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BUREAU OF MINES

METHODS OF ANALYZING AND TESTING COAL AND COKE

By Staff, Office of the Director of Coal Research

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Walter R. Hibbard, Jr., Director

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METHODS OF ANALYZING AND TESTING COAL AND COKE

by

Staff, Office of the Director of Coal Research [1]

Abstract

THIS bulletin presents all analytical and test methods regularly used by Bureau of Mines laboratories for characterizing coal and coke. To provide better service to coal producers and consumers, the scope of this bulletin has been expanded to include important test methods used to evaluate coal properties for commercial processing. The methods described will prove valuable to all persons interested in analyzing and testing coal and coke.

Introduction

Since its creation by Congress in 1910, the Bureau of Mines has been engaged in the development of methods for analyzing and testing coal and coke. Methods used for analysis and testing were first published in January 1912, as Technical Paper 8. Improvements and modifications in analytical procedures were included in subsequent papers published in 1913, 1926, 1929, 1938, and 1951.

Efforts to improve the precision of analytical procedures and to develop rapid methods to reduce time requirements were continued by the Bureau. To aid the consumer in the selection of coals for commercial processing, numerous test methods have been developed in this country and abroad to appraise coal properties more intelligently. This bulletin includes the analytical and test methods which are used regularly by the Bureau of Mines.

Analytical methods included for the first time are the flame spectrophotometric method for the determination of alkali oxides, and potentiometric determination of chlorine in coal, as well as rapid methods for analysis of coal ash. Additional test methods include the determination of the grindability of coal, equilibrium moisture in coal, and float-and-sink analysis. Plastometric and dilatometric methods to determine the coking properties of coals are described, as well as assay procedures for the appraisal of low-temperature carbonization yields.

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[1] Compiled by Walter H. Oppelt, Project coordinator, Coal Utilization and Preparation, Pittsburgh Coal Research Center, Bureau of Mines, Pittsburgh, Pa.

Work on manuscript completed January 1966.

METHODS OF ANALYZING AND TESTING COAL

PREPARATION OF LABORATORY SAMPLE WITH PRELIMINARY DRYING

The coal samples are received at the laboratory in galvanized steel containers, height 11½ inches, diameter 3¼ inches. Each container has a close-fitting screw cap and rubber gasket to assure no moisture loss while in transit. The methods of collecting and shipping samples are described in a Bureau of Mines handbook.[2] After the sample is received at the laboratory, it is given a laboratory number and placed in a tared aluminum pan 10 inches wide, 14½ inches long, and 2 inches deep. The sample is weighed and then put in the air-drying room, shown in figure 1. This is a controlled temperature (30–35° C) room with forced air moving over the samples. The sample is dried under these conditions until the loss in weight between two successive weighings, made 20 to 24 hours apart, does not exceed 3.5 percent by weight. The purpose of drying is to reduce the moisture in the sample to approximate equilibrium with the air of the laboratory and thus minimize changes in moisture content during sample preparation and analysis.

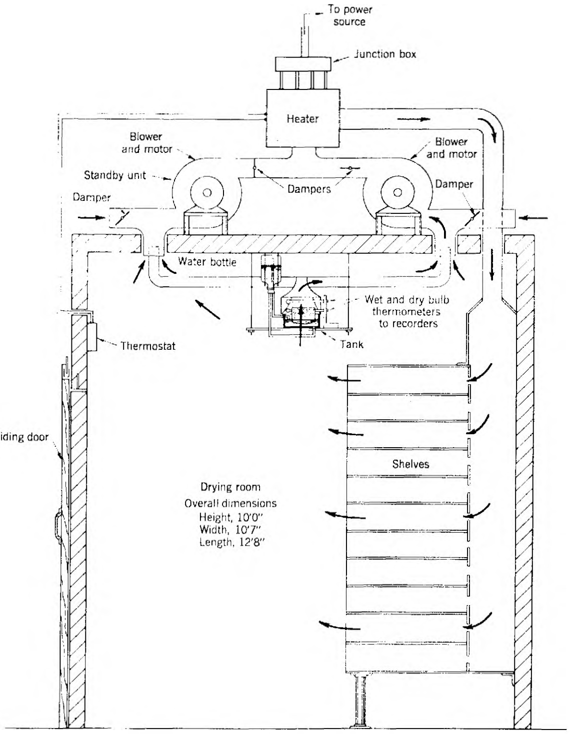

FIGURE 1.—Air-Drying Room.

The loss in weight by air-drying is not the total moisture, but this moisture combined with the moisture determined in the analysis sample at 105° C gives the total moisture of the sample.

Immediately after the last weighing, the entire air-dried sample is pulverized to pass a No. 60 sieve (250 micron), by passing it through an impact pulverizing mill. This sample is then reduced to about 50 grams with a laboratory riffle shown in figure 2 (thirty-six ¼-inch openings).

The sample is then passed quickly through a No. 60 sieve. Normally all the sample will pass through the sieve, but if any particles

FIGURE 2.—Laboratory Riffle.

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[2] Snyder, N. H. (revised by S. J. Aresco). Coal Sampling. Revision of Technical Paper 133. Bureau of Mines Handbook, 1957, 16 pp.

do remain on the sieve, they are reduced to pass the No. 60 sieve on a bucking board and added to what passed through the sieve. This 50-gram portion is put in a rubber-stoppered, wide-mouth, 4-ounce bottle, and constitutes the laboratory sample. The above procedure is carried out as rapidly as possible, to minimize change in moisture.

Before portions for the various analytical determinations are weighed, the sample is mixed thoroughly. The bottle containing the sample is placed on the 36-bottle-capacity mixing wheel shown in figure 3 and rotated for 20 minutes. The wheel is 30 inches in diameter and makes 25 revolutions per minute. The sample bottles are held by spring clips on the periphery of the wheel at an angle of 45° with the axis. The bottle is not more than three-fourths filled, and the speed of rotation is slow enough to prevent centrifugal action from hindering the thorough mixing of the pulverized coal.

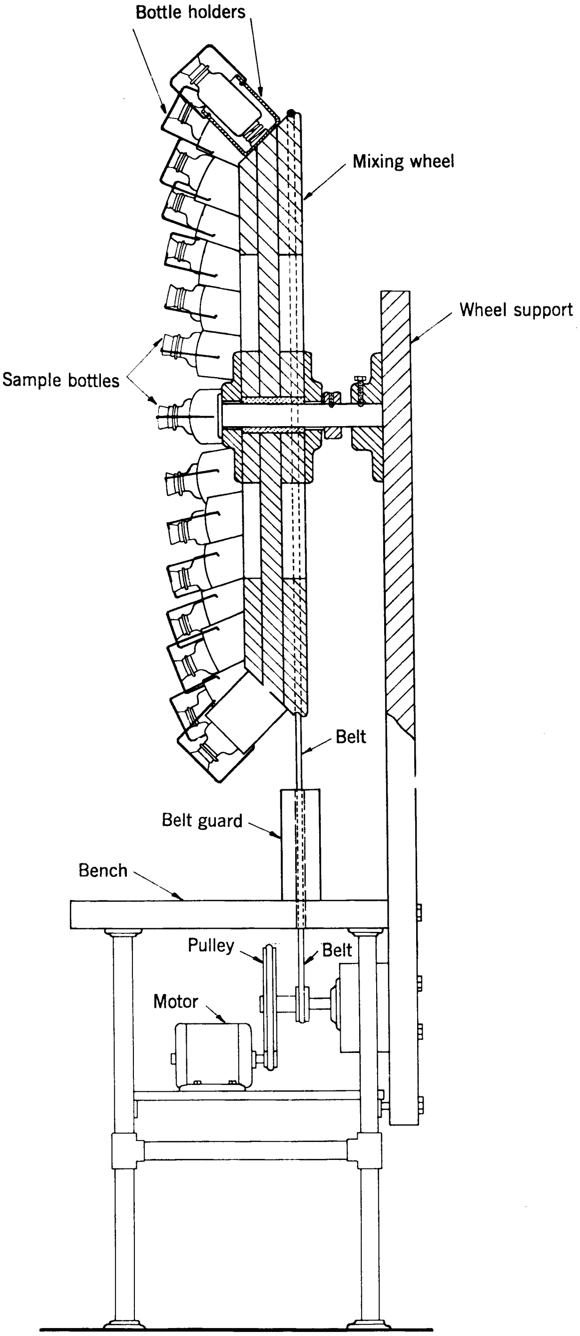

FIGURE 3.—Mixing Wheel.

METHODS OF ANALYSIS

Proximate Analysis

Proximate analysis is the determination, by prescribed methods of moisture, volatile matter, fixed carbon (by difference), and ash.

Moisture by Oven Method

APPARATUS.—The moisture oven is a large copper cylinder containing seven identical small copper cylinders arranged as in figure 4. The oven is 12 inches wide, 19 inches high, and 26 inches long, and each of the 7 copper cylinders accommodates 12 porcelain capsules. The space between the outer and the inner cylinders is filled with a 1:1 solution of ethylene glycol and water. The solution is heated with four electric strip heaters, and the temperature is controlled by a thermostat. A reflux condenser allows for expansion, and also keeps the water from evaporating. A current of air dried by passing through concentrated sulfuric acid and preheated by passing through copper tubes surrounded by the ethylene glycol solution is forced through the inner cylinders of the oven and over the sample at a rate of two to four volume changes per minute; it takes up moisture from the samples and escapes through small openings in the front of the oven. It has been found that some coals oxidize on heating in the presence of air, and therefore the determined moisture may be somewhat low. Using nitrogen instead of air as the sweep gas would eliminate this slight error. A distillation procedure[3] that also minimizes oxidation effects is sometimes used for low-rank coals and lignites. It involves collection and measurement of the

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[3] Goodman, John B., Manuel Gomez, and V. F. Parry. Determination of Moisture in Low Rank Coals. BuMines Rept. of Inv. 4969, 1953, 20 pp.

