pumps were driven by steam cylinders with complicated Corliss valve gear.

Coupled with these features was the general lack of knowledge of the volumetric efficiency of such pumps. In contradistinction to the ease with which tests can be run on jet and whirling air pumps, tests on reciprocating pumps require more expensive installation and equipment.

According to the *Industrial World*, 47, No. 16, a new reciprocating pump has been placed on the market by a Pittsburgh firm. This air pump, which is illustrated above, has no mechanically operated valves on the air cylinder, but has instead automatic valves of the multi-ported plate type. There are no flash ports and no large clearance spaces due to such flash ports. It is claimed that the valves require no attention and no oiling; they are said to open and close independent of any adjustment.

The New Mesta Reciprocating Pump was tested for reliability and economy by W. Trinks. His results seem to show that the reciprocating air pump should be used wherever sufficient amount of exhaust steam for feed water heating is available from other sources.

A NEW GAS SCRUBBER

W. R. Heslewood, of Berkeley, Cal., has devised an apparatus for scrubbing flue gases, wherein the scrubbing is effected by water traversing a closed cycle, impelled by a centrifugal pump. The centrifugal pump delivers the water through a nozzle into

a gas case composed of two reducers, bolted together at their large ends and making up the suction line. The water proceeds from the second reducer into an expanding nozzle, from which it is delivered into a tank through a perforated pipe. The centrifugal pump then draws its feed from the same tank. There is suction produced in the gas case by the jet of water, with the result that the flue gases are thereby drawn in, scrubbed and discharged through the holes in the exit pipe. While the

apparatus may be useful for scrubbing out soluble liquids, solids, or gases, it should be determined whether any large amounts of insoluble flue dust would clog the pump and exit holes.

SCIENTIFIC SOCIETIES

PRELIMINARY REPORT FOR THE COMMITTEE ON COAL ANALYSIS OF THE AMERICAN SOCIETY FOR TESTING MATERIALS AND THE AMERICAN CHEMICAL SOCIETY

By W. A. NOYES

INTRODUCTION

Sometime ago committees were appointed by the American Society for Testing Materials and the American Chemical Society for the purpose of revising the standard methods of coal analysis. During the fall of 1911 the two committees were

organized as a joint committee consisting of the following members: W. A. Noyes, *Chairman*, Perry Barker, H. C. Dickinson, A. F. Fieldner, Frank Haas, W. F. Hillebrand, S. W. Parr, S. S. Voorhees, A. H. White.

At the Washington meeting of the American Chemical Society in December, 1911, this committee met and after a careful discussion of the problems to be considered appointed the following sub-committees:

1. Preparation of samples, including loss of moisture in

sampling—Mr. Fieldner, *Chairman*, Haas, Hillebrand, Voorhees, Parr and Barker.

2. Moisture—Dr. Hillebrand, *Chairman*, Fieldner, Parr.

3. Deterioration—Professor Parr, *Chairman*, Fieldner, Haas, Dickinson.

4. Volatile Matter—Professor Parr, *Chairman*, Fieldner, Haas, Dickinson.

5. Fixed Carbon and Ash—Professor Parr, *Chairman*, Fieldner, Hillebrand.

6. Sulfur—Mr. Barker, *Chairman*, Voorhees, Dickinson.

7. Phosphorus—Dr. Hillebrand.

8. Ultimate Analysis—Mr. Fieldner, *Chairman*, Parr, White.

9. Calorimetric Determination—Mr. Dickinson, *Chairman*, Haas, Barker.

10. Interpretation and Computation—Whole Committee.

These sub-committees have been actively at work and at the Milwaukee meeting in March it was decided to publish at the present time a preliminary report of the work of each sub-committee, which it is hoped will furnish the basis for discussion on the part of members of the committee and of others who are interested in the matter, to the end that it may be possible at the Rochester meeting in September to carry the discussion far enough to make it possible to present a final report in the near future. The reports of the sub-committees, which are given below, are in all cases the results of a considerable amount of correspondence and discussion, but it is to be clearly understood that these recommendations are not final and have not been endorsed by the committee as a whole, and indeed in several cases it has not been possible to carry the discussion far enough so that it can be said that the report represents fully the sentiment of the sub-committee. In other words the chairmen are primarily responsible for these reports in their present form.

Every one interested in the subject of coal analysis is earnestly urged to read these reports and to send to the chairman any suggestions which he thinks may be of value to our committee. As an introduction to these reports the following items, which are partly the result of the discussion at Milwaukee, may be mentioned:

It can not be emphasized too strongly that in coal we have an extremely complex mixture of organic compounds, many of which are easily changed by oxidation and otherwise by exposure to the air, and containing water in such condition that a part of it is usually lost with the greatest ease, while the material after complete drying is excessively hygroscopic, probably even more so than calcium chloride. These actual conditions give rise to variations in analysis very far beyond those which most analysts, who have not studied the matter carefully, realize. It has seemed necessary, therefore, to the committee to place rather liberal estimates on the allowable variations in the analysis, and in addition to this we wish to impress it upon every analyst that it is necessary for him to convince himself by personal experiment (1) *that the variations in his own method of procedure do not cause errors greater than the allowable amount, and (2) if possible, that the methods give results which will agree with those of other analysts.*

Sampling.—A committee of The Society for Testing Materials on coal specifications, of which Mr. J. A. Holmes, of the Bureau of Mines, Washington, is chairman, has charge of the questions relating to the sampling of coal under different conditions, in the mine, on cars, in bins, etc. By mutual agreement that committee considers all questions up to the point of furnishing to the laboratory a five-pound sample, which our committee think should be of one-eighth inch size and which, of course, must be submitted in a sealed can under conditions to prevent loss of moisture and deterioration. It was the consensus of opinion at Milwaukee that in the preparation of this five-pound sample at least fifty pounds of coal should be crushed to one-

eighth inch size by a suitable mill. A mill which is suitable for this purpose is sold at a price of \$7.50 by the Enterprise Manufacturing Company, Philadelphia. In sampling and analyzing it is necessary to emphasize again the fact that coal is an extremely changeable substance, that all operations should be carried out as rapidly as possible, and that the analysis should be made as soon as practicable after the sample reaches the laboratory.

Moisture.—It is probably impossible to secure an actually exact determination of the amount of moisture present in coals, especially in those of the bituminous or lignite type, partly because some compounds in the coal decompose readily with loss of water, and partly because of the rather rapid oxidation of such coals when heated in the air. The determination of moisture is, therefore, to be considered as empirical rather than theoretical, and we should strive at conditions that should give concordant results, the agreement of different analysts being of more importance than a determination of the actual amount of moisture in the coal, since the calorific value of the "pure coal" depends on the method of determining moisture in such a manner that it is unimportant whether some of the moisture is counted as moisture or as a part of the coal.

Volatile Matter.—The determination of volatile matter is empirical even to a much greater extent than that of moisture, and here again the point that must be aimed at is to secure conditions which can be accurately reproduced by different analysts. The most important change which seems necessary from the procedure recommended by the committee of the American Chemical Society in 1899 is the application of a gentle heat at first to those lignites which undergo a large mechanical loss if the full heat is applied at once.

Ash.—Practically it is expected that for the present, at least, the ash which will be reported by coal analysts will be that which is found by careful burning of the coal at a temperature finally reaching about 700–750° C. Theoretically, however, the ash should include all substances in the coal other than moisture and organic compounds which are combustible. It seems desirable, therefore, to introduce as a basis for careful work, especially for the calculations of engineers, a "corrected ash" which would include iron pyrites, sulfur, calcium carbonate, calcium sulfate, ferrous sulfate and the water of hydration of clayey matters which is not expelled at 110°.

Calorimetric Determination.—As brought out by Mr. Fieldner, under conditions of actual practice coals are always burned in such a manner that the water escapes as vapor. It is probably not possible at once and perhaps not soon to induce engineers to change their practice of basing their calculations on the calorific value of coals burned to liquid water, but we think that in all cases in the future the statement of calorific values should have appended to it either the words "liquid water" or "vapor of water at 20°."

