon." There have also been numerous publications on the testing of tar products, emanating from various sources, such as the Office of Public Roads, the U. S. Department of Agriculture, the American Society for Testing Materials, the American Gas Institute, etc., and also from many individuals, but we do not intend to present here a bibliography of the literature on coal-tar product methods of analysis, but merely to indicate under a few of the tests published the main sources from which we have drawn.

About a year and a half ago, we realized that the directions of our testing methods were more or less incomplete in detail and that in many cases important points were left unemphasized. Accordingly, a chemists' committee was formed, consisting of S. R. Church, F. J. Gerty, J. B. Hill, K. B. Howell, H. E. Lloyd, J. G. Miller, M. R. Walczak, and the writer, whose purpose it was to revise and standardize the existing tests. A description of each test was prepared by one or another of the committee and sent for comment to each member of the committee, a majority of whom were actual laboratory workers of long experience. The comments were compiled and, where necessary, experimental work was instituted to settle points which were in dispute. The methods were not put into final form until the committee was substantially unanimous regarding all the details of the methods.

We are presenting in this paper a selected list of methods which we believe are of very general interest

to all engaged in the manufacture or use of coal-tar products. This paper will be followed by three others, one dealing with the methods of test for refined tars and pitches, another with methods of test for creosote oils and carbolic oils, and the last, benzols and light oils.

Many of the tests are widely used throughout the country and have been adopted by a majority of the producers and consumers of tar products. A number of these tests are the standard methods of such associations as the American Railway Engineering Association, American Society for Testing Materials, etc. We are presenting them in the belief that it will be helpful to those engaged in the testing of tar products to have these standard methods collected together in compact form convenient for reference. The illustrations are mainly assembly drawings, but the special apparatus can now be obtained through almost any apparatus house. We have furnished detailed plans and specifications of all our special laboratory apparatus to every chemical glassware manufacturer and laboratory supply house of whom we were cognizant.

For each test on which we have carried out sufficient exhaustive research, to enable us to do so, we have made a statement as to its accuracy.

SAMPLING

Before considering the tests in detail a few words on sampling would not be out of place.

The sole practical purpose of laboratory testing or analysis is to obtain information as to the composition, quality, and properties of a given material. Usually, this material is in large bulk. To make the desired test on the entire bulk of material would obviously be impracticable as well as necessitating frequently the destruction of the material. It therefore becomes necessary to select from the bulk of a material, a portion or sample of same, which shall be representative of the entire bulk and which can be tested and its properties determined. Obviously, the interest and commercial values attach to the properties and qualities of the bulk of material and only to the properties and qualities of the sample as far as the sample is representative of the bulk. It is therefore necessary to take every possible precaution to see that the sample is *in every case representative*. The laboratory methods, apparatus, and technique may be perfect and the results recorded may be accurate as to the quality of the sample tested. If, however, that sample is not representative of the bulk, the value of the test is commercially nil. The entire theory of sampling is therefore based on the principle

¹ THIS JOURNAL, 3 (1911), 227.

² *Ibid.*, 5 (1913), 195.

³ *Ibid.*, 6 (1914), 279.

of obtaining a sample which shall be and remain representative.

Materials may be grouped as homogeneous and heterogeneous. A homogeneous material is a material which is uniform in quality and composition throughout. A heterogeneous material is one which varies in quality or composition throughout. There is, of course, no such thing as a perfectly homogeneous material, except in the cases of pure chemical compounds, true solutions, and mixtures of perfect gases. Obviously, a sample taken from any part of a homogeneous material will be representative of the entire bulk. Sampling of homogeneous materials therefore becomes a relatively simple matter.

LIQUIDS—The sampling of liquids presents a somewhat more difficult problem. Where the liquid is thin, non-viscous, and does not contain immiscible constituents, a homogeneous condition usually exists, and a sample from any part of the bulk is usually representative of the whole. Where, however, viscous or immiscible materials are present, the constitution is usually heterogeneous.

Most of the liquids handled by the coal-tar chemist fall into this latter class. In such cases, great care must be taken to obtain thoroughly representative samples. While it is impossible to set absolute standards as to the methods of sampling these materials, the following methods represent good practice.