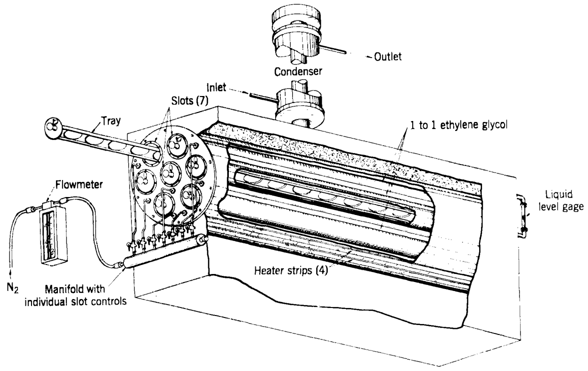

FIGURE 4.—Moisture Oven.

water resulting from heating the coal in a liquid that has a boiling point higher than water and is immiscible with it.

OVEN METHOD FOR COAL CRUSHED TO PASS A NO. 60 SIEVE.—In this case the moisture is determined on the air-dried sample.

Place a 1-gram sample (all weighings made to 0.1 mg) of the coal in a weighed porcelain capsule (22.5 mm in depth, 42.5 mm in diameter, glazed inside, unglazed outside botom) and heat for 1 hour at 105° ± 5° C in a preheated oven. The capsule is then removed from the oven, immediately covered with an aluminum cover, and cooled in a desiccator over concentrated sulfuric acid. This step must be carried out without delay. The loss in weight multiplied by 100 is recorded as percent moisture.

OVEN METHOD FOR COAL CRUSHED TO PASS A NO. 20 SIEVE.—In this case, if requested, the moisture is determined on the as-received coal without preliminary air drying.

Place a 5-gram sample (weighed to 1 mg) in the same capsule as used for the 1-gram sample and heat for 1½ hours; otherwise, the procedure is the same as for the coal crushed to pass a No. 60 sieve.

On laboratory samples crushed to pass a No. 60 sieve

	Permissible differences, percent
Moisture content, percent:	
Under 5	0.15
5–10	.20
10–15	.30
Over 15	.40

On laboratory samples crushed to pass a No. 20 sieve

	Permissible differences, percent
Moisture content, percent:	
Under 5	0.2
Over 5	.3

Ash

APPARATUS.—The muffle furnace to burn the coal (fig. 5) is a heavy duty electric hairpin-type furnace with an air aspirator installed at the back of the muffle. The aspirator maintains an ample supply of air in the muffle at all times to insure complete oxidation and to provide circulation through the muffle to remove the products of combustion formed during ignition of the sample.

The door of the furnace is kept open 6 to 8 mm from the bottom to provide circulation of air through the muffle.

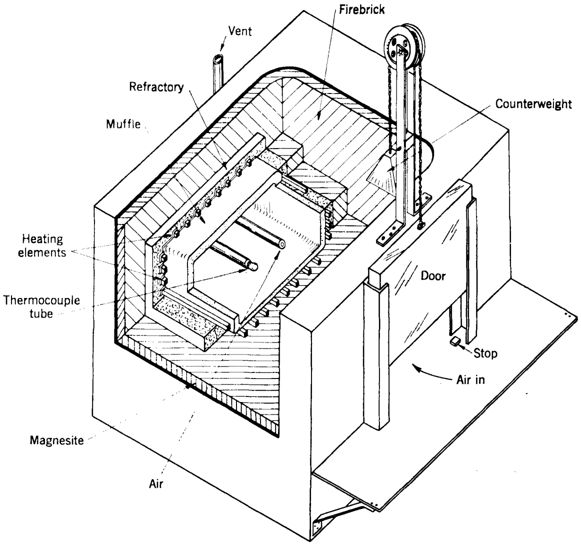

FIGURE 5.—Muffle Furnace for Determining Ash.

PROCEDURE.—Place the porcelain capsule containing the residue from the moisture determination by the oven method, or a 1-gram sample weighed to 0.1 mg of air-dried coal ground to pass a No. 60 sieve when moisture is determined by the distillation method in the cold muffle furnace, and heat gradually so that the temperature reaches 500° C in 1 hour and 750° C in 2 hours. Continue the ignition in the muffle at 750° C for 1½ hours. Remove the capsule with its contents from the muffle, cover with an aluminum cover, cool on an asbestos tray, and weigh. Replace the capsule and contents in the muffle at 750° C, heat for ½ hour, cool, and weigh again. If the change in weight is 0.5 mg or less, the last weight of the capsule and residue minus the empty capsule multiplied by 100 is percent ash. If the change is greater than 0.5 mg, heat the residue again for 30 minutes and repeat the process until the change in weight is 0.5 mg or less.

Slow heating of the coal as described prevents difficulty in obtaining satisfactory check results for coals that contain considerable calcite and pyrite because of varying amounts of sulfur retained as calcium sulfate in the ash.[4] Slow heating also avoids coking the sample, which makes burning difficult; furthermore, if a coal high in volatile matter is heated rapidly, the gas generated tends to puff within the capsule and thus mechanically to carry off portions of the sample. Ash determined by this method represents ignited mineral matter remaining after the combustible substances of the coal are burned.

Precision.—The following tabulation gives permissible differences in percent, of ash from the same laboratory and same sample.

Ash, percent:	*Permissible differences, percent*
0–15	0.15
15–25	.20
25–50	.30
Over 50	.40

Volatile Matter

Apparatus.—All volatile-matter determinations at the Pittsburgh laboratory are now made in specially designed electric furnaces of the vertical type shown in figure 6. The heating element consists of 36 feet of nickel-chromium resistance wire (No. 17 B. & S. gage, 0.324 ohms per foot) wound on a helical grooved ($\frac{5}{32}$-inch pitch) refractory furnace core 6 inches long by 3½ inches wide with semicircular sides of ¾-inch radius. A current of about 10 amperes at 115 volts is required to reach a temperature of 950° C (± 20° C) in 15 to 20 minutes. With an electric proportioning stepless controller package, 7 amperes are required to maintain the 950° C temperature. The life of the heating element under daily operation is 20 to 24 months. A base metal thermocouple is permanently installed through the bottom of the furnace so that the hot junction is just below the platinum crucibles. In calibrating the furnace, 1 gram of ignited silica or alumina is substituted for the coal to avoid possible contamination of the thermocouple. A thermocouple is placed in the crucible so that the hot junction is in contact with the bottom of the interior of the crucible. The furnace controller is then adjusted until a constant temperature of 950° C is registered by the thermocouple in the crucible. The temperature of the fixed thermocouple of the furnace is recorded, and this temperature corresponds to 950° C in the crucible zone when two crucibles are in the furnace. In making this comparison the usual platinum cover is replaced by one that is perforated to admit the thermocouple leads.

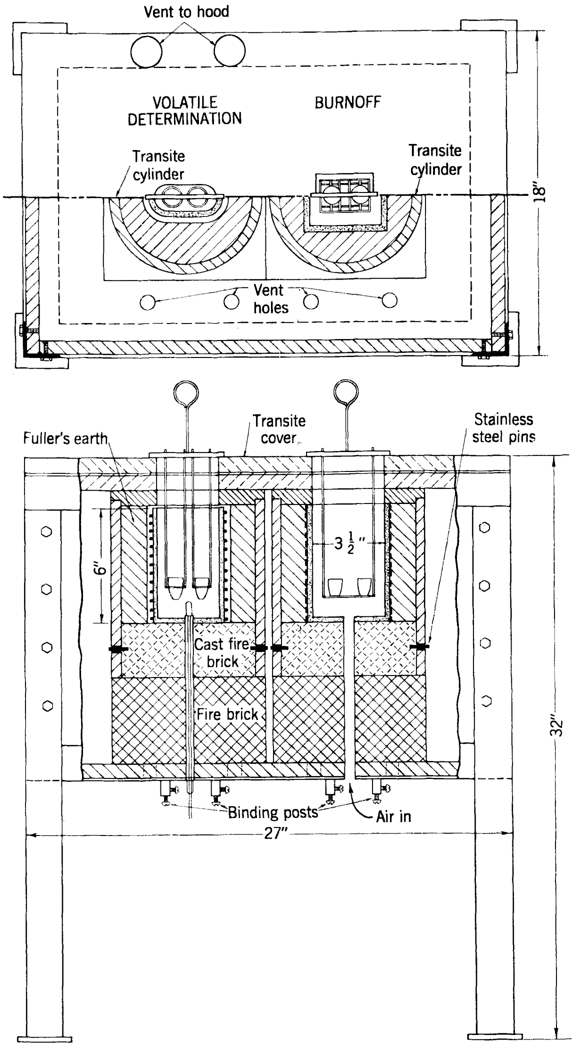

FIGURE 6.—Electric Furnace for Determining Volatile Matter.