In conclusion, I wish to express our thanks to many chemists not members of our committee who have coöperated with us and participated in our discussions, especially to H. C. Adams, Horace C. Porter, W. H. Blauvelt, J. D. Davis, William Brady, W. B. Wiley, L. A. Touzalin and A. C. Parsons.

PREPARATION OF LABORATORY SAMPLES

By A. C. FIELDNER, *Chairman*

AMOUNT AND FINENESS OF SAMPLE FOR TRANSMITTAL TO THE LABORATORY

Assuming thorough mixture, accuracy in the reduction of gross samples to a convenient quantity for transmittal to the laboratory, is largely dependent on crushing the extraneous impurities of slate, pyrite, etc., to such a degree of fineness before each process of mixing and dividing, that the inclusion of a few pieces more or less in the various divisions can not materially change the character of the final sample.

That there should be a nearly constant ratio between the largest particle of heaviest impurity and the weight of sample, in the various stages of reduction is essential, otherwise excessive errors are introduced at the particular point in the process where this ratio is exceeded. Hence the quantity of sample to send 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.

Bailey¹ places the following limits beyond which samples should not be divided when crushed to different sizes:

Size of impurities	Minimum weight of sample
2-mesh.....	8300 grams (18.3 lbs.)
4-mesh.....	1100 grams (2.5 lbs.)
8-mesh.....	120 grams

His table is based on a ratio of 0.02 per cent between the weight of the largest pieces of slate and the minimum weight of sample. For the above limits of reduction in the case of samples containing 5 per cent ash as free impurities, Bailey computes the probable error in ash at 0.20 per cent and the maximum possible error occurring once in 10,000 times at 1.00 per cent ash.

Somermeier² gives the following table as a guide in selecting and reducing samples containing pieces of pyrite equivalent to cubes of different sizes:

Size in inches	Weight of sample	
	Grams	oz. or lbs.
1/64.....	1	1/28 ounce
1/32.....	8	2/7 ounce
1/16.....	64	2 2/7 ounces
1/8.....	510	1 1/8 pounds
3/16(a).....	1700	3 3/4 pounds
1/5(a).....	2090	4 3/5 pounds
1/4.....	4090	9 pounds
3/8.....	13700	30 pounds
1/2.....	32700	72 pounds

(a) Interpolated by the writer. Size of openings in 4-mesh sieves vary from 3/16 inch to 1/5 inch, depending on thickness of the wire.

The above table is based on a ratio of 0.019 per cent between the weight of ash resulting from the largest particle of pyrite and the weight of sample.

This ratio according to Somermeier is sufficiently small to keep the error in ash less than 0.5 per cent, provided the sample is thoroughly mixed and properly reduced.

The results of a considerable number of sampling experiments made by the Bureau of Mines indicate that the quantities of sample given in the above table for various sizes of particles are none too large.

The sub-committee, therefore, recommends the following minimum weight of sample for transmittal to the laboratory.

Size of largest impurities	Minimum weight of sample
1/2 inch.....	75 pounds
3/8 inch.....	30 pounds
1/4 inch.....	9 pounds
3/16 to 1/5 inch (a) (4-mesh).....	5 pounds
1/8 inch.....	3 to 5 pounds

(a) The usual 4-mesh screen has openings of 3/16 inch to 1/5 inch in length.

SPECIAL MOISTURE SAMPLES

Unless special crushing and sampling apparatus is available, much moisture is lost during the reduction of the gross sample to the smaller sizes given above. Therefore, when the moisture content is important, a special moisture sample should be accumulated by placing in a hermetically sealed receptacle small parts of the freshly taken increments of the gross sample.³

¹ "Accuracy in Sampling Coal," by E. G. Bailey, *THIS JOURNAL*, **1**, 176 (1909).

² "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 67, McGraw Hill Book Co. (1912).

³ See page 29, *Bull.* **63**, Bureau of Mines, "Sampling Coal Deliveries," by G. S. Pope (1913).

These parts should be broken to about 1/2 inch size as accumulated. If possible, the mixing should be done in the closed receptacle, and an average sample of about 3 pounds quickly transferred to a moisture-tight container for shipment to the laboratory.

Mine samples when reduced in the mine do not require a special moisture sample, owing to the usual high humidity of mine atmospheres.

CONTAINERS FOR SHIPMENT TO LABORATORY

Samples in which the moisture content is important should always be shipped in moisture-tight containers. 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, but require very careful packing to avoid breakage in transit.

Samples in which the moisture content is of no importance need no especial protection from loss of moisture.

PREPARATION OF LABORATORY SAMPLES

The method of preparing a suitable sample for the various analytical determinations that are required in coal analysis must conform as nearly as practicable to the following requirements:

(1) A uniform distribution of coal and impurities must be maintained throughout the process of reducing to the final powdered sample. This should be insured by thorough mixing between each dividing or quartering process, and by having due regard to the ratio of size of largest impurities and weight of sample as given in the preceding tables.

(2) Changes in moisture during the procedure of sampling must be reduced to a minimum.

Coal, especially when in a pulverized condition, is exceedingly susceptible to change in moisture content. The general tendency is loss of moisture on dividing to finer sizes. This may amount to several per cent in coal that has not been previously air-dried.

The equilibrium point of the moisture in pulverized coal varies with the temperature and humidity of the air. Coal that has reached equilibrium with respect to moisture in an atmosphere of low humidity will reabsorb moisture if placed in an atmosphere of higher humidity.¹ Hence to reduce the loss of moisture to a minimum the sample received by the laboratory should be brought to an approximately air-dry condition, before it is pulverized and reduced to the final sample for analysis. Furthermore, the unavoidable exposure of the sample to the air of the sampling room both before and after the air-drying period must be limited to the shortest possible time. The use of an air-tight grinding apparatus such as the ball mill is essential for the final pulverization.

The results² of a considerable number of experiments comparing the ball mill and bucking board at the United States Fuel Testing Plant show that air-dried samples rubbed down on a bucking board may gain or lose moisture, depending on the extent of previous air-drying and the humidity conditions of the sampling room.

If the sample has not been air-dried, or if a ball mill is not available, a special moisture sample should be taken after the coal has been rapidly reduced to 10- or 20-mesh size. The main portion of the sample may then be pulverized and reduced by any suitable apparatus without regard to further moisture changes. The sample obtained by this method will be more susceptible to loss of moisture while weighing out portions for analysis, than air-dried samples. The moisture must, of course, be accurately determined in both samples to bring the calculations to the same wet or dry basis.

¹ For experimental data on moisture changes in coal samples, see *Bull.* **28**, Bureau of Mines, "Experimental Work of the Chemical Laboratory," by N. W. Lord.

² "Experimental Work of the Chemical Laboratory," by N. W. Lord, *Bull.* **28**, Bureau of Mines, and *Bull.* **323**, U. S. Geological Survey.

(3) Due regard must be given to the tendency of coal to absorb oxygen and deteriorate in heating value.

That appreciable quantities of oxygen are absorbed during prolonged air-drying at 35° C. is shown by the following experimental results obtained by H. C. Porter, of the Bureau of Mines.

OXYGEN¹ ABSORBED BY 100 GRAMS OF COARSELY CRUSHED COAL (AS RECEIVED) ON EXPOSURE TO AIR AT 35° C., REPLENISHING THE OXYGEN OF THE AIR INTERMITTENTLY AS ABSORBED

Fresh mine sample of bituminous coal from Pittsburgh bed. Air-drying loss (usual method)=2.5 per cent			Fresh mine sample of sub-bituminous coal from Wyoming. Air-drying loss (usual method)=14.2 per cent		
Days	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentages by weight of oxygen absorbed	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentage by weight of oxygen absorbed	
1.....	43	0.06	81	0.12	
2.....	71	0.10	155	0.22	
3.....	71	0.10	204	0.29	
4.....	87	0.13	264	0.38	
5.....	100	0.14	312	0.45	
6.....	109	..	..	..	
7.....	..	..	377	0.54	
8.....	123	..	419	..	
Correction(a).....	6	—	64	—	
8.....	117	0.17	483	0.70	

(a) Based on analysis of air in container, before and after.