METHOD I—A $1\frac{1}{2}$ in. sampling pipe shall be inserted in the line through which the oil is being pumped, on the discharge side of the pump, preferably in a rising section of the pipe line. This sampling pipe shall extend half way to the center of the main pipe and with the inner open end of the sampling pipe turned at an angle of 90° and facing the flow of the liquid. This pipe shall be provided with a plug cock and shall discharge into a receiver of 50 to 100 gal. capacity. The plug cock shall be so adjusted that, with a steady continuous flow of the oil, the receiver shall be filled in the time required to pump the entire shipment. The receiver shall be provided with a steam coil sufficient to keep the contents at a temperature not exceeding 120° F. Immediately upon completion of the pumping, the contents of the receiver shall be very thoroughly agitated and a duplicate 1 qt. sample taken immediately for the test. The amount of the drip sample collected shall be not less than 1 gal. for each 1000 gal. of oil handled, except in the case of large boat shipments, where a maximum of 100 gal. is sufficient. Care must be taken that the bleed cock does not shut off partially or entirely during the pumping. It is necessary to insure a *uniform flow* of material throughout.

METHOD II—Where the material to be sampled is handled by gravity flow, Method I can frequently be employed by inserting a drip sampler into the end of the discharge nipple. Where this is for any reason impracticable, an alternate method, II, consists in taking dipperful samples at *frequent* and *regular* intervals, from the open stream. These dipperful samples should be combined in a covered receiver. The combined gross sample should be not less than 0.1

per cent of the whole material of which the sample is representative. The combined gross sample should be placed in a receiver, in which the material can be kept fluid, and stirred thoroughly to homogeneous consistency. Small samples may then be taken for analysis.

While it is preferable to take a sample of material during passage through a pipe or in gravity flow, it is also necessary to take samples of materials while at rest, as in storage tanks, mixing tanks, etc. In such cases, Method III or IV shall be employed.

METHOD III—Small bottles weighted with metal should be fitted with tight stoppers to which strings are attached. The bottle shall be lowered to a fixed depth into the liquid, whereupon the cork shall be pulled from the bottle by the string and the bottle allowed to fill with material. After sufficient time for the filling of the bottle, it is pulled up. A cut of a suitable arrangement in use at several of our plants is shown in Fig. I.

FIG. 1

Bottled samples should be taken from a sufficient number of different depths in the liquid to insure obtaining a combined sample which is representative of the whole. The combined sample should then be agitated and a similar sample taken from it for analysis. In case the cross-sectional area of the container

varies throughout the vertical depth of the liquid, a number of samples should be taken at different levels, the number at each level being proportional to the cross-sectional areas at such levels.

In tank cars for all ordinary cases we recommend that samples be taken from three zones, *viz.*, the top foot section of the car, the middle foot section, and the bottom foot section. These should be combined in various proportions depending on the diameter of the car. We recommend that composite samples be made up as shown in the following table:

Diam. of car Feet	Zone	Proportionate weight to be given sample
6	Top	11
	Middle	25
	Bottom	11
7	Middle	1
	Bottom	2
	Bottom	1
8	Top	1
	Middle	3
	Bottom	1

Of course, if free water is present in large amount, this should be noted separately and care be taken not to include it in the samples taken.

METHOD IV—Many storage tanks, particularly large ones, are equipped with sample cocks along the side of the tank and arranged at one-foot intervals. After taking samples by this method an equal amount is drawn from each cock and the samples thoroughly mixed before the final laboratory sample is taken. (This, of course, assumes that the tank is one of uniform cross section.) In taking a sample by this means, the nipple from each cock shall extend at least 6 in. inside from the shell of the tank and the operator shall allow sufficient material to flow through the cock to clear the line before taking his final sample. We would caution the operator, however, that samples from the side of the tank should not be taken too close to the bottom of the tank. This will avoid inclusion of the sediment normally present in the bottom of the tank.

SOLIDS—Solids are almost always heterogeneous in constitution. It is impossible to advise definite and arbitrary methods for obtaining samples. Each case must be worked out for itself, bearing in mind the particular conditions in the case. It is usually preferable to take samples during the unloading of cars or the transit of the material in conveyors. In such cases, a number of small samples should be taken at *frequent* and *regular* intervals from the material in transit and these samples combined to form a representative combined sample.

Occasionally, solids are tested as received, in bags or barrels. In such cases, it is desirable to take a small sample from every *n*th bag or barrel combining same to obtain the representative combined sample.