Procedure.—Place a 1-gram sample (weighed to 0.1 mg) of air-dried coal ground to pass a No. 60 sieve in a 10-ml platinum crucible with a close-fitting capsule cover, shown in figure 7, in which *A* is the cover and *B* is the crucible. Heat the crucible and contents at 950 ° C (± 20° C) in the electric furnace for exactly 7 minutes. Remove the crucible from the furnace, cool it rapidly by placing it on an air-cooled steel plate, and

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[4] Rees, O. W., and W. A. Selvig. Determination of Ash in Coals Unusually High in Calcite and Pyrite. Ind. and Eng. Chem., anal. ed., v. 14, 1942, pp. 209–212.

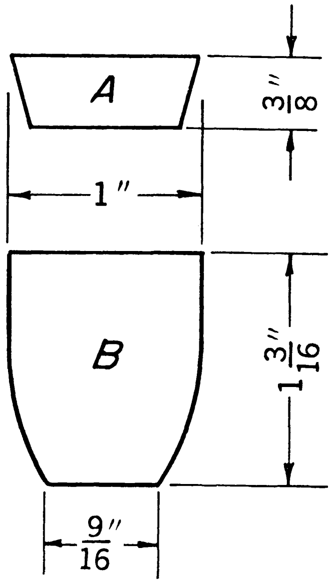

FIGURE 7.—Ten-Milliliter Platinum Crucible for Determining Volatile Matter. *A*, crucible cover. *B*, crucible.

weigh. The loss in weight minus the weight of moisture determined at 105° C times 100 equals the percentage of volatile matter.

With some strongly caking low- and medium-volatile bituminous coals the coke button may be broken with explosive violence because of liberation of volatile matter within the button. This is designated "popping." It may blow the lid off the crucible and cause mechanical losses of the coked material. When popping is observed, reject the determination and repeat the test until popping no longer occurs.

Mechnical losses are incurred when peat, lignite, and subbituminous coal are heated rapidly; such losses also occur with some low-temperature cokes, green cokes, chars, anthracites, and semianthracites. This mechanical loss is usually called sparking, and is caused by particles of the fuel being ejected from the crucible by the too-rapid escape of steam or volatile matter.[5] These particles become incandescent in the flame of the burning volatile constituents and may be seen around the edge of the crucible cover, sometimes only ¼ inch above the crucible and at other times shooting several inches to the top of the furnace. In severe sparking, ash deposits and occasionally unburned material are found on the crucible cover. Small deposits of ash are sometimes found on the crucible cover with moderately sparking fuels. All fuels that do not cake when volatile matter is determined are watched closely for sparking during the heating period; at the end of the test the crucible cover is inspected for ash deposits, and any found are considered as evidence of sparking.

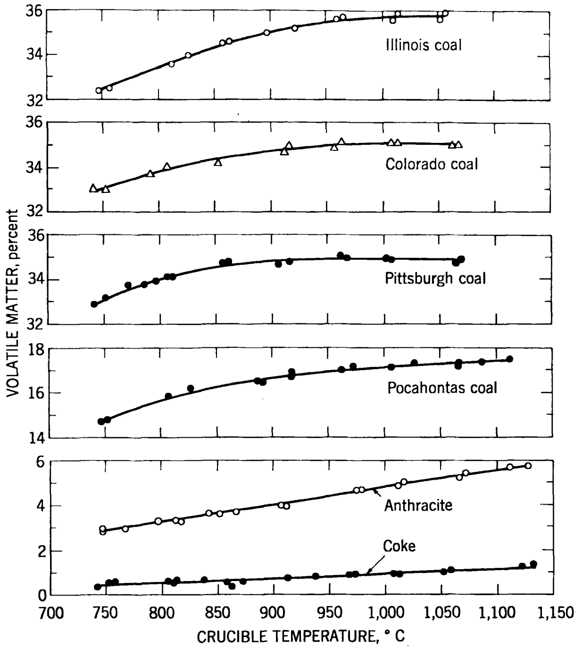

FIGURE 8.—Percentage of Volatile Matter From Different Coals at Various Temperatures.

All fuels that spark appreciably when volatile matter is determined by the prescribed method are given a gradual (linear) heating so that the temperature reaches 650° C in 6 minutes. The crucible is then lowered to its regular position for exactly 6 minutes at 950° C. A statement is included in the analytical report when the modified method is used.

It should be clearly understood that the volatile matter does not represent any definite compound in the coal. The method of determination is wholly empirical, and any variation in temperature or rate of heating will change the amount of volatile matter determined.

This fact is illustrated graphically by the curves in figure 8, which represent the amount of volatile matter obtained by heating several portions of a single sample of coal or coke at various temperatures between 750° and 1,100° C.[6]

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[5] Cooper, H. M., F. D. Osgood, and R. E. Solomon. Determination of Volatile Matter in Low-Temperature Cokes, Chars, and Noncaking Coals. BuMines Rept. of Inv. 3168, 1932, 17 pp.
Lord, N. W. Experimental Work Conducted in the Chemical Laboratory of the United States Fuel-Testing Plant at St. Louis, Mo., January 1, 1905 to July 31, 1906. Geol. Survey Bull. 323, 1907, 49 pp.; reprinted as BuMines Bull. 28, 1911, pp. 6–7.

[6] Fieldner, A. C., and A. E. Hall. Influence of Temperature on the Determination of Volatile Matter in Coal. Proc. 8th Internat. Cong. Appl. Chem., v. 10, 1912, p. 139.

Precision.—The following gives the permissible difference for the same sample from the same laboratory.

	Permissible differences, percent
Volatile matter:	
High-temperature coke	0.2
Anthracite	0.2
Semianthracite, bituminous coal, low-temperature coke, and chars	0.5
Subbituminous coal	0.5
Lignite and peat	0.5

The fixed carbon is found by subtracting the sum of the percentages of moisture, ash, and volatile matter from 100.

Ultimate Analysis

The ultimate analysis supplies information on the elemental composition of coals in terms of ash, carbon, hydrogen, nitrogen, oxygen, and sulfur.

Carbon and Hydrogen

Apparatus.—Schematic diagrams of apparatus and electrically heated furnace used for determining carbon and hydrogen in solid fuels are shown in figures 9 and 10. The furnace consists of three independent heaters (*G*, *H*, and *I*) mounted on wheels so that they are movable along the combustion tube.

The three heaters are similar in construction, and differ only in length and in resistance wire used in their heating elements. Heater *G* is 8 inches (203 mm) long and is wound with 15 feet of B. & S. No. 33 nickel-chromium No. II ribbon (1.1520 ohms per foot) on a fused alumina tube $7\frac{3}{4}$ inches (197 mm) long, $1\frac{1}{4}$ inches (32 mm) inside diameter, and $1\frac{1}{2}$ inches (38 mm) outside diameter; heater *H* is 14 inches (356 mm) long and is wound with 26 feet of B. & S. No. 28 nickel-chromium No. V ribbon (0.676 ohms per foot) on a tube $13\frac{3}{4}$ inches (349 mm) long; and heater *I* is 6 inches (152 mm) long and is wound with 10 feet of B. & S. No. 20 nickel-chromium No. 4 wire (0.615 ohm per foot) on a tube $5\frac{3}{4}$ inches (146 mm) long. The combustion furnace operates on 110–115 volts, and the temperature of each heater is controlled by a separate voltage regulator, *D*, of the variable transformer type.

The combustion tube is a fused-silica tube glazed inside and outside. Its internal diameter is about 18 mm, wall thickness about 2 mm, and total overall length about 112 cm; one end is rounded for insertion of a rubber stopper, and the other end is drawn out to about 6 mm outside diameter and 30 mm in length for rubber tubing connection with the absorption train. To permit observation the tube has a 12 cm transparent section that begins about 35 cm from its large end. The first part of the tube up to the end of the transparent section is empty; following the transparent section is a roll of copper gauze about 2 cm long; the next 33 cm is filled loosely with copper oxide wire; a second roll of copper gauze separates the wire from 18 cm of fused lead chromate (3 by 10

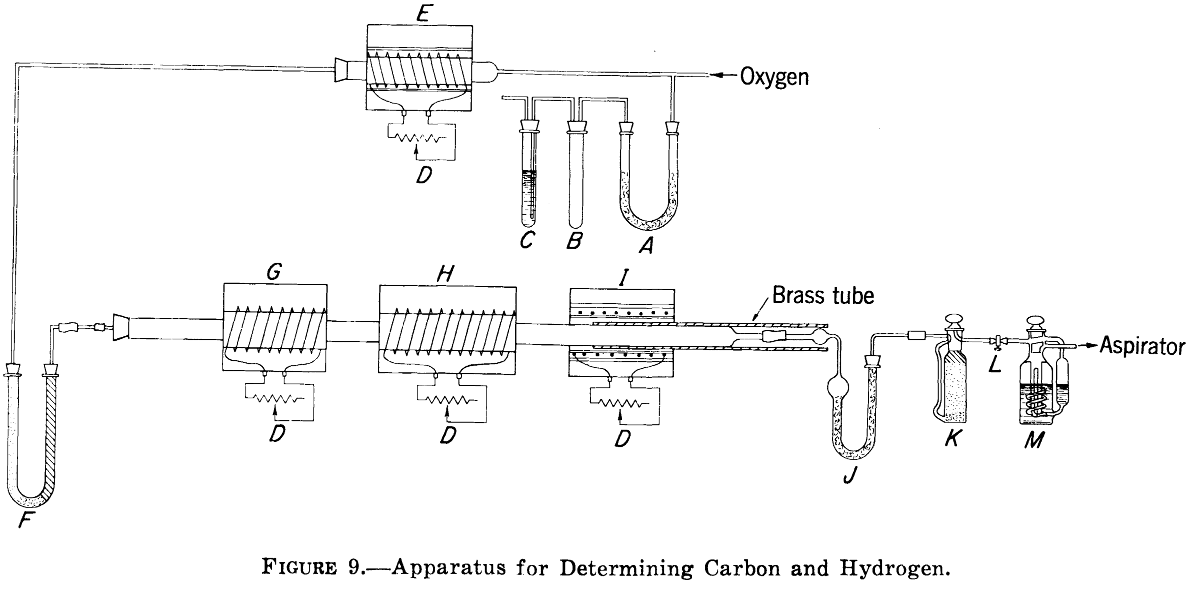

Figure 9.—Apparatus for Determining Carbon and Hydrogen.