MOISTURE REMOVED DURING TEST

Pittsburgh coal.....	2.46 per cent
Wyoming coal.....	5.27 per cent

"The coal in the above tests was used in the condition as received from the mine sampler, having been crushed by him so as to pass through a 2-mesh screen. The sample was mailed to the laboratory in a galvanized iron can, sealed moisture-tight.

"There are two sources of error in these tests, both of which tend to lessen the oxygen absorption: (1) the coal was in a confined space with no circulation of air, so that the moisture vapor arising from the coal was not displaced by air as readily as in the usual air-drying process; and (2) the normal oxygen content of the air was not maintained constantly, the supply of fresh oxygen being admitted only once in 24 hours.

"The results show, however, that the oxidation error during air-drying at 35° C. may amount in the case of a sub-bituminous coal to at least 0.4 per cent in 4 days and 0.7 per cent in 8 days. The calorific values determined on such an air-dried sample will be in error to a somewhat larger extent, owing to the neutralizing effect of oxygen on the hydrogen and carbon of the coal."

Mine samples of coal crushed to 4 mesh ($\frac{3}{16}$ inch to $\frac{1}{8}$ inch) and spread out to a depth not exceeding 1 inch, in circulating air at 10° C. above room temperature will become approximately air-dry in the following periods of time:

Appalachian coals.....	8 to 24 hours
Illinois and similar coals.....	12 to 48 hours
Sub-bituminous coals and lignites.....	48 to 72 hours

Lignites and some sub-bituminous coals continue to lose moisture over longer periods of time than given above; however, in view of Porter's experiments, the above maximum limits should not be exceeded.

METHODS OF SAMPLING RECOMMENDED BY THE SUB-COMMITTEE

The following alternate methods of preparing laboratory coal samples are recommended as conforming to the theoretical requirements set forth in the preceding paragraphs, and as being commercially practicable for technical coal analysis.

METHOD 1

Samples of coal received by the laboratory which exceed 5

¹ Quoted from private communication from H. C. Porter.

pounds in weight, or 4 mesh (length of openings in sieve not to exceed 0.20 inch) in size should be rapidly crushed to 4 mesh, mixed and reduced to not less than 5 pounds. This portion is then transferred to a weighed sheet-metal pan, spread out to a depth of 1 inch and at once weighed. The pan is placed in a special drier¹ and the coal allowed to air-dry in circulating air at 10° C. to 15° C. above the sampling room temperature, until the rate of moisture loss is less than 0.1 per cent per hour, as shown by two weighings made at intervals of 2 to 4 hours. The time limits already given in this report should not be exceeded. In most cases bituminous coal and anthracite will be air-dry if left in the drier over night.

Immediately after the last weighing has been made, the entire sample should be rapidly pulverized to 10-mesh size, mixed and reduced to 500 grams with an enclosed riffle sampler² whose sub-divisions are not more than $\frac{1}{2}$ inch apart. This 500-gram portion is at once transferred to the porcelain jar (8.95 in diameter and 9.65 inch high) of an Abbé ball mill, sealed air-tight and pulverized to 60-mesh. Bituminous coals require about $\frac{1}{2}$ hour and anthracites about 2 hours to pulverize to 60 mesh.

The jar should contain about one-third of its volume of 1-inch, well rounded flint pebbles, and should be rotated at about 60 revolutions per minute. The coal is removed from the porcelain jar by emptying the contents on a $\frac{1}{2}$ inch screen, which is vigorously shaken a moment to detach the coal from the pebbles. The sample is then reduced to the final laboratory sample of approximately 60 grams by successively halving it with a small, enclosed riffle sampler. All of the final sample should then be put through the 60-mesh sieve, and at once transferred to a 4-ounce wide-mouthed bottle which is securely closed with a well fitting rubber stopper. To avoid moisture change the sieve should be covered while sifting. Usually a few particles of coarse material remain on the sieve. These must be rubbed down on a bucking board or mortar to 60-mesh, and thoroughly mixed with the sample. (If one could be certain that all of each sample would pass the 60-mesh sieve it would be preferable to omit sieving, since it has a tendency to segregate the particles of slate and pyrite and offers an opportunity for change in moisture content. On the other hand, if the sieving is omitted there is great danger of rather coarse particles of slate and pyrite being present in the final sample.) The mixing and reducing of the sample after removal from the ball mill should be done rapidly to minimize loss or absorption of moisture. The total time elapsing from the opening of the ball-mill jar to the stoppering of the laboratory sample bottle need not exceed two or three minutes.

The total loss in weight of samples while air-drying is reported as air-drying loss

METHOD II

Samples of coal if larger than 4-mesh (0.20 inch) should be rapidly reduced to 5 pounds at 4-mesh or finer as in Method I.

This 5-pound portion is quickly passed through a suitable crushing apparatus—rolls or enclosed coffee mill type of grinder, adjusted to crush to 10- or 20-mesh size. A 60-gram moisture sample should be taken, without sieving, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 10- or 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

¹ For details of air-drying oven see *Bull.* 9, 4th series, Ohio Geological Survey, "Coal," by Bownocker, Lord and Somermeier (1908), page 312, or *Technical Paper* 8, Bureau of Mines, "Methods of Analyzing Coal and Coke," by F. M. Stanton and A. C. Fieldner (1912), page 4, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 71, McGraw-Hill Book Co. (1912).

² For details of riffle sampler see *Bull.* 9, 4th series, Ohio Geological Survey, page 313, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 73.

The main portion of the sample is further pulverized until all passes through a 20-mesh sieve. It is then thoroughly mixed and reduced on the riffle to about 120 grams, which is pulverized to 60-mesh by any suitable apparatus without regard to loss of moisture. After this sample has been passed through the 60-mesh sieve it is again mixed and divided on a small riffle to 60 grams. The final sample should be transferred to a 4-oz. rubber-stoppered bottle.

Coal containing visible superficial moisture should be spread out in weighed pans and allowed to air-dry as in Method I, or at room temperature, otherwise considerable loss of moisture will take place while crushing to 10-mesh size. The percentage of loss in weight is recorded and the analysis of the air-dried sample corrected to the "as received" basis.

Notes on Method I.—(1) This method of preparing coal samples was developed by Lord and Somermeier at the Fuel Testing Plant of the U. S. Geological Survey at St. Louis. It has been used for several years by the Bureau of Mines in connection with the analysis of mine samples of coal, where especial consideration must be given to loss of moisture during the sampling process. The Bureau of Mines uses a chipmunk jaw crusher for crushing the sample received at the laboratory to 4-mesh size, and a Sturtevant roll crusher for reducing the 4-mesh material to 10- or 20-mesh size. The rolls have one disadvantage, in that with some coals, flakes are formed which must be broken up by rubbing through a sieve before the sample can be reduced on the riffle. On the other hand, the rolls have a large capacity and are easily cleaned.

Coffee or bone mill types of grinders may be used for grinding to 10- or 20-mesh size. They should be entirely enclosed and provided with a covered hopper and receptacle of sufficient capacity to hold the entire 5-pound sample.