Generally, samples taken from the bulk, in piles or cars, are unreliable and not representative. Where it is necessary to take such samples before the unloading of the car, small samples should preferably be taken from at least twelve spots throughout the bulk and these small samples collected to form the representative combined sample.

In taking such small samples, it is desirable to take 8 samples from the corners of the car, 4 near the bottom, and 4 near the top of the material. To these should be added 4 samples from the center of the car, 2 from the top, and 2 from the bottom of the material.

The combined representative sample taken by any of the above methods should be in amount at least 0.1 per cent of the total bulk of material sampled. These combined samples should be carefully mixed and reduced in size to a convenient laboratory sample, by the standard method of quartering. In carrying out this quartering, a hard clean surface should be selected, free from cracks and protected from rain, snow, wind, and beating sun. Do not let cinders, sand, chips from floor, or any other material get into the sample. Protect the sample from loss or gain in moisture. The combined sample should be carefully mixed, spread out on this surface into a circular layer and divided into four equal quadrants. Two opposite quadrants should be combined to form the representative reduced sample. If this sample is still too large for laboratory purposes, the quartering operation shall be repeated. In this manner, the sample shall finally be reduced to a size suitable of handling by the laboratory.

GENERAL PRECAUTIONS—Scarcely second in importance to the necessity of obtaining a representative sample, is the necessity of preventing the composition or property of the sample from changing during handling or storage prior to laboratory analysis. Some materials are very hygroscopic and must be kept in tightly stoppered bottles to prevent absorption of moisture. This is particularly true of dry felt, lime, and finely divided mineral materials. Other materials are volatile and must be kept in tightly closed cans or bottles to prevent loss of their lighter constituents.

A great many samples are taken of hot materials in process of distillation where the high temperature has produced a high vapor pressure which will cause considerable loss of the more volatile constituents when exposed to the atmosphere. Usually in the case of these materials, the volatilization of oil is apparent by the vapor rising from the liquid and becoming condensed in the cold atmosphere to a cloud. In the case of some of the lower-boiling materials, however, a high vapor pressure is produced at moderately low temperatures and a volatilization of the sample is continually going on, although this may not be so apparent by reason of the fact that the vapors from this material are not readily condensed in the atmosphere.

It is, therefore, particularly desirable to watch the sampling of such materials carefully and make sure that the sample is kept in a tightly covered container until it has cooled to a point where it exhibits an inappreciable vapor pressure.

CRUDE TAR TESTS

TEST B2—WATER

APPARATUS—Copper still, 6 in. by 3½ in. Ring burner to fit still. Connecting tube. Condenser

trough. Condenser tube. Separatory funnel. Thermometer, 0°–250° C. See Fig. II.

FIG. II

METHOD—Fifty cc. of coal-tar naphtha or light oil shall be measured in a 250 cc. graduated cylinder. 200 cc. of the tar to be tested shall be added. The contents shall be transferred to the copper still, the cylinder shall be washed with 100–150 cc. more of naphtha, and the washings added to the contents of the still. The lid and clamp shall be attached, using a paper gasket, and the apparatus set up as shown in Fig. II. The condenser trough shall be filled with water. Heat shall be applied by means of the ring burner, and distillation continued until the vapor temperature has reached 205° C. (401° F.). The distillate shall be collected in the separatory funnel, in which 15 to 20 cc. of benzol have been previously placed. This effects a clean separation of the water and oil. The reading shall be made after twirling the funnel and allowing to settle for a few minutes. The percentage shall be figured by volume.

PRECAUTIONS—When fresh supplies of naphtha or light oil are obtained, they shall be tested to determine freedom from water.

ACCURACY—One-tenth of 1 per cent.

NOTE—For works-control an iron still of the same size and shape as the copper still specified above may be used. Some laboratories omit the use of the thermometer and judge when the water is off by the appearance of the distillate. These variations must never be applied where check test is required or in case of dispute.

TEST B3—DEHYDRATION (PREPARATION OF DRY TAR)

APPARATUS—Same as Test B2.

METHOD—About 300 to 400 cc. of tar shall be placed in the copper still without the addition of naphtha. The apparatus shall be set up as in Fig. II, except that an ungraduated separatory funnel may replace the special graduated one. The distillation shall be carried on cautiously at first to prevent foaming and continued until the vapor temperature reaches 170° C. (338° F.). Any oil which has distilled over shall be separated from the water (warming sufficiently, if crystals are present, to insure their solution). This separated oil shall be thoroughly mixed back into the residual tar in the still, after the latter has cooled to a

moderate temperature. The dehydrated tar shall be then transferred to a suitable container.