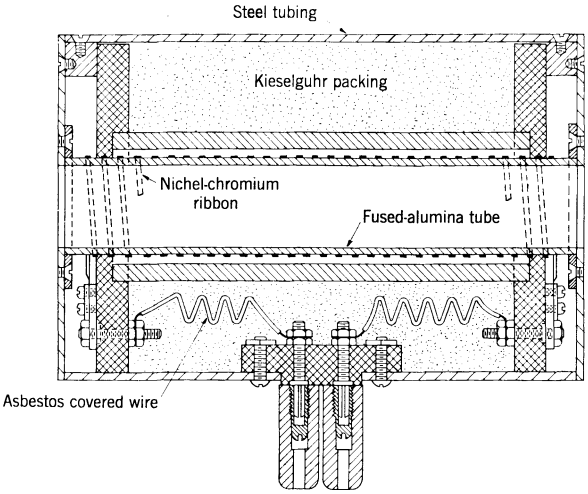

FIGURE 10.—Electric Furnace for Determining Carbon and Hydrogen.

mesh) which is held in place by a plug of glass wool extending to the constricted end of the tube.

The oxygen before entering the combustion tube is purified by passing it through a silica tube filled with copper oxide wire and heated to 750° C by heater *E*, then through U-tube *F* filled with sodium hydroxide-asbestos in the entrance side separated by a glass-wool plug at the bottom from anhydrous magnesium perchlorate in the exit side. Heater *E* is identical with heater *G* except that it is mounted permanently. The purification may be eliminated if the oxygen is known to be pure. The sodium hydroxide-asbestos and anhydrous magnesium perchlorate used in purification tube *F* are the same as those used in the absorption train connected to the exit end of the combustion tube.

Combustion and subsequent aspiration are carried out with oxygen, and the combustion tube is under pressure of about 3 inches of water controlled by the depth of water in tube *C*. This tube acts not only as a safety valve to prevent excess oxygen pressure in the combustion tube but also as an indicator to insure an ample supply of oxygen in case of rapid combustion of the sample. Tube *B* is empty and serves as a safety device to prevent water from tube *C* reaching the anhydrous magnesium perchlorate in U-tube *A*. When the current is interrupted or the oxygen flow is stopped, atmospheric pressure is established in the system by loosening the stopper in the top of tube *B*.

First in the absorption train is a Marchand tube, *J*, filled with granular anhydrous magnesium perchlorate to absorb water. Nesbitt absorption bulb *K* is connected to magnesium perchlorate tube *J* to absorb carbon dioxide. This bulb contains sodium hydroxide-asbestos which has approximately ¼ inch of magnesium perchlorate on top. The Nesbitt bulb *K* is connected to a Vanier bulb, *M*, filled with water, to indicate the rate of flow, and the Vanier bulb in turn is connected to an aspirator.

A small screw clamp, *L*, on the rubber tube connecting Nesbitt bulb *K* to Vanier bulb *M* regulates the rate of aspiration through the combustion tube. The rate is maintained at 50 to 75 ml per minute or 2 to 3 bubbles per second through the Vanier bulb *M*. The volume does vary somewhat because of variation in the diameter of the glass spiral in different bulbs. After aspiration has been regulated to the desired rate the combustion tube and absorption train are tested for tightness by temporarily closing the large end of the combustion tube with a rubber stopper or by placing a pinch clamp on the rubber connection at this point. More than 3 bubbles per minute through the Vanier bulb *M* indicates a leak.

PROCEDURE.—Run a blank for the same length of time and in the same manner as a regular determination after the system has been idle for some hours or after changes have been made in the chemicals in the absorption train or after the combustion tube has been recharged. If in the blank aspiration the change in weight of tube *J* and bulb *K* is less than 0.5 mg each, the apparatus is in proper condition for use. A compound of known carbon and hydrogen content, such as sucrose, is used regularly to check the operation.

To start a series of determinations, attach tube *J* and bulb *K* with short pieces of tightly fitting rubber tubing, regulate the oxygen aspiration, and energize heaters *E*, *H*, and *I*. Pull partly out of the heater a brass tube, which fits over the exit end of the combustion tube and moves freely in heater *I*, to cover the connection between the combustion tube and Marchand tube *J*. This brass tube conducts enough heat from the heater to prevent deposition of moisture in the connection. The temperature of heater *H* reaches 800° C in about 90 minutes, and the temperature of heater *I* over the lead chromate is about 400° C. Remove tube *J* and bulb *K* from the train, wipe with a clean cloth, and cool to room temperature. Connect another set of tube *J* and bulb *K* in the apparatus and aspirate for 15 to 20 minutes. Place a 0.2-gram air-dried sample, crushed to pass a No. 60 sieve, weighed to 0.1 mg, in a porcelain boat and put in a glass weighing tube, which is immediately closed with a stopper to minimize moisture changes. After the first set of tube *J* and bulb *K* have cooled to room temperature, open bulb *K* for a moment to allow the oxygen in the bulb to reach atmospheric pressure) weigh, and replace them in the train. Quickly transfer the boat containing the sample from the weighing tube to the transparent section of the combustion tube. Energize heater *G*, and move it from the left end of the track to cover about half of the boat containing the sample. If the heater *G* has been cooling from a previous determination, its temperature is reduced under 200° C before another test is started. Gradually increase the temperature of heater *G* to 850° C at such a rate that the coal burns slowly and evenly. At the same time, move the heater forward slowly so that it finally covers the entire clear section in the combustion tube and contacts heater *H*. This burning operation requires 20 to 25 minutes. After full heat is continued 15 minutes, deenergize heater *G* and return it to its original position to cool for the next determination.

Continue the aspiration for 15 to 20 minutes. Remove Marchand tube *J* and Nesbitt bulb *K* and replace them with another set for the next determination. Wipe the tube *J* and bulb *K* with a clean cloth, cool to room temperature, and weigh. The increase in weight of the Marchand tube *J* multiplied by 55.95 gives the percentage of hydrogen, and the increase in weight of the Nesbitt bulb *K* multiplied by 136.45 gives the percentage of carbon. Remove the boat and inspect the residue for carbon. If coke or carbon is present, the determination is repeated. The total time required for a determination after heaters *H* and *I* have reached the proper temperature is 50 to 60 minutes.

PRECISION.—Permissible differences of same sample from the same laboratory are as follows.

	Permissible differences, percent
Ultimate analysis:	
Carbon	0.30
Hydrogen	.07

Nitrogen

The well-known Kjeldahl-Gunning method is used to determine nitrogen. Boil one gram of the air-dried coal sample ground to pass a No. 60 sieve and weighed to ± 1 mg with 30 ml of concentrated sulfuric acid (H_2SO_4), 7 to 10 grams of potassium sulfate (K_2SO_4), and 0.6 to 0.8 gram of mercury in a 500-ml Kjeldahl flask until all particles of coal are oxidized and the solution is nearly colorless. For coke, about 0.1 gram of chromic oxide (CrO_3) is added to the mixture before boiling. Continue the boiling at least 2 hours after the solution has reached the straw-colored stage. The total time of digestion will be 3 to 4 hours except for coke and anthracite, which require much longer digestion. Add a few crystals of $KMnO_4$, after the solution has cooled enough to avoid violent reaction, to insure complete oxidation. After the solution has cooled, dilute it to about 250 ml with cold water. Add twenty-five milliliters of potassium sulfide solution (40 grams K_2S per liter) to precipitate the mercury, and several granules of 20-mesh zinc to prevent bumping. Add gradually enough strong sodium hydroxide (NaOH) solution to make the solution distinctly alkaline.

The danger of loss of ammonia is minimized by holding the flask in an inclined position while the sodium hydroxide solution is being added. The alkaline solution runs down the side of the flask and forms a layer below the lighter acid solution. After the alkaline solution is added, connect the flask at once to the condensing apparatus, and mix the solution by gently shaking the flask. Distill over the ammonia (NH_3) into a measured amount (10 ml) of standard sulfuric acid solution (0.3568 *N*), to which has been added enough cochineal indicator for titration. Continue the distillation until 150 to 200 ml of distillate has passed over, and titrate the distillate with 0.1784 *N* ammonia (NH_4OH) solution (20 ml NH_4OH solution = 10 ml H_2SO_4 solution = 0.05 gram nitrogen).

In routine work the determinations are made in sets of 12, the digesting and distilling apparatus being designed for 12 flasks. One flask in each set contains a blank determination in which 1 gram of pure sucrose (cane sugar) is substituted in place of the usual coal sample. The nitrogen found in this blank determination is deducted from the nitrogen found in each of the 11 determinations that were made in the same set.

Usually the sodium hydroxide and potassium sulfide are dissolved in a single stock solution. Twenty pounds of electrolytic caustic soda are dissolved in water in a stoneware jar. A solution containing 175 grams of potassium sulfide in water is added, and the resulting solution is made up to 22 liters. About 100 ml of this alkali solution is used for a nitrogen determination.