(2) A new porcelain jar ball mill and pebbles should always be tested for abrasion before use. This may be done by grinding 500 grams of sugar for a period of 2 hours, and then determining the ash in the sugar; or by keeping a record of the loss in weight of jar and pebbles and the weight of coal ground. No trouble has ever been experienced by the Bureau of Mines in the use of the ball mill.¹

(3) A large number of duplicate sampling experiments by Method I, beginning with a 3- to 5-pound 4-mesh sample have

A COMPARISON OF TOTAL MOISTURE IN DUPLICATE SAMPLES OF COAL

DESCRIPTION OF COAL	Sample no.	TOTAL MOISTURE		Difference
		Sampled by Method I Per cent	Sampled by Method II Per cent	
Bituminous, Pittsburgh bed, dry	10	1.99	1.74	-0.25
Bituminous, Pittsburgh bed, dry	11	1.97	1.76	-0.21
Bituminous, Pittsburgh bed, dry	12	1.97	1.74	-0.23
Bituminous, Pittsburgh bed, wet	13	3.46	2.92	-0.54
Bituminous, Pittsburgh bed, wet	14	3.62	2.74	-0.88
Bituminous, Pittsburgh bed, wet	15	3.55	2.84	-0.71
Bituminous, Pittsburgh bed, dry	16	2.80	2.58	-0.22
Bituminous, Pittsburgh bed, dry	17	2.67	2.56	-0.11
Bituminous, Pittsburgh bed, dry	18	2.81	2.57	-0.24
Sub-bituminous, Wyoming, dry	19	15.99	15.56	-0.43
Sub-bituminous, Wyoming, dry	20	16.21	15.61	-0.60
Sub-bituminous, Wyoming, dry	21	15.89	15.62	-0.27

been made by the Bureau of Mines on a wide range of coals. The variations in moisture usually range from 0 to 0.20 per cent and the variations in ash from 0 to 0.4 per cent.

Notes on Method II.—(1) This method requires less special apparatus (such as air-drier, and ball mills) than Method I, and, therefore, can be more readily adapted to the apparatus at hand in the ordinary analytical laboratory. The sample can be prepared for analysis in a much shorter time than by Method I.

¹ For experimental data on abrasion in ball mills see paper on "Accuracy and Limitations of Coal Analysis," by A. C. Fieldner, *THIS JOURNAL*, 5, 281 (1913).

The moisture obtained by this method is usually somewhat lower than by Method I, as shown in the preceding table of experimental results obtained on duplicate samples analyzed by Methods I and II.

(2) The Bureau of Mines has used this method during a period of several years in the Fuel Inspection Laboratory at Washington. The samples as received, if larger than $\frac{1}{4}$ inch, are first pulverized with a jaw crusher to about $\frac{1}{8}$ inch and then by a roll crusher to 20 mesh. A planetary disk grinder is used for pulverizing to 60 mesh. This machine, on account of heating, can not be used for anthracite.

Duplicate samples almost invariably check within 0.4 per cent in ash.

(3) For crushing samples in the field S. W. Parr recommends a small portable mill which will reduce the samples to $\frac{1}{8}$ inch size before quartering.

(4) S. W. Parr and W. A. Noyes recommend that all samples should be crushed to $\frac{1}{8}$ inch size in the field and reduced to not less than five pounds before transmittal to the laboratory.

(5) The size to which the final laboratory sample should be pulverized is best indicated by showing the deviation in ash and sulfur that is caused by one particle more or less of cubes of pyrite equivalent to the openings in the various sizes of sieves.

Nominal size of sieve	Length of opening, mm.	Weight of pyrite cube equivalent to opening, Gram	Weight of sulfur in this cube, Gram	Weight of ash produced from this cube, Gram
40 mesh	0.42	0.00037	0.00019	0.00024
60 mesh	0.34	0.00020	0.00011	0.00013
80 mesh	0.23	0.00006	0.00003	0.00004

An inspection of the above table shows that 40 mesh is obviously too coarse to insure satisfactory duplication, inasmuch as a deviation of only 10 particles of pyrite in the 1-gram sample would cause a difference of 0.19 per cent sulfur and 0.24 per cent ash. Even 60 mesh is scarcely fine enough for high-sulfur coals. In such cases 80 mesh would be preferable.

MOISTURE

By W. F. HILLEBRAND, *Chairman*

In view of our own experience and that of the chemists who coöperated with a subcommittee of the International Committee on Analyses¹ it seems needless to strive at present in ordinary work for a very high degree of refinement in the determination of moisture. So sensitive are coals to humidity changes of the air that it is evidently only by chance that two or more analysts will reach the same results for moisture in a given coal, especially if they live in different cities or make the tests on different days in the same place. To the truth of this the report of the above-mentioned International Committee bears abundant testimony. The variations therein shown are probably due, in part to lack of realization on the part of many of the analysts of the magnitude of the changes in moisture content that may arise during the transfer of the coal from the containing vessel to the drying receptacle and during the weighing operation. Nevertheless, the chances of variation are so serious that the opening statement above is fully justified.

A. APPROXIMATE METHOD

Use a pair of shallow weighing capsules with ground caps or other well-fitting covers. Suitable forms are indicated below. Heat these under the conditions at which the coal is to be dried, stopper or cover, cool over concentrated sulfuric acid for 30 minutes and weigh.

Dip out with a spoon or spatula from the container two portions of coal of about 1 gram weight each, put these quickly into the drying vessels, close, and weigh at once.

¹ *Proceedings 8th Intern. Congr. Appl. Chem.*, 25, 41.

An alternative procedure (more open to error), after transferring an amount slightly in excess of 1 gram, is to bring to exactly 1 gram weight (± 0.5 mg.) 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.

Further procedure:

(a) *For Anthracite and Bituminous Coals*

Quickly place the vessels open in a preheated oven (at $104-110^{\circ}$ C.) through which passes a current of air dried by concentrated sulfuric acid. Close the oven at once and heat for one hour. Then open the oven, cover the capsules quickly and place in a desiccator over concentrated sulfuric acid. When cool, weigh.

(b) *For Sub-bituminous and Lignitic Coals*

Instead of air use a current of dry carbon dioxide, both for the preliminary heating of the capsules as well as for the drying of the coal. After the hour's heating, open the oven, cover the capsules and place them in a vacuum desiccator over concentrated sulfuric acid. Exhaust the desiccator to remove the carbon dioxide from the capsules. When cool, slowly let in dry air and weigh at once.

Notes on Method A.—(1) Although watch glasses ground to fit, and with clamp, are most effective drying vessels on account of their shallowness, it is probable that glass capsules as used by S. W. Parr and as recommended by the International Committee will be found most convenient. The capsules themselves should be about $2\frac{1}{2}$ cm. wide and $1\frac{1}{2}$ cm. deep. The shallower they are, consistent with convenient handling, the quicker and more perfect the drying. The Parr capsules have the upper part of the wall ground on the outside and the cap is ground on the inside, leaving a smooth edge, a feature which facilitates transfer of the coal to the ashing vessel.

A porcelain cup (Eimer and Amend, No. 2657) is preferred at the Bureau of Mines, where it is used with a well fitting aluminum cover. It has the disadvantage of greater depth as compared with the glass capsule, but if demand arose this defect could be remedied. Its only advantage over the glass capsule lies in permitting the ash determination to be made on the moisture sample without transfer.

(2) The oven must be so constructed as to have a uniform temperature in all parts and a minimum of air space. The air current must be rapid enough to renew the gas in the oven frequently when the oven holds from 6–12 vessels of coal.

The cylindrical form of oven shown in *Technologic Paper* 8, of the Bureau of Mines, p. 5, and holding 6 crucibles, is well adapted for the purpose; also a new rectangular oven of the same Bureau, holding 12 crucibles and measuring inside $1\frac{1}{2}$ inches high by 4 inches wide and $14\frac{1}{2}$ inches long. The approximate air space in each of these ovens is 0.05 cubic foot. With this type of oven, of small air space, it has been found at the Bureau of Mines that the air must be renewed from 2 to 4 times a minute to obtain the maximum loss in weight from the coal in 1 hour.

S. W. Parr uses an oven 12 inches in each of the three directions, and here the renewal of air need not be so rapid, 8 to 10 times in an hour being probably sufficient.

(3) Although carbon dioxide is absorbed by coal at room temperature there is no absorption above 100° C. The need for modifying the procedure for sub-bituminous and lignitic coals arises from the fact that such coals undergo very many times the amount of oxidation that Appalachian coals suffer. Nitrogen gas is to be preferred to carbon dioxide because its density is so near that of air that it will be unnecessary to displace it from the capsules before final weighing. If this gas is used, a vacuum desiccator is unnecessary.