NOTE—A temperature of 170° is used because this is sufficiently high to expel all water from the still. In Test B2 a higher temperature is used to insure flushing out the condenser tube.

TEST B4—SPECIFIC GRAVITY (SPINDLE)

APPARATUS—Hydrometer: special, calibrated against water at 15.5° C. (60° F.), of suitable scale range.

Cylinder: see Fig. II.

METHOD—It is not usually possible to make the test by this method at 15.5° C. (60° F.) as ordinary tars are not sufficiently liquid at this temperature. The cylinder shall be filled with the dry tar (see B3), the latter thoroughly stirred, and the temperature noted. The hydrometer shall be inserted and the reading taken. Care shall be taken that the hydrometer does not touch the sides or bottom of the cylinder and that the surfaces of the tar are free from froth and air bubbles. For every degree centigrade above 15.5° C., at which the test is made, add 0.000685 to the observed reading. (This is equivalent to 0.00038 for every degree Fahrenheit above 60° F.) Unless instructed to the contrary, report results at 15.5° C. (60° F.).

ACCURACY—This method is not recommended as an accurate method. If accuracy is desired, use Test B5 or B6. It is sufficiently accurate for ordinary testing of incoming tar shipments.

NOTE—The hydrometer used, when first obtained, should be standardized.

TEST B5—SPECIFIC GRAVITY (PYCNOMETER)

APPARATUS—Modified Hubbard Bottle (Fig. III).

FIG. III

STANDARDIZATION OF BOTTLE—The bottle shall be weighed empty, filled with water, and held in a bath at 15.5° C. (60° F.) until the volume becomes constant. The water shall then be adjusted to the mark, the bottle dried superficially, and weighed. Each bottle used in the laboratory should be numbered and a

record kept of its weights—empty, and filled to the mark with water at 15.5° C. (60° F.).

METHOD—Tar, dehydrated as under B₃, shall be used. Introduce 10 g. of dry tar into the bottle at 40° to 50° C.; allow to cool and weigh. *Freshly boiled* distilled water shall then be added and the bottle kept in a bath at 15.5° C. (60° F.) until no further volume change takes place. (This usually takes about 30 min.) The water shall then be adjusted to the mark, the bottle dried superficially, and weighed.

Let A = weight of bottle.

B = weight of bottle + water at 15.5° C.

C = weight of bottle + tar

D = weight of bottle + tar + water at 15.5° C.

Then: Sp. gr. at 15.5° C. = $\frac{C - A}{(B - A) - (D - C)}$

PRECAUTIONS—The use of freshly boiled distilled water is essential to accurate results.

ACCURACY—Within 0.003.

NOTE—In exceptional cases tar is very liquid, and, upon the addition of water, partially floats through the water, giving an oily film on the surface. In such cases, do not add water, but fill the bottle with tar, hold at 15.5° C. (60° F.) until the volume becomes constant, adjust to the mark and weigh. The weight of the tar divided by the weight of water necessary to fill the bottle to the mark at 15.5° C. (60° F.) gives the specific gravity.

TEST B6—SPECIFIC GRAVITY (PLATINUM PAN)

APPARATUS—Special platinum pan (Fig. III).

STANDARDIZATION OF PAN—The clean pan shall be ignited, cooled, and suspended by a waxed thread on the left-hand arm of an accurate chemical balance. Its weight in air and its weight in freshly boiled, distilled water at 15.5° C. shall then be noted in the usual way.

METHOD—The clean pan shall be filled with tar and suspended from the balance by the same thread as was used in the standardization. The weight of the pan plus tar should be noted, first in air and second in freshly boiled, distilled water at 15.5° C.

Let A = weight of pan in air

B = weight of pan in water at 15.5° C.

C = weight of pan and tar in air

D = weight of pan and tar in water at 15.5° C.

Then: Sp. gr. at 15.5° C. = $\frac{C - A}{(C - A) - (D - B)}$

PRECAUTION—Allow the pan and tar to remain in water at 15.5° C. for 10 min. before taking the water reading.

ACCURACY—Within 0.003.