PRECISION.—Permissible differences of the same sample, same laboratory, follow.

	Permissible differences, percent
Ultimate analysis:	
Nitrogen	0.05

Sulfur

ESCHKA METHOD.—The method consists of incinerating coal and coke with Eschka mixture (2 parts of light calcined magnesium oxide (MgO) and 1 part of anhydrous sodium carbonate (Na_2CO_3)). Thoroughly mix a sample of air-dried coal ground to pass a No. 60 sieve and weighing 1.3737 grams, weighed to 0.1 mg, in a 30-ml platinum or porcelain crucible with about 3 grams of Eschka mixture, and spread over the top about 3 grams of Eschka mixture to form a cover. Place the crucible with its contents in a cold muffle furnace, and heat slowly to 800° ± 25° C in about 1½ hours. Slow heating during this preliminary period is essential to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulfur. Maintain the maximum temperature of 800° ± 25° C for about 1½ hours.

Remove the crucible from the muffle and stir the contents thoroughly. If any black particles remain, return the crucible to the muffle and heat until all the particles are burned out, a condition that indicates that the process is complete. Allow the crucible and contents to cool, transfer the contents to a beaker, and digest with 100 ml of hot water for at least 30 minutes. Filter into a beaker; wash the insoluble residue in the beaker twice with hot water by decantation and after transferring it to the filter paper, wash it with small quantities of hot water until the volume of solution in the beaker is about 200 ml. Add enough hydrochloric acid (2:1) to make the solution slightly acid. Precipitate the sulfur as barium sulfate ($BaSO_4$) by adding slowly 10 to 20 ml of a hot 10-percent solution of barium chloride ($BaCl_2 2H_2O$). Allow the solution containing the precipitate to stand for at least 2 hours at a temperature just below boiling.

After cooling, filter the solution through an ashless filter paper and wash with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. The test for assuring excess barium chloride is made by adding a few drops of sulfuric acid solution to the filtrate. Ignite the precipitate in a porcelain crucible, free access of air being allowed and the paper being folded over the precipitate only loosely to prevent spattering. Smoke the paper off gradually at first, and do not heat above a dull redness for the final heating. After burning off the paper completely, continue the heating for a few minutes; then cool the crucible and weigh the $BaSO_4$ precipitate. The weight in grams of barium sulfate after deducting the weight of barium sulfate found in a blank determination using the same reagents, multiplied by 10, equals the percentage of sulfur in the sample.

BOMB-WASHING METHOD.—Sulfur can be determined in the washings from the oxygen bomb calorimeter after the calorimetric determination. The results have been found to check closely with those of the Eschka method.[7] The method saves considerable time over the Eschka method, so it is also used in the coal-analysis laboratory of the Bureau of Mines.

Allow the bomb to stand in the calorimeter water for not less than 5 minutes after firing. Remove the bomb, and open the valve carefully to allow the gases to escape at an approximately even rate so that the pressure is reduced to atmospheric in not less than 1 minute. Too rapid release of the gases results in a loss of sulfur. Bombs equipped with valves other than needle valves, such as compression valves, are provided with a device for controlling the valve to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If you find any, repeat the test. Wash all parts of the interior of the bomb, including the tray, with a fine jet of distilled water containing 1 ml per liter of a saturated solution of methyl orange until no acid reaction is observed. It is essential to wash through the valve openings of bombs equipped with compression valves or other types of valves with large openings, as considerable spray may collect in such openings.

Collect the washings in a 250-ml beaker and titrate with standard ammonia solution (0.00652 g per ml) to obtain the acid correction for the heating value, as specified under the calorimetric determination. Heat the solution to boiling, filter, and wash the residue and filter paper thoroughly five or six times with hot distilled water. Add to the filtrate and washings, amounting to about 200 ml, enough hydrochloric acid (2:1) to make the solution slightly acid. Heat the

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[7] Selvig, W. A., and A. C. Fieldner. Sulfur in Coal and Coke; Check Determinations by the Eschka, Bomb-Washing and Sodium Peroxide Fusion Methods. Ind. and Eng. Chem., v. 19, 1927, pp. 729–733.

solution and precipitate the sulfur with barium chloride solution as described in the Eschka method.

$$\frac{(\text{Weight of BaSO}_4 - \text{blank}) \times 13.74}{\text{Weight of sample}} = \text{percentage of sulfur}$$

Permissible differences of the same sample, same laboratory follow:

Ultimate analysis of sulfur, percent:	Permissible differences, percent	
	Eschka method	Bomb-washing method
0–2	0.05	0.10
2–4	.08	.15
Over 4	.10	.20

Oxygen

In the ultimate analysis, the composition of coal is expressed in percentages of ash, sulfur, carbon, hydrogen, nitrogen, and oxygen. The sum of these constituents is taken to equal 100 percent. As there is no simple, direct method for the determination of oxygen, it is estimated by subtracting the sum of the other five constitutents from 100. This method throws upon the oxygen the summation of all the errors incurred in the other determinations.

In the consideration of an ultimate analysis one must remember that the hydrogen and oxygen of the moisture in the sample are included with the hydrogen and oxygen of the dry-coal substance. Usually before comparisons are made ultimate analyses are computed to a dry-coal basis to give the relative proportions of hydrogen and oxygen in the dry coal.

Determination of Sulfur Forms in Coal

Three forms of sulfur are recognized in coal: (1) Sulfur combined with iron as pyrite or marcasite and known as pyritic sulfur, (2) sulfur combined with the coal substance as organic sulfur, and (3) small quantities of sulfate sulfur in the form of calcium sulfate or iron sulfate. Freshly mined coal usually contains only small quantities of sulfate sulfur. These forms of sulfur are determined on samples of air-dried coal crushed to pass a No. 60 (250 μ) sieve by modifications of methods developed by Powell.[8]

The sulfate sulfur is extracted from the coal with dilute hydrochloric acid. The pyritic sulfur is extracted from the hydrochloric acid residue with dilute nitric acid. The pyritic sulfur is then determined (1) from the nitric acid soluble sulfur, or (2) by calculation from the pyritic iron which is the nitric acid soluble iron. The organic sulfur is the difference between the total sulfur and the sum of the pyritic and sulfate sulfur.

Sulfate Sulfur

Weigh out a 2.0000-gram sample, weighed to 0.1 mg, and place it in a 250-ml beaker. Add 3 ml of 1:3 ethyl alcohol and swirl to wet the sample. Cover the sample carefully with 50 ml of hydrochloric acid (1:3). Cover with a watch glass and place on a hotplate to boil.

At the end of 20 minutes, filter the contents of the beaker, retaining the coal material left on the filter, after washing six times with cold water, for the pyritic sulfur determination. To the filtrate add 10 ml of bromine water and heat almost to boiling. Add 20 to 25 ml of 1:1 ammonium hydroxide, and let stand on a hotplate for 20 minutes. Filter while hot, discarding the residue left on the filter after washing five or six times with hot water. Increase the volume of the filtrate to 200 ml with distilled water.

Neutralize the filtrate with hydrochloric acid (2:1) and add an excess of 5 ml, using methyl orange indicator. Heat the solution to boiling, add slowly 20 ml of hot 10 percent barium chloride solution, and allow to stand for several hours. Filter and wash the precipitate with hot water until free of chlorides, ignite the filter paper, and weigh the barium sulfate. The weight of barium sulfate, in grams, multiplied by 6.868 represents the percentage of sulfur combined as sulfate in the coal.

Pyritic Sulfur

Macerate the coal residue and filter paper from the hydrochloric acid separation in 100 ml of 25 percent by volume nitric acid and allow to stand, with occasional stirring for 12 to 24 hours at room temperature. Filter and discard the coal residue after washing several times with cold water. Add 3 ml of concentrated hydrochloric acid to the filtrate and evaporate to dryness on a water bath.

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[8] Powell, Alfred R. The Analysis of Sulfur Forms in Coal. BuMines Tech. Paper 254, 1921, 21 pp.

Dissolve the residue in 5 ml of concentrated hydrochloric acid and 25 ml of water. Pour this acid solution into a 250-ml beaker and add 25 ml of hot ammonium hydroxide (1:1) making sure that ammonium hydroxide is in excess. Filter while hot and wash several times with hot water.

Sulfur in the filtrate is determined by the method used for sulfate sulfur.

Dissolve the precipitate of ferric hydroxide off the filter with the least possible quantity of concentrated hydrochloric acid, added drop by drop, and wash with small amounts of water. Heat the acid solution contained in a 250-ml beaker almost to boiling and add stannous chloride (10 grams of stannous chloride dissolved in 20 ml of hot concentrated hydrochloric acid and diluted to 200 ml with water) drop by drop from a burette until the solution is colorless, adding 3 or 4 drop in excess. Cool the solution rapidly and transfer it to a 600-ml beaker containing 250 ml of cold water. Add 10 ml of a saturated solution of mercuric chloride, stir the solution thoroughly, then add 20 ml of titrating solution (144 grams of manganous sulfate, 1,040 ml of water, 280 ml of sulfuric acid, 1.84 specific gravity, and 280 ml of phosphoric acid, 1.71 specific gravity) and stir until well mixed. Titrate at once with 0.02 *N* potassium permanganate until the faintest pink color lasts for 10 seconds. The number of milliliters of 0.02 *N* potassium permanganate used, multiplied by 0.0558, gives the percentage of pyritic iron in the coal. The percentage of pyritic iron multiplied by 1.148 gives the percent sulfur as pyrite in the coal. Comparison is made with the gravimetric determination of pyritic sulfur, and if the calculated percentage is lower than that obtained directly, the calculated value is considered to be the correct one.