(4) The International Committee in its report recommends,

when using air, to remove one of the capsules from the oven at the expiration of 30 minutes, to continue heating the other for 30 minutes longer, and to accept the higher loss in weight, if a difference is shown, as may happen with certain coals. Our committee has not deemed it advisable to adopt this precaution, both on account of the added labor involved in testing four portions of a sample instead of two and because the probable error in the determination of the true moisture content is so large as to render the precaution of doubtful value.

B. METHODS OF GREATEST ACCURACY

(1) Heat as in Method A, but in a current of dry nitrogen that is free from oxygen. Instead of a shallow vessel a U-tube with well ground stoppers may be used, which tube can be hung in an oven at the temperature of $104-110^{\circ}$. Fill the tube with nitrogen before taking its weight empty, and weigh always with a counterpoise tube of about the same displacement and weight. Introduce about a gram of the coal quickly through a short and wide-stem funnel without attempt to secure a weight of exactly 1 gram. Before hanging the tube in the preheated oven pass nitrogen to displace all air, and continuously while heating. When the last trace of moisture has disappeared from the outlet of the tube, remove from the oven and let cool with the gas still passing. When cool close the cocks, hang in the balance case for 15 minutes and after opening one cock weigh with the counterpoise. The counterpoise need not be filled with nitrogen.

As a check the water given off may be collected in sulfuric acid and weighed, care being taken to keep the absorption vessel full of nitrogen. The weight of water thus obtained is a little higher than that found indirectly.

Ba. ALTERNATIVE METHOD (FOR USE WHEN TIME DOES NOT PRESS)

Dry in a vacuum desiccator over sulfuric acid of maximum concentration for 3 and 7 days, longer if necessary.

The vacuum should be high—not over 3 millimeters of mercury pressure—and should be checked by a manometer. The capsules mentioned above may be used. Before evacuating fill the desiccator with an inert gas, and before opening the desiccator carefully let in air dried by sulfuric acid. Weigh immediately.

This method is easy of execution and is sound in principle since a possible error due to loss of gaseous constituents is negligible.

It has not been deemed advisable to recommend the xylene method of Constam (boiling a large weight of coal with xylene and collecting and measuring the water that distills over) since, though promising, the method has not been subjected to exhaustive test.

ALLOWABLE VARIATIONS

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

VOLATILE MATTER

By S. W. PARR, *Chairman*

It is recommended that for volatile matter determinations a 10-gram platinum crucible be used having a capsule cover, that is, one which fits inside of the crucible and not on top. The crucible with one gram of coal is placed in a muffle maintained at approximately 950° C. for 7 minutes. With a muffle of the horizontal type, the crucible should not rest on the floor of the muffle but should be supported on a platinum or nichrome triangle bent into a tripod form. After the more rapid discharge of the volatile matter, well shown by the disappearance of the luminous flame, the cover should be tapped lightly to

more perfectly seal the cover and thus guard against the admission of air.

ALTERNATE METHOD

One gram of coal is placed in a platinum crucible of approximately 20 cc. capacity (35 mm. in diameter at the top and 35 mm. high). The crucible should have a capsule cover which will readily adjust itself to the inside upper surface of the crucible. The crucible is placed in the flame of a Méker burner, size No. 4, having approximately an outside diameter at the top of 25 mm. and giving a flame not less than 15 cm. high. The temperature should be from 900° to 950° C. determined by placing a thermocouple 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.). The crucible is placed in the flame about 1 cm. 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.

For lignites a preliminary heating of 5 minutes is carried out, during which time the flame of the burner is played 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 the crucible is placed in the full burner flame for 7 minutes as above described.

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
Bituminous coals.....	0.5	1.0
Lignites.....	1.0	2.0

DETERMINATION OF ASH

By S. W. PARR, *Chairman*

In any outline for the determination of ash the attempt must be made to meet the conditions of the widely varying mineral constituents of coals. Those of the Illinois type perhaps have disturbing constituents in greatest amount. These are (a) calcium carbonate, (b) iron sulfate, (c) iron pyrites.

Concerning the extent to which carbonates are present, out of 500 samples of Illinois coal examined, only 9 per cent were found to have calcium carbonate present in an amount less than 0.2 per cent. Very nearly half of the samples have this constituent in excess of 1 per cent. One-fifth of the samples have more than 2 per cent of calcium carbonate and a very considerable number were found to have over 4 per cent with a few isolated cases reaching as high as 10 per cent of calcium carbonate in the raw coal.

Concerning the distribution of sulfate, investigations show this constituent practically always present and in the form of ferrous or ferric sulfate. In the fresh coal the amount varies from a few tenths up to 1 per cent. There is a rapid increase in the content of sulfate in the laboratory sample ground to 60 mesh. In a large number of cases examined, the amount of this constituent had doubled during six months of laboratory storage. An examination of the samples which had been retained in storage in the buckwheat size without fine grinding showed that the increase in sulfate was practically confined to the finely divided particles; that is to say, in that part of the sample which will pass a 60-mesh screen practically all of the increase in sulfate is found. That part of the sample which is retained on a 20-mesh and which passes through a 10-mesh has very little if any increase in sulfate, and the next larger size has so little increase that it may be considered as having the normal content as found in the vein sample.

As to sulfur in the form of sulfide it must be looked upon as an additional element of disturbance in the presence of cal-

cium carbonate, for the reason that any temperature adequate for burning off of carbon will result in the burning also of the sulfur to sulfur dioxide and part or all of the calcium carbonate to calcium oxide. Under these conditions calcium sulfate is inevitably formed. If this reaction were complete or definite in amount, the proposition would be much simplified. An additional point to be observed is the fact that calcium oxide may further increase in weight from absorption of sulfur from the gas flame.

In the final method for ash determination the following items should be borne in mind.

First, Calcium carbonate begins rapid decomposition at and above 900°; below that temperature the decomposition is partial but evident at temperatures above 600° C., or a dull red, and must be considered.

Second, Calcium oxide in the presence of iron pyrites readily takes up sulfur and retains the same in the form of calcium sulfate. Attention should be called in this connection also to the fact that where calcium oxide is present the sulfur from the gas flame may be readily absorbed, with the formation of calcium sulfate.

Third, If high temperatures are maintained during the process of burning off the carbon the quantity of sulfate is seriously modified by reduction in the presence of red-hot carbon.

Fourth, Temperatures which are carried to the fusion point will further modify normal constituents by the formation of calcium silicate and the liberation of sulfur trioxide.

Fifth, Ferrous sulfate is decomposed at 550 to 600° C. and ferric sulfate at 700° C. With the temperature necessary for burning off the carbon there is likely to be a transfer of sulfur trioxide to the calcium oxide. The decomposition of calcium sulfate does not occur rapidly below 1100° C. in the absence of carbon, but may occur to a disturbing extent at 900° C. or above.

Sixth, Sulfur in the form of iron pyrites is completely oxidized at the low temperatures indicated, along with the burning out of the carbon. If it is so discharged it does not operate to disturb the values by uniting with calcite, but in so far as calcium oxide develops, it is retained.

METHOD FOR DETERMINING ASH

Unless the coal is of a type known to be free from carbonates the amount of carbon dioxide must be determined. A five-gram sample, recently boiled distilled water and dilute hydrochloric acid are employed, making use of any convenient apparatus for collecting, absorbing and measuring accurately the carbon dioxide discharged from the coal. It is most convenient to obtain the factor as in the form of carbon.

One gram of coal, either freshly weighed or that which has been used for the moisture determination, is ignited in a shallow capsule or porcelain crucible by placing directly in a muffle maintained at a dull or cherry-red temperature between 700 and 750° C. and retained at this temperature for 20 or 30 minutes or until all of the carbon is burned out. The capsule is cooled in a desiccator and weighed. In the absence of a muffle the desired temperature may be obtained by placing the capsule at first just above the tip of a Bunsen flame turned down to about 2 or 3 inches in height. After the larger part of the carbon is burned off in this manner the flame is increased so that the tip comes well into contact with the bottom of the capsule.