TEST B7—INSOLUBLE IN BENZOL (FREE CARBON)

APPARATUS—Extraction flask. Condenser and cover, wire support. See Fig. III. Extraction thimble (prepared by operator¹). Cap of filter paper or alundum.

¹ These shall be made of Whatman No. 50 filter paper. To make a cup, two 15 cm. circles shall be taken and one cut down to a diameter of 14 cm. A round stick about 1 in. in diameter shall be used as a form. The stick shall be placed in the center of the circles of filter paper, the smaller inside, and the papers folded symmetrically around the stick to form a cup about 2½ in. long. A little practice enables the operator to make these evenly and quickly. After being made they shall be soaked in benzol to remove grease due to handling, drained, dried in a steam oven at 97° to 100° C., cooled in a desiccator and kept there until used.

The latter are 30 mm. inside diameter by 14 mm. high. Balance: an ordinary analytical balance accurate to 0.0005 g. Steam bath, water bath, or electric hot plate. Beakers, 100 cc. Carbon filter tubes, 37 mm. size. Weighing bottle, 32 mm. by 70 mm. Camel's hair brush, 14 mm.

METHOD—Tar dried as under B₃ shall be used. After drying, it shall be passed hot through a 30-mesh sieve to remove foreign substances. The amount of tar to be taken for test depends on the content of insoluble material and shall be:

Less than 5 per cent, 10 g.

5 per cent to 20 per cent, 5 g.

Above 20 per cent, 3 g.

If the content of insoluble material cannot be approximated, the larger amount shall be taken. The amount shall be weighed into a 100 cc. beaker and digested with pure toluol at 90° to 100° C. for a period of *not over thirty minutes*. The solution shall be stirred to insure complete digestion. A filter cup prepared as described shall be weighed in a weighing bottle and placed in a filter tube supported over a beaker or flask. The thimble shall be wet with toluol and the toluol-tar mixture decanted through the filter. The beaker shall be washed with toluol until clean, using the camel's hair brush as a policeman to detach solid particles adhering to the beaker. All washings shall be passed through the filter cup. The filter cup shall then be given a washing with pure benzol and allowed to drain. The cap shall then be placed on the cup and the whole placed in the extraction apparatus and extracted with pure benzol until the descending benzol is completely colorless. The cup shall then be removed, the cap taken off, and the cup dried at 97° to 100° C. After drying, it shall be allowed to cool in a desiccator and weighed in the weighing bottle. The increase in weight represents matter insoluble in benzol.

PRECAUTIONS—If the first filtrate shows evidence of insoluble matter, it should be refiltered. The 30-min. period allowed for digestion must not be exceeded.

ACCURACY—5 per cent of insoluble matter present. In other words, with 20 per cent of "free carbon" present, a 1 per cent accuracy may be expected.

NOTE—Where *only approximate* results are desired, tars containing not over 5 per cent of water may be tested without dehydration and the results calculated back to a dry tar basis.

TEST B8—FIXED CARBON¹

APPARATUS—Platinum, Rhotanium, or Palau crucible, 20 cc., standard shape, provided with a tightly fitting cover.

METHOD—Dry tar (see B₃) shall be used. One gram of tar shall be placed in the crucible, the cover applied, and the crucible placed on a platinum, nichrome, or fireclay triangle over a Bunsen burner, with the bottom of the crucible 6 to 8 cm. from the top of the burner. The burner flame shall be regulated to a height of 20 cm. when burning free. The tar

¹ Based on report of Committee on Coal Analysis, *J. Am. Chem. Soc.*, 21 (1899), 1116, *et seq.*

shall be heated gently until the tendency to foam has passed and shall then be exposed to the 20 cm. flame of the burner for 7 min. At the end of this period the flame shall be removed, the crucible transferred to a desiccator, and allowed to cool. The residue in the crucible, less ash, is "fixed carbon."

PRECAUTIONS—The test shall be carried out in a part of the laboratory free from draughts. The upper surface of the crucible cover should be free from carbon at the end of the ignition period.

ACCURACY—1 per cent.

NOTE—The loss on ignition in the above test is called "volatile combustible matter" and may be reported if desired.

TEST B9—ASH

APPARATUS—Open platinum, porcelain, or silica crucible.

METHOD—Tar dried as under B3 shall be used. Weigh 10 g. of tar into the crucible and incinerate to constant weight. The residue in the crucible is ash.