Organic Sulfur

Organic sulfur is determined by subtracting the sum of the sulfate and pyritic sulfur from the percentage of total sulfur in the coal determined by the Eschka method.

Determination of Chlorine in Coal and Coke by the Bomb Combustion Method

This analytical method is used for the determination of chlorine in coals, cokes, and chars. The chlorine in the sample is converted to a chloride by combustion with oxygen in the bomb and determined volumetrically by potentiometric titration with a standard $AgNO_3$ solution.

Procedure

Mix a 1-gram sample of air-dried coal, ground to pass a No. 60 sieve, and weighed to 0.1 mg, thoroughly with 1-gram of Eschka mixture (a special 2:1 mix of low chloride MgO and Na_2CO_3) and put in a nickel crucible. Place 10 ml of water in the bottom of the bomb to absorb the acid gases from the vapor phase. Admit oxygen slowly into the bomb until the pressure reaches 25 atmospheres. Immerse the bomb in a container of distilled water and fire with an ignition unit. Use a 10-cm length of iron wire for ignition. After 10 minutes, remove the bomb from the water and rotate so that maximum washing is accomplished by the liquid in the bomb. After the pressure is released at a uniform rate (requiring approximately 1 minute) open the bomb and inspect for unburned coal. If unburned particles are found, discard the determination; otherwise rinse the interior of the bomb and crucible thoroughly with a fine stream of hot distilled water into a 400-ml beaker until approximately 250 ml of wash water is collected. Take special care not to lose any wash water.

Allow the bomb washing to come to room temperature; add 2 to 3 drops of methyl orange indicator to the solution and acidify to a permanent pink color with freshly boiled 1:1 HNO_3. Add approximately 14 to 16 drops of excess acid to get the solution to a pH of 2. (It is not necessary to measure the pH, because experiments have shown that the required pH of 2 is obtained by the addition of 14 to 16 drops of excess acid.) Balance the titrating meter at a scale reading of 500 millivolts and set the scale to the predetermined millivolt equivalence point (see calibration). Place the silver and silver-silver chloride electrodes in the solution and actuate the stirring mechanism. Carry out the titration with standard $AgNO_3$ (0.0141 *N*) to the end-point and record the volume of titrant consumed.

Make a blank determination following the same procedure and using the same amounts of all reagents.

Calculation

To calculate the percentage of chlorine for a 1-gram sample and a 0.0141 *N* solution of $AgNO_3$ use:

(A-B) × 0.05 = percentage of chlorine, where
A = ml of $AgNO_3$ solution required to titrate sample, and
B = ml of $AgNO_3$ solution required to titrate blank.

Calibration

To calibrate the titrating meter for the potentiometric end-point, dilute a standard solution of 10.00 ml of 0.0141 *N* NaCl with 200 ml of distilled water and acidify with 1:1 HNO_3 to a pH of 2. Add to this 0.0141 *N* $AgNO_3$ solution in 8 increments of 1 ml each, 8 increments of 0.5 ml each, and then 6 increments of 1 ml each. Record each increment with its particular dial reading. Plot a curve by using the volume as the abscissa and the dial settings as the ordinate. Take the end-point from this curve as the point of inflection or the middle of the steepest portion of the curve.

Having determined this end-point, routine determinations can be carried out rapidly by setting the dial to a value preceding this point and titrating till the cathode ray tube opens. The dial is then set to the exact end-point and the titration carried out drop-wise until the tube opens again. Continue stirring for a few seconds before recording the volume of titrant used.

Determination of Carbon Dioxide in Coal

Small amounts of mineral carbonates occur in many coals and comparatively large amounts in some coals. The determination of carbon dioxide is required in estimating the mineral-matter content of high-carbonate coals for classification[9] purposes.

Carbon dioxide is determined by boiling the coal with dilute hydrochloric acid and absorbing the liberated carbon dioxide in a situable absorbent.

Apparatus

The apparatus used for the determination is shown in figure 11. A 300 ml Erlenmeyer flask, *A*, is fitted with socket joint No. 35/20. To this is fitted a straight adapter tube, *B*, with ball and socket joints No. 35/20, and center tube of about 8 mm OD. The inner (8 mm) tube of the adapter extends almost to the bottom of the Erlenmeyer flask. The other end of the small tube is attached to a three-way stopcock having a separatory funnel, *C*, on one end and an aspirator bottle, *D*, attached to the third end, which is an acid reservoir. Separatory funnel *C* and aspirator bottle *D* are provided with a glass cylinder, *E*, filled with soda lime to free the incoming air from carbon dioxide. The large tube of the adapter, *B*, is connected to a 300 mm Graham coil-type condenser, *F*, with ball and socket joint No. 35/20; this is connected to an absorption bulb, *G*, having a layer of glass wool on the bottom and filled with 8-mesh anhydrous calcium chloride saturated with carbon dioxide. Bulb *G* is followed by another absorption bulb, *H*, filled about two-thirds full with pieces of pumice impregnated with anhydrous copper sulfate.

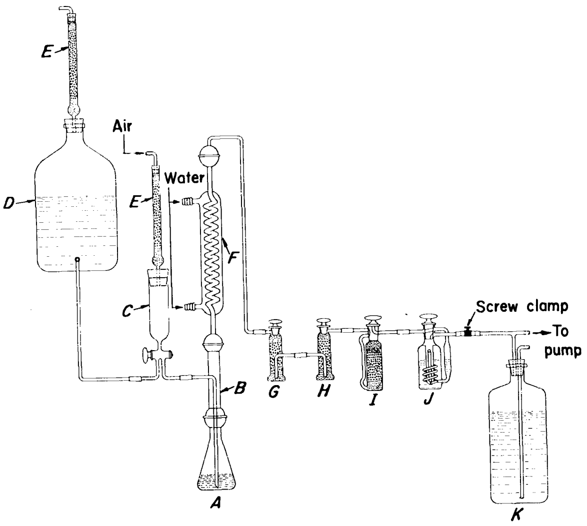

FIGURE 11.—Apparatus for Determining Carbon Dioxide.

The impregnated pumice is prepared as follows: Crush pumice to approximately ¼-inch size, sieve free from dust, and transfer 60 grams to a casserole. Cover with a concentrated solution of 30 to 35 grams of copper sulfate, evaporate to dryness while stirring constantly, and then heat for 3 to 4 hours at 150° to 160° C in an air bath. Cool in a desiccator and preserve in a glass-stoppered bottle.[10]

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[9] American Society for Testing and Materials. Carbon Dioxide in Coal. D 1756-62 in 1965 Book of ASTM Standards: Part 19, Gaseous Fuels; Coal and Coke. Philadelphia, Pa. 1965, pp. 312-315.

[10] Hillebrand, W. F., and G. E. F. Lundell. Applied Inorganic Analysis. John Wiley & Sons, Inc., New York, 1929, pp. 42-43.

The pumice impregnated with copper sulfate absorbs any hydrogen sulfide and hydrochloric acid that may be present. The remainder of bulb *H* is filled with 8-mesh anhydrous calcium chloride saturated with carbon dioxide. Nesbitt bulb *I* contains sodium hydroxide-asbestos which has approximately ¼-inch of magnesium perchlorate on top with a layer of glass wool on the top and bottom of the bulb. Vanier bulb *J* is half-full of water and is used to indicate the rate of flow only. Suction is applied to the Vanier bulb by a filter pump through a Mariotte flask *K*. The flask keeps the pressure constant; the rate of flow is regulated by a screw clamp placed between the bulb and Mariotte flask.

Procedure

Insert the Nesbitt bulb into the absorption train and displace the air by aspirating carbon dioxide-free air for about 15 minutes at a rate of 2 to 3 bubbles a second, as indicated in the Vanier bulb. Remove the Nesbitt bulb, weigh, and insert into the absorption train. Place a 10-gram sample of coal, weighed to 0.1 mg and ground to pass a No. 60 sieve, in the Erlenmeyer flask and add 100 ml of hot, recently boiled distilled water. Shake the flask to wet the sample and connect it to the apparatus. Turn the stopcock to allow 30 ml of dilute hydrochloric acid (1:3) to flow from the reservoir, *D*, to the separatory funnel, *C*, and by turning the stopcock add the dilute acid slowly to the flask. Heat the Erlenmeyer flask until the contents boil gently and continue the boiling for 10 minutes. Maintain the current of carbon dioxide-free air through the apparatus during this period and for an additional 15 minutes to insure that all the carbon dioxide is swept into the Nesbitt bulb. Remove the Nesbitt bulb, wipe with a clean cloth, allow to stand 10 minutes at room temperature and weigh. The increase in weight is the carbon dioxide in the coal sample.

Precision

Carbon dioxide, percent	Permissible differences, percent	
	Same laboratory, same sample	Different laboratory, duplicate sample
Under 1.0	0.05	0.10
Over 1.0	0.10	0.20

Determination of the Calorific Value of Coal

Apparatus

The multiple unit calorimeter [11] used by the Bureau of Mines is of the isothermal oxygen bomb type shown in figure 12. The combustion bomb is made of stainless steel, which will not be attacked by nitric or sulfuric acid. The calorimeter consists of an oxygen bomb, an inner pail, a calorimeter can with cover, a stirring device, a platinum resistance thermometer, a resistance bridge, a galvanometer, a constant-temperature bath, and a large automatic pipette.