For coals having carbon dioxide present in an amount to exceed 0.2 per cent, the ash after cooling is moistened with a few drops of sulfuric acid (diluted 1 : 1) and again carefully brought up to 750° C. and retained at that temperature for 3 to 5 minutes. The capsule is cooled in a desiccator and weighed. Three times the equivalent of carbon present as carbon dioxide is subtracted from the ash as weighed in order to restore the weight of the calcium sulfate formed to the equivalent of calcium carbonate.

A full discussion of the determination of ash will be published soon.

CORRECTED ASH

The application of a correction for sulfur present in the iron pyrites depends largely upon the use to be made of the results. For technical purposes it may well be omitted. For comparative purposes, especially where use is to be made of the pure coal or unit values, it should be applied. Five-eighths of the sulfur present in the pyritic form if added to the ash would restore the iron sulfide to the original form as weighed.

While with certain types of coal, especially those extensively used for steaming purposes, averaging 15 to 20 per cent ash, it is evident that there is a volatile ash constituent of considerable importance due to hydration of clayey material, in our present state of information as to the uniform distribution of this constituent it does not seem advisable to incorporate it in technical analyses. For a comparative study, however, a correction for this type of ingredient cannot be avoided. The factor which has received extended application is an increase of 8 per cent of the ash as weighed to represent this volatile constituent.

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
No carbonates present.....	0.2	0.3
Carbonates present.....	0.3	0.5
Coals with more than 12 per cent ash..	0.5	1.0

SULFUR

By PERRY BARKER, *Chairman*

In view of the close agreement of results obtained in the experimental work on various types of coal, the Subcommittee recommends that a choice of the following three methods for the determination of sulfur be permissible:

- The Eschka method.
- The Atkinson method of fusion with sodium carbonate.
- The method of fusion with sodium peroxide in the Parr calorimeter bomb.

I. THE ESCHKA METHOD

The essentials of this method as described by G. L. Heath¹ have been modified as given in the former report of the Committee of the American Chemical Society on Coal Analysis.² Additional directions for application when city gas is used are also included in the method herein recommended.

Thoroughly mix on glazed paper 1.3737 grams of coal and 6 grams of Eschka mixture. This mixture is prepared by thoroughly incorporating two parts of magnesium oxide with one part of sodium carbonate by passing through a 40-mesh screen. By this method of preparation the mixture attains a uniformity comparable with that of the laboratory sample of coal and thorough incorporation is, therefore, more easily effected. Transfer to a No. 1 Royal Berlin porcelain crucible and cover with about two grams of the Eschka mixture.

On account of the amount of sulfur contained in artificial gas, it is preferable to heat the crucible over an alcohol, gasoline or natural gas flame or in an electrically heated muffle. 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 sulfur. Heat the crucible slowly for about 30 minutes, gradually increasing the temperature and occasionally stirring until all black particles disappear, which is an indication of the completeness of the procedure.

Mixture use of artificial gas for heating the coal and Eschka mixture is permissible, provided the crucibles are heated in a

muffle and a blank determination of the amount of sulfur absorbed from the gas is made.

Place the crucible in a cold gas muffle and gradually raise the temperature to about 870° or 925° C. (cherry-red heat) in about one hour. Maintain this maximum temperature for about one and a half hours and then allow the crucible to cool in the muffle. Remove and empty the contents into a 300 cc. beaker and digest with 200 cc. of hot water for one-half to three-quarters of an 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 cc. with 10 to 20 cc. of saturated bromine water and make slightly acid with concentrated hydrochloric acid. Transfer the beakers to the hot plate and, upon boiling, precipitate the soluble sulfates by adding slowly from a pipet with constant stirring 10 cc. of a 10 per cent solution of barium chloride. Continue boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter through an ashless filter paper and wash first with hot water containing 1 cc. of hydrochloric acid per liter and then 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 sulfate in a weighed platinum or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. The paper should be smoked off gradually at first. After the paper is practically consumed raise the temperature to approximately 925° C. and heat to constant weight. In case artificial gas is used as a heating agent, a blank to correct for contamination due to sulfur in the gas is carried through the process in the manner described above, using the same amounts of Eschka mixture, wash water, bromine water, hydrochloric acid and barium chloride solution as employed in the regular determination. A large number of tests using a mixed coal and carburetted water gas containing not more than 25 grains of sulfur per 100 cubic feet show blanks averaging 0.003 gram of barium sulfate. These blanks include the impurities in the form of sulfur compounds in the reagents, which amount to nearly one-half of the total weights. The percentage of sulfur is obtained by deducting the blank, provided artificial gas is used, and multiplying the resulting figures by ten.

II. THE ATKINSON METHOD¹

Thoroughly mix on glazed paper 1.000 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. Raise the temperature of 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 ten or fifteen 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 appear, the dish should be replaced and heated for a short time. When all carbon is burned, remove the dish and digest the contents with 100 to 125 cc. of warm water. 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 washing should be continued until the filtrate shows no alkaline reaction. Make the filtrate slightly acid with sufficient concentrated hydrochloric acid and precipitate the sulfates with barium chloride

¹ *J. Am. Chem. Soc.*, **20**, 630.

² *Ibid.*, **21**, 1127.

¹ *J. Soc. Chem. Ind.*, March 29, 1886. *J. Iron and Steel Inst.*, No. 2 (1896). *J. Am. Chem. Soc.*, **21**, 1128 (1899).

as described under the Eschka method. No oxidizing agent is required.

III. THE PEROXIDE FUSION METHOD

This method is most conveniently carried out in the bomb which is a part of the Parr calorimeter.¹ The sodium peroxide and potassium chlorate used in the fusion mixture should be of the grade especially prepared for the determination of heating values with this apparatus.

Before mixing the coal and chemicals for the fusion, thoroughly dry the bomb and warm slightly in order to be sure that all traces of moisture have been removed. Place one gram of potassium chlorate, about ten to twelve grams of specially prepared sodium peroxide and one-half gram of the laboratory sample of coal, which has previously been air-dried, in the bomb and seal quickly to avoid the absorption of moisture by the sodium peroxide. Shake the bomb thoroughly and rap sharply on the laboratory table to remove the portions of the mixture which may adhere to the top of the bomb on the terminals. Place in a vessel containing sufficient water to completely submerge the portion of the bomb containing the mixture, allowing the stem to protrude sufficiently to attach the terminals of the ignition circuit. Ignite the wire with a current of 15 to 20 volts either from a lighting circuit, four-cell storage battery or four or five dry cells in series. After the bomb has cooled, remove, dry, and open over a four-inch watch glass placed on top of the beaker in which the fusion is to be dissolved. The bottom of the bomb is removed and the fused mass is knocked out upon the watch glass with the special rod furnished with this apparatus. The portions of the fusion which adhere to the sides and top of the bomb are washed into the beaker with hot water, the remainder of the fused mass is added and completely dissolved. The solution is acidified with hydrochloric acid in such a manner as to give approximately 5 cc. of free acid in the entire volume, which should amount to 250 to 300 cc. of liquid. Heat the solution, filter through a qualitative filter and wash several times with hot water. Heat the filtrate to boiling and precipitate the soluble sulfates by slowly adding 10 cc. of the hot solution of barium chloride. Continue the boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter, wash and ignite as described under the 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.

Experimental Results.—The above recommendations have been made after careful consideration of all the available methods for the determination of sulfur in coal. In order to make careful tests of such methods, a number of samples were prepared which represented various types of coal having sulfur contents ranging from one to four per cent. The results of comparative tests for the various methods are given in Table I. This same set of samples was submitted to two other members of the committee for comparative tests. One member employed the Eschka method essentially as given in this report while the other followed the Peroxide Fusion method. The results of these determinations, together with the original figures from Table I for the various methods are given in Table II.

In connection with the report on the various methods for the determination of sulfur in coal, the results of comparative tests by a member of the committee² are of particular interest. The results of these tests on 35 samples of coal show an average difference of 0.02 per cent of sulfur between the Peroxide Fusion method and the Eschka method on the samples which averaged slightly over two per cent of sulfur. The average results from the bomb washings were 0.16 per cent lower than by the Per-

oxide Fusion method, while the results by the special Photometric method were 0.11 per cent. lower than by the Peroxide Fusion method.