PRECAUTION—The heating shall be conducted so as to avoid foaming at the start or carrying away of ash during the ignition. It should be carried out in a part of the laboratory away from currents of air.

TEST B10—VISCOSITY (ENGLER)

APPARATUS—Engler viscosimeter: A. H. T. 41352; E. & A. 4790, or improved model A. H. T. 41360; E. & A. 4792. The latter type differs from the former in that the inner container is totally immersed in the outer bath and the top of the inner container is double-walled. The outer bath is also larger and provided with a stirrer. It is easier to maintain a uniform temperature with the latter instrument, but with careful temperature regulation identical results are obtained with both instruments. Sugar flasks, 100 cc. Stopwatch.

METHOD—Tar dried as under B3 shall be used. Before use it shall be screened through a 20-mesh wire gauze to remove extraneous matter. The tar shall be heated on a steam bath to approximately the correct temperature before introduction into the viscosimeter. The outer bath shall be kept at a temperature of from 1° to 3° C. above the inner temperature desired. The tar shall be filled in up to the top of the fixed points in the viscosimeter. (This requires approximately 250 cc. of tar.) The tar shall be kept at the proper temperature for 3 min., the plug released, and the time of flow (in seconds) of 100 cc. noted.

PRECAUTIONS—In allowing the material to run from the viscosimeter, it is better to let it impinge on one side of the measuring flask, as this avoids the formation of bubbles and consequent obscurity of the reading. After each test the aperture should be examined to make sure that it is free from obstruction.

The aperture should be cleaned with a soft piece of tissue paper and not with rough twine or any other material which may scratch or damage the aperture.

Up to 80° C., water may be used as the bath in the outside jacket; above this, it is better to use a heavy lubricating oil.

NOTES—The temperature differential to be maintained between the inner and outer baths varies with the temperature of test and the room temperature. The temperature of the inner bath usually drops after the material has flowed out to a point sufficient to uncover the thermometer bulb (more particularly with the old type of Engler viscosimeter), but if the outer bath remains constant, this apparent drop does not affect the results.

Some specifications require the use of 200 cc. In this case use 200 cc. sugar flasks and note the time of flow of 200 cc., otherwise the procedure is the same.

Specific viscosity is sometimes required. This is a ratio and is obtained by dividing the time of flow of the material by the time of flow of an equal volume of water at the same temperature. Unless otherwise stated, the volumes compared should be 200 cc.

TEST B11—SULFUR

APPARATUS—Crucible 50 cc. platinum, nickel, or silica. Usual inorganic, gravimetric, analytical apparatus.

METHOD—One gram of material shall be weighed into the crucible and 1.5 g. of Eschka mixture added. (Eschka mixture consists of 2 parts of pure magnesium oxide and 1 part of pure anhydrous sodium carbonate. The mixture should be light and fluffy.) The tar and Eschka mixture shall be intimately mixed and the crucible placed over a very low Bunsen flame. The crucible shall be set in a round hole in a 6 in. sq. asbestos board so that the flame impinges only on the bottom of the crucible and the products of combustion from the burner are deflected from the open top of the crucible.

The heating of the crucible shall be conducted very slowly until no more fumes are given off. This requires 5 to 6 hrs. The heat shall then be gradually increased and the mixture stirred with a platinum rod or wire until all the carbon particles are burnt off and the mass is white. At the close of the ignition the bottom only of the crucible shall not be more than at a dull red heat. The white residue shall be washed into a beaker with 200 cc. of water, 20 cc. of pure bromine water added, boiled for 5 min., and filtered. The precipitate on the filter shall be washed with boiling water until the filtrate gives no test for bromides with nitric acid, and silver nitrate solution. The filtrate and washings shall be combined, acidified with 5 cc. of pure concentrated hydrochloric acid, and the excess of bromine removed by boiling. 10 cc. of 10 per cent pure barium chloride solution shall then be added drop by drop to the boiling solution and the precipitated barium sulfate allowed to collect and agglomerate by standing in a warm place over night. The barium sulfate shall be filtered out in a Gooch crucible, using suction, washed with hot water until free of chlorides (test with nitric acid and silver nitrate), ignited, cooled in a desiccator, and weighed. From the weight of barium sulfate, deduct the weight obtained in a blank test. (see Notes below) and multiply by 0.13734 to obtain the weight of sulfur.