Standardization of the Calorimeter

The first detail to be considered in calorimetric work is the correct determination of the water-equivalent of the apparatus.

Among others, the most convenient and accurate method of calibrating commercial calorimeters is by the combustion of standard substances, the calorific values of which have been accurately determined in calorimeters calibrated by electrical methods. Benzoic acid of certified calorific value may be obtained from the National Bureau of Standards.[12]

In using this method the water-equivalent is an average of at least five determinations, which are carried out with the thermometer used in daily work. The weight of benzoic acid taken for combustion is about 1.2 grams; this amount gives approximately the same rise of temperature as is obtained in the combustion of 1 gram of coal. The benzoic acid is pelleted, weighed, and immediately placed in the bomb.

The determination is divided into three periods—the preliminary period, the combustion period, and the final period. The preliminary period usually requires five readings taken 1 minute apart, or until the rate of change per minute is nearly constant. After the fifth reading has been taken the current at 32 volts is turned on for about half a second, and the combustion period begins. The first two readings in this period are taken half a minute apart, because the change in temperature is so great. The temperature rises to a maximum and then begins to fall; after its rate of fall becomes uniform,

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[11] Davis, J. D., and E. L. Wallace. A Convenient Multiple-Unit Calorimeter Installation. BuMines Tech. Paper 91, 1918, 48 pp.

[12] National Bureau of Standards. Reference Materials: Catalog and Price List of Standard Materials Issued by the National Bureau of Standards. Misc. Publication 260, October 1, 1965.

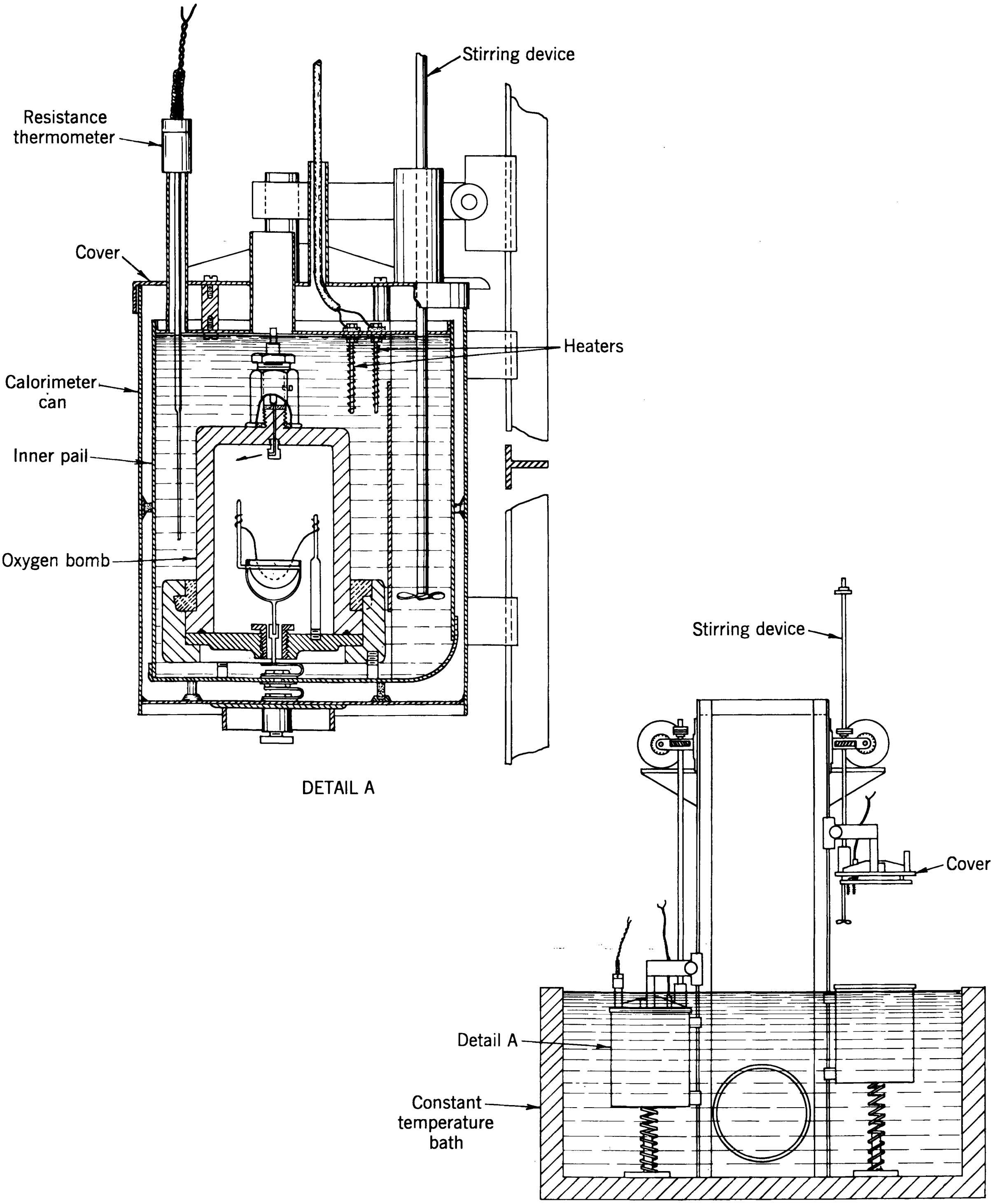

FIGURE 12.—Multiple-Unit Calorimeter.

readings are taken every minute for 5 or 6 minutes. The final reading of the combustion period is the first reading after the rate of fall becomes uniform.

The following figures are from an actual determination and show the method of calculating the results and the corrections applied:

Method of calculating water equivalent from calorimeter readings
(Benzoic acid: 1.2000 grams weighed to 0.1 mg)

Time, min	Reading,[1] ° C	Change from previous reading	Temperature change at each reading, computed rate per minute	Temperature correction for heat loss or gain during each interval
		PRELIMINARY PERIOD		
0	0.201	—	—	—
1	.205	0.004	—	—
2	.211	.006	—	—
3	.218	.007	—	—
4	.224	.006	—	—
5	.232	.008	—	—
Net	—	.031	+.0062	+.0028
		COMBUSTION PERIOD		
5.5	0.637	0.405	+0.0049	+0.0013
6	2.502	1.415		—.0013
7	3.109	1.057	—.0029	—.0031
8	3.248	.139	—.0033	—.0034
9	3.268	.020	—.0034	—.0034
10	3.269	.001	—.0034	—
Net	—	3.037	—	[2]—.0071
		FINAL PERIOD		
11	3.265	+.0004	—	—
12	3.262	—.003	—	—
13	3.258	—.004	—	—
14	3.255	—.003	—	—
15	3.252	—.003	—	—
Net	—	—.017	—0.0034	—

[1] Starting at approximately 28° C.
[2] Algebraic sum.

Reading at 10 minutes	° C	3.269
Reading at 5 minutes	° C	.232
Observed change	° C	3.037
Radiation loss	° C	.0071
Corrected change	° C	3.0441
Heat of combustion of 1 gram of benzoic acid	Btu	11,373
Weight of sample	grams	1.2000
Heat of combustion of sample	Btu	13,648
Heat from titer [1]	Btu	20
Total heat	Btu	13,668
Water equivalent of heat from titer (13,668/3.0441)	Btu	4,493

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[1] 2 ml. titer (1 ml=10 Btu)	Btu	20
0.0 g sulfur (0.01 g=23.4 Btu)	Btu	0
		20

The reading 0.201°, taken at 0 minutes, is the first reading of the preliminary period. The temperature reading 0.232° is the last reading of the preliminary period and was taken 5 minutes after the first reading; hence, 0.232° — 0.201° = 0.031°, or total change in temperature during the preliminary period; also 0.031° ÷ 5 = 0.0062°, or rate of change per minute during the preliminary period.

The rate of change per minute in the final period is found in like manner to be

—0.0034°; hence, 0.0062° — (—0.0034°) = 0.0096°, or change in rate during the combustion period.

The observed change in temperature during the combustion period is 3.037°; the change in rate per degree of temperature change in the combustion period is therefore equal to

$$\frac{0.0096^\circ}{3.037^\circ} = 0.0032^\circ.$$

The change in temperature during the first half minute of the combustion period is 0.405° and 0.405° × 0.0032° = 0.0013°, the change in rate during first half minute of combustion period. The rate of temperature change at reading at 5½ minutes is 0.0062° — 0.0013° = 0.0049°.

The rate of change for each succeeding reading in the combustion period is calculated in the same way.

The temperature correction for the heat loss during the half-minute readings is made by dividing the algebraic sum of the rates by 4, and for the minute readings the algebraic sum is divided by 2, because the temperature correction for heat loss during each interval is the mean rate per minute of temperature change multiplied by the time of the interval in minutes. For example, at 5 minutes the rate per minute of temperature change is + 0.0062°, and at 5½ minutes the rate per minute of temperature change is + 0.0049°; therefore the mean rate per minute of temperature change for the half-minute interval is

$$\frac{0.0062 + (+\ 0.0049)}{2} = 0.0056^\circ,$$

and ½ × (+ 0.0056) = + 0.0028, which is the correction for heat loss taking place during the half-minute interval. The algebraic sum of all the temperature corrections for heat loss during each interval is added to the observed temperature change.

Correction for radiation, (heat loss or gain), and acidity are made as shown previously. After the corrected change of temperature (3.0041 in the specimen calorimeter determination) has been obtained the water equivalent is computed by the following formula:

$$E = \frac{HW+C}{T}$$

in which

E = water equivalent of calorimeter,
H = heat of combustion of 1 gram of the standard substance,
W = Weight in grams of sample taken,
C = correction for heat from formation of nitric acid, and
T = change of temperature, corrected for radiation.