After careful consideration of the various methods, together with the data which are given herewith, the Subcommittee recommends that the method of precipitation from bomb washings be discarded and endorse a choice between the (1) Eschka method, (2) the Atkinson method and (3) the method of fusion with sodium peroxide in the Parr calorimeter.¹

TABLE I—COMPARATIVE TESTS
Determination of Sulfur in Coal by Various Methods
Percentages Refer to Dry Coal Basis

SAMPLE	I	II	III	IV	V	VI	VII	
							(a)	(b)
1.....	1.02	0.000	1.01	1.00	1.03	1.06	1.01	1.02
2.....	1.99	0.017	2.00	2.02	1.94	2.01	1.79	1.92
3.....	2.98	0.004	3.02	2.99	2.93	3.04	3.00	3.13
4.....	3.95	0.019	3.97	3.96	3.87	3.94	3.91	3.94
(Dup.).....	3.96							

I. Eschka method: Samples heated in gas-fired muffle, corrected for blank determination due to sulfur in gas, which averaged 0.025 per cent. This process is regularly in use in the laboratory where these tests were made.

II. Residual sulfur on extracting residue from Eschka method with hydrochloric acid.

III. Eschka method, according to methods for coal analyses adopted by the American Chemical Society in 1899, using the alcohol lamp.

IV. Atkinson's fusion method: "Method of Fusion with Sodium Carbonate," *J. Am. Chem. Soc.*, **21**, 1128.

V. Precipitation from washings obtained by combustion in oxygen bomb calorimeter.

VI. "Parr's Method of Combustion and Fusion in Bomb with Sodium Peroxide," *THIS JOURNAL*, **1**, 689 (1909).

VII. "Precipitation of Soluble Sulfates from Washings Resulting from Combustion of Coal in Oxygen Bomb Calorimeter by means of Barium Hydrate and Subsequent Neutralization and Titration with Standard Alkali and Acid," *Z. chem. Apparatenkunde*, **2**, 542; (a) and (b) are duplicate determinations on same sample.

TABLE II
Determination of Sulfur in Coal (Results on Standard Samples)
Percentages Refer to Dry Coal Basis

SAMPLE	Eschka method		Peroxide fusion method	
	Table I	Analyst A	Table I	Analyst B
1.....	1.02	1.03	1.06	1.02
2.....	1.99	1.98	2.01	2.01
3.....	2.98	2.92	3.04	3.01
4.....	3.95	3.86	3.94	4.03

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
For coal.....	0.05	0.1
For coke.....	0.03	0.05

DETERMINATION OF THE CALORIFIC POWER

By H. C. DICKINSON, *Chairman*

The specifications are to be of two classes, (a) and (b). The procedure specified under (a) may be followed in tests where a tolerance of at least 1 per cent is allowed. The procedure under (b) is to be used in all cases where the limit of tolerance is less than 1 per cent, and is to be followed in all cases of dispute. Under (b) any three determinations made at the same time on the same sample may be required to fall within a range of 0.3 per cent.

Combustion Bombs.—The Atwater, Emerson, Mahler, Peters, Williams or similar bombs may be used. For (a) the lining material of the bomb need not be specified. The Parr calorimeter may also be used, but only on condition that both parties to the contract agree to its use. For (b) the bomb shall have a lining of platinum, gold, porcelain enamel or other material

¹ A simpler, inexpensive bomb is described in *Am. Chem. J.*, **25**, 184 (1903); see also Noyes, "Organic Chemistry for the Laboratory," p. 21.

² *THIS JOURNAL*, **1**, 689 (1909).

¹ Mr. Fieldner recommends that precipitation from the bomb washings be permitted when both parties agree to its use, especially for coals used for steaming or heating purposes.

which is not attacked by nitric and sulfuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter (except the Parr) 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. For (b) the water in the jacket must be kept within 2 or 3 degrees of the temperature of the room 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. For (b) a motor-driven screw or turbine stirrer is recommended and the speed should not be sufficient to hold the temperature of the calorimeter more than 0.3° or 0.4° C. above that of the jacket, when the stirrer is allowed to run continuously. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is too irregular. The portion of the stirring device immersed in the calorimeter should be separated from that outside by nonconducting 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 the corrections given on the certificate. This shall also apply to electrical resistance or thermoelectric thermometers. For (b) 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° are required. Such thermometers should be tapped lightly just before each reading to avoid errors due to 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.—Oxygen used for combustions shall be free from combustible material and for (b) it shall not contain more than 5 per cent nitrogen and argon together. 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 cm. (preferably 5 cm.) should be used at a time. A correction of 1600 calories per gram weight of iron wire burned is to be subtracted from the observed number of calories. Except, however, that this correction may be omitted from both the standardizations of bomb and coal combustions, provided the same amount of wire is used in all cases.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of standard substances such as the 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 and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of such 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 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. For (b) in the case of any disagreement between contracting parties a check standardization shall be made at the time of test, but such standardization may consist of two or more combustions of standardizing samples.

Manipulation.—1. **Preparation of sample:** The ground sample, which is in approximate moisture equilibrium with the atmosphere, is to be thoroughly mixed in the bottle and an amount, approximately one gram, is to be taken out and weighed in the crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. Standardizing samples are also to be briquetted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation when naphthalene is used.

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 1/2 cc. 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 coal or briquet of standard material. For the combustion of standardizing samples 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 coal 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, viz., at least 5 grams per gram of coal, or other combustible. When feasible, the bomb may be exhausted before filling to remove the nitrogen of the air, thus reducing the amount of the nitric acid formed.

4. **Calorimeter Water.**—The calorimeter is to be filled with the required amount of water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. For (b) distilled water should be used and the amount determined by weighing. The amount must be kept the same as that used in standardization of the apparatus, or a correction applied for the difference in weight.

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 degree, preferably about 1/2 degree, above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be very small when the rise of temperature is 2° or 3°, 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 E. M. F. of not more than 12 volts. The circuit should be closed by means of a switch which should remain closed for not more than two seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out. For (b) the E. M. F. of the firing battery shall not exceed 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.

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 two minutes after the stirrer is started, temperatures are read at one-minute intervals for five minutes and the charge is then fired, noting the exact time of firing. Observations of temperature are then made at intervals de-

pending 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 one-minute intervals for five minutes to determine the cooling rate.

8. *Titration*.—After a 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 and the washings titrated 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. If the sulfur content of the coal is determined the amount of sulfuric acid should be computed and an *additional* correction of 1220 calories per gram of H_2SO_4 should be subtracted, for the excess of the heat of formation of the sulfuric acid over that of nitric acid.

Computation of Results.—The following method of computation is recommended, to take the place of the Pfaundler or other similar formulas for computing the cooling correction (radiation correction).

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for four or five 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, sixty per cent of the expected temperature rise, and noting the time when this point is reached), observe (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some five minutes after firing, (5) the final rate of cooling (r_2) in degrees per minute for five minutes.

The rate r_1 is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature were *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 were *rising* at the time c and later) to the thermometer reading taken at 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. This result, corrected for the heats of formation of nitric and sulfuric acids 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 B.t.u. per lb. *See example.

The results should be reduced to calories per gram or B.t.u. 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.

For an accurate comparison of different coals from the calorimeter determinations it is evident that the results should be reduced in each case by the heat of evaporation (preferably at 20° C.) of the water formed by combustion of the coal, since in the bomb this water is condensed and the heat of condensation is included in the measurement, while in nearly all commercial conditions the water vapor passes off uncondensed and the heat is lost. On account of the additional time required to determine the hydrogen content of coal samples the correction necessary to reduce to the above basis or "net" heat of combustion is not generally applied, although it may amount to several per cent in extreme cases.

Combustion of Anthracites and Coke.—For anthracites and

coke, which have a high ash content and do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The coal is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

* EXAMPLE

Observations

Water equivalent 2550 g.

Weight of charge 1.0535

Approximate rise of temp. 3.2°

60 per cent of approximate rise 1.9°

Time	Temp.	Corrected temp.
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) 27-12	17.2° ¹	
¹ The initial temperature is 15.27°; 60 per cent of the expected rise is 1.9°. The reading to observe is then 17.2°.		
(c) 31	18.500°	18.497°
32	.498	
33	.497	
34	.496	
35	.494	
36	.493	

Computation

$r_1 = 0.028^\circ \div 5 = 0.0056^\circ$ per minute. $b - a = 1.2$ minutes

The corrected initial temperature

is $15.276^\circ + 0.0056^\circ \times 1.2 = 15.283^\circ$.

$r_2 = 0.007^\circ \div 5 = 0.0014^\circ$ per minute; $c - b = 3.8$ minutes

The corrected final temperature is $18.497^\circ + 0.0014^\circ \times$

3.8.....	= 18.502°	
Total rise 18.502° — 15.283°.....	= 3.219°	
Total calories 2550 × 3.219.....	=	8209
Titration, etc.....	=	—7
Calories from 1.0535 grams coal.....		8202
Calories per gram.....	7785	
or B.t.u. per lb.....	14013	

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.

ALLOWABLE VARIATIONS

	Per cent	Per cent
Same analyst.....	0.3	Different analysts..... 0.4

Parr Calorimeter.—The essential conditions for the operation of the Parr or peroxide calorimeter are as follows:

The coal should be finely pulverized. While 60 mesh is sufficient for bituminous coals, anthracites should be ground to at least 100 mesh.

The sodium peroxide used should be received in solder sealed tins and of a size suitable for emptying completely into the container for use, preferably a glass jar with lever sealed cap.

In addition to the reaction the peroxide serves as a diluent and the ratio necessary for a quiet reaction should be maintained, preferably 0.5 gram of coal to approximately 10 grams of peroxide. One gram of pulverized potassium chlorate is also used to advantage. It is first thoroughly mixed with the coal in such a manner as to avoid any possibility of lumping of these two substances. A thorough and uniform mixing with the peroxide is then assured by shaking in the closed cartridge.

Coals with moisture above 2 or 3 per cent must be oven-dried at 110° C. in the usual manner after weighing out, and before mixing with the chemicals.

The correction factors to be subtracted are as follows:

For each per cent of ash.....	0.00275° C.
For each per cent of sulfur.....	0.005° C.
For 1 gram of KClO ₃	0.130° C.
For electric fuse wire.....	0.008° C.
For oxygen of bituminous coals for 0.5 gram.....	0.025° C.
For oxygen of brown lignites for 0.5 gram.....	0.050° C.
For oxygen of benzoic acid for 0.5 gram.....	0.124° C.

The products of combustion, CO₂ and H₂O, combine with the chemical with the formation of heat, which amounts in each case to 27 per cent of the total heat of the reaction.

The corrections for ash, fuse wire, etc., in terms of the temperature rise together with radiation and thermometer corrections must first be subtracted from the indicated rise in temperature. The formula for the final calculation then becomes:

$$\text{Corrected thermometer rise} \times 0.73 \times \text{total water} = \text{calorific value.}$$

0.5 gram coal

Detailed directions for use of the calorimeter accompany each instrument and may be found in numerous handbooks such as the new edition of Hempel's "Gas Analysis," Olsen's "Quantitative Analysis," etc.

THE IRON AND STEEL INSTITUTE FELLOWSHIP

The Iron and Steel Institute of Great Britain have awarded the Carnegie Research Fellowship to Dr. Alcan Hirsch, of New York, for the purpose of carrying out investigations in connection with electric furnaces as applied to the heating of bars, billets and ingots.

This award carries a stipend of \$500.00.

The investigations will be carried out in Dr. Hirsch's laboratory in the Chemists' Building, New York City, and the results of his research will be presented before the Iron and Steel Institute at the annual meeting in May, 1914.

AMERICAN CHEMICAL SOCIETY—SEPTEMBER MEETING

The regular annual meeting of the American Chemical Society will be held in Rochester, New York, September 9th to 12th, inclusive. All members should keep these dates in mind and plan to be at the meeting.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

SIXTH SEMI-ANNUAL MEETING, BOSTON, JUNE 25-28, 1913

PROGRAM OF PAPERS

Meetings to be held at Engineers' Club.

Presidential Address. DR. T. B. WAGNER.

Effect of Climate on Plant Location. WM. M. BOOTH.

The Power Plant. MR. P. BARKER, of Arthur D. Little, Inc.

Relation of the Manufacturer to the Patent System. DR. WM. M. GROSVENOR.

General Efficiency in Dyehouses and Bleach Works. DR.

LOUIS J. MATOS.

Depreciation and Obsolescence. RICHARD K. MEADE.

Some Peculiar Functions of the Retained Expert. DR. WM.

M. GROSVENOR.

Legal Control of Dangers to Health in Factories. DR. CHAS.

F. MCKENNA.

Import Duties on Chemicals and their Influence on Chemical Industry. DR. F. W. FRERICH.

The Drying of Linseed Oil and Red Lead with Special Reference to Painting Steel. DR. J. C. OLSEN AND A. H. CALLAGHAN.

EXCURSIONS

Hood Rubber Co., Watertown, Mass.

U. S. Arsenal, Watertown, Mass.

Laboratory and Experimental Paper Mill of A. D. Little, Inc., Boston.

Pacific Mills (Cotton Goods and Prints), Lawrence, Mass.

E. Frank Lewis' Wool Scouring Establishment, Lawrence

Russell Paper Co. (Wood Pulp by Soda and Sulfite Processes, and Manufacture of Book and Print Paper), Lawrence

New England Gas and Coke Co., Everett, Mass.

New Power Plant of Boston Elevated Railroad.

Gorham Manufacturing Co. (Silversmiths and Goldsmiths, Plated Ware, Bronzes, etc.), Providence, R. I.

United States Finishing Co. (Large Cotton Finishing Plant. Bleaching, Dyeing, Printing), Providence.

BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., has now ready for distribution samples of acid open hearth steel with 0.8 per cent and 1.0 per cent carbon, the fee being \$2.00 per bottle holding about 150 grams.

May 19, 1913

ANOTHER PLATINUM THIEF

On the night of May 16th, our laboratory was broken into and all of our platinum ware stolen, presumably by a professional platinum thief. I have advised our company's plant managers and some other laboratories in this vicinity. The crook engineered the trick in a way somewhat similar to that used by the thief who was caught early this spring at Sparrows Point, Md. The man we suspect answers to the following description: about thirty-five years of age, very dark complexioned, smooth face, about five feet ten inches tall, weight about one hundred and forty pounds. He was neatly dressed, but not stylishly. He speaks fluent English, and one would probably take him to be either German or Jewish, but his accent would not reveal any particular race as far as I could detect.

L. SELMI, Chief Chemist

LAKE SUPERIOR IRON AND CHEMICAL CO.
ASHLAND, WIS.

BOOK REVIEWS

Chemical Industries of Belgium, Netherlands, Norway, and Sweden. By THOMAS H. NORTON. Bureau of Foreign and Domestic Commerce, Department of Commerce and Labor. Special Agents Series No. 65. Washington: Government Printing Office. 1912. 8vo. 85 pp. 21 tables.

It has been said that "the primary function of a consul is to extend the trade of the country which he represents..... It is his duty to be a close student of current events." The present report by Dr. Norton, who, through his extensive experience as a chemical works manager, teacher and original investigator, is familiar with the methods of scientific enquiry, deals in a most comprehensive manner, considering the extent of the field covered, with the supply of raw materials used in

the chemical industries, the methods of manufacture, the costs of production, and the foreign and domestic trade of each of the countries considered. Dr. Norton makes pertinent observations on the prospects of improving the chemical goods trade with the United States, and his accounts of the processes in operation in certain of the industries disclose many facts which will be new to some American manufacturers and teachers. The monograph makes extremely interesting reading, and demonstrates that the policy of detailing experts as special commercial agents is indeed a most commendable one.

The accounts of the Norwegian and Swedish industries, given by Dr. Norton, were published in full in THIS JOURNAL, 4, 51 and 691.

W. A. HAMOR