An oxygen bomb calorimeter, standardized by the combustion of benzoic acid, gave the following concordant results:

Seven determinations with benzoic acid (Btu value, 11,373) gave water equivalent values of 4,495, 4,501, 4,491, 4,492, 4,495, 4,496, and 4,493, or an average of 4,495.

Procedure

Place a 1-gram sample of coal, weighed to 0.1 and ground to pass a No. 60 sieve, in a platinum tray the bottom of which is covered with a piece of asbestos paper that has been ignited. The use of this asbestos mat avoids trouble in completely burning anthracite. Put about 0.5 ml of water in the bottom of the bomb to saturate with moisture the oxygen used for combustion. Attach one of the platinum terminals of the firing circuit to the tray. Connect the terminals by a piece of platinum wire 85 mm long and 0.10 mm in diameter, weighing about 15 mg. Attach the ends of the wire to the terminals (which must be clean) simply by wrapping the wire tightly around them. Bend down the platinum wire so as to touch the coal sample on the mat within the tray. Put the bell on the bomb plate and engage the locknut. Admit oxygen slowly into the bomb until the pressure within the bomb is 20 to 30 atmospheres, depending on the size of bomb used. For the larger bombs a pressure of 20 atmospheres is sufficient, while smaller bombs may require as much as 30 atmospheres to furnish enough oxygen for complete combustion. The bomb should contain at least 5 grams of oxygen per gram of coal or other combustible. The oxygen is admitted very slowly so that no particles of coal dust are blown out of the tray. When extremely light materials such as peat are used, best results are obtained by briquetting the sample, and using a weighed portion of the broken briquets instead of the powdered sample.

Place the bomb in the brass inner pail containing 1,880 grams of distilled water and put the inner pail in the calorimeter can. The temperature of the water is 2.5° C below the temperature of the water bath. Adjust the stirring apparatus so that it touches neither pail nor bomb, and insert the platinum resistance thermometer so that the tip is about 5 cm from the bottom of the bucket and does not contact any metal parts of the apparatus. After the stirrer has been in motion about 1 minute, or when the water has been mixed thoroughly, read the temperature with the platinum resistance thermometer attached to a bridge and galvanometer which is calibrated to 0.001° C, required for accurate calorimetric work. Continue the stirring at a uniform rate throughout the determination which should be rapid enough to insure thorough mixing. In covered calorimeters never allow the temperature to rise more than 1° C above the temperature of the water jacket.

The actual determination is made by recording only two readings, the initial reading at 28° C before the sample is ignited and the final reading 5 minutes later. Subtracting the initial from the final reading gives the observed temperature change and the radiation correction is applied (see Radiation Correction) to give the total temperature change. This multiplied by the water equivalent will give the total heat developed.

Further corrections are made for heat due to formation of aqueous nitric acid and sulfuric acid. The correction for sulfur burned to sulfuric acid (H_2SO_4) is 13 calories per 0.01 gram of sulfur. The correction for nitrogen to aqueous nitric acid is made by titrating the acidity of the bomb liquor with standard ammonia solution (0.00652 gram NH_3 per milliliter) and is equivalent to 5.56 calories (10 Btu) per milliliter.

DETERMINATION OF SULFUR-CORRECTION FOR ACIDITY.—After combustion of the coal, wash the bomb calorimeter thoroughly, and titrate the washings with standard ammonia solution (0.00652 gram per millilter), methyl orange being used as an indicator. The acidity is due to the nitric acid (HNO_3) formed from the nitrogen of the coal and the nitrogen of the air in the bomb and also to the sulfuric acid (H_2SO_4) obtained from the combustion of the sulfur in the coal. The sulfur can be easily determined by precipitation as barium sulfate ($BaSO_4$). The ammonia solution is of such strength that 1 ml is equivalent to 0.00537 gram of nitrogen, since this weight of nitrogen burned to nitrogen pentoxide (N_2O_5) plus water generates 5.56 calories (10 Btu) of heat.

The calorific value of nitrogen burning to N_2O_5 + water is 1,035 calories per gram; 1,035 calories: 5.56 calories: : 1 gram : 0.00537 gram. Therefore, 0.00537 gram of nitrogen generates 5.56 calories (10 Btu) of heat when burned to aqueous nitric acid.

The ammonia solution is made up according to the equation

$$HNO_3 + NH_3 = NH_4NO_3.$$

Since $N = 14$ and $NH_3 = 17$,

$$14 : 17 = 0.00537 \text{ gram} : 0.00652 \text{ gram}.$$

Therefore, 0.00652 gram of NH_3 is equivalent to 0.00537 gram of nitrogen, which when burned to aqueous nitric acid (HNO_3) releases 5.56 calories (10 Btu) of heat. The standard solution contains 6.52 grams of NH_3 per liter. The solution, when used to titrate the bomb liquor after combustion of a coal sample, must satisfy not only the nitric acid formed but also any sulfuric acid resulting from the combustion of the sulfur in the coal.

The strength of the ammonia solution in terms of sulfur in the form of sulfuric acid (H_2SO_4) is determined by the following equation:

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

$$2NH_3 : S = 34 : 32 = 0.00652 \text{ gram } NH_3 : 0.0061 \text{ gram S}.$$

The heat of combustion of sulfur to aqueous sulfuric acid (H_2SO_4) is 4,450 calories per gram of sulfur. This reaction takes place in the bomb calorimeter when the fuel is burned in an atmosphere of oxygen under high pressure.

In the ordinary combustion of coal under a boiler the sulfur burns to sulfur dioxide (SO_2), the heat of formation of which is 2,250 calories per gram of sulfur. The difference between these two calorific values (4,450 calories — 2,250 calories) is 2,200 calories per gram of sulfur. Therefore, a correction of 2,200 calories per gram of sulfur must be made in the calorimeter determinations, owing to the formation of aqueous sulfuric acid. As 1 ml of the ammonia solution is equivalent to 0.0061 gram of sulfur, 0.0061 times 2,200 equals 13.49 calories, the heat correction to be made if all the acidity of the liquor from the bomb represented sulfuric acid (H_2SO_4).

Hence, the ammonia solution containing 0.00652 gram NH_3 per milliliter is equivalent to 5.56 calories (10 Btu) for nitrogen converted to aqueous nitric acid (HNO_3) or to 13.49 calories for sulfur converted to aqueous sulfuric acid (H_2SO_4). A further correction, therefore, is applied for the sulfur that is determined separately. This correction is a function of the differences between the value of the ammonia solution in terms of sulfur (13.49 calories) and its value in terms of nitrogen (5.56 calories), of 7.93 calories. The difference, 7.93, divided by 0.0061, the value of 1 ml of ammonia solution in grams of sulfur, equals 1,300 calories per gram of sulfur, or 13 calories for each 0.01 gram of sulfur.

The total acidity correction is the number of milliliters of ammonia (NH_3) solution multiplied by 5.56 (10 Btu, the factor for nitric acid) plus the number of centigrams of sulfur multiplied by 13 (23.3 Btu).

Radiation Correction.—The change in radiation loss from one sample to another is due only to the difference in temperature change after a sample is ignited. The previous statement holds true only if the equipment is not changed in any way and the ignition temperature remains the same.

The Bureau of Mines ignites all samples when the water temperature is at 28° C (± 0.1), and by doing this a radiation correction chart is printed for each calorimeter unit. After a temperature rise is recorded for a sample, the radiation loss is taken from the chart which compares with that temperature rise. The radiation loss is then applied to the observed temperature change to give the corrected change of temperature. The chart is made from a graph which is plotted with radiation correction vs. observed temperature change. By using 0.8, 1.2, and 1.6 grams of benzoic acid, three points on the graph are found, and the curve is then plotted. Three to five runs are made using each weight, and the average of them is used. These determinations are run as shown under the Standardization of the Calorimeter.

The permissible difference for the same laboratory, same sample, is 40 Btu/lb.

Method of Calculating and Reporting Analyses [13]

Calculation from analysis of "air-dried" coal to coal "as received"

As all the analytical determinations are made on the air-dried sample, the analysis of the coal as received at the laboratory is calculated from the analysis of the air-dried coal in the following manner:

$$\text{Moisture} \times \frac{(100\text{-air-drying loss})}{100} + \text{air-drying loss} = \text{moisture as received.}$$

$$\text{Volatile matter} \times \frac{(100\text{-air-drying loss})}{100} = \text{volatile matter as received.}$$

$$\text{Fixed carbon} \times \frac{(100\text{-air-drying loss})}{100} = \text{fixed carbon as received.}$$

$$\text{Ash} \times \frac{(100\text{-air-drying loss})}{100} = \text{ash as received.}$$

$$\text{Sulfur} \times \frac{(100\text{-air-drying loss})}{100} = \text{sulfur as received.}$$

$$\text{Hydrogen} \times \frac{(100\text{-air-drying loss})}{100} + 1/9 \text{ air-drying loss} = \text{hydrogen as received.}$$

$$\text{Carbon} \times \frac{(100\text{-air-drying loss})}{100} = \text{carbon as received.}$$

$$\text{Nitrogen} \times \frac{(100\text{-air-drying loss})}{100} = \text{nitrogen as received.}$$

$$\text{Oxygen} \times \frac{(100\text{-air-drying loss})}{100} + 8/9 \text{ air-drying loss} = \text{oxygen as received.}$$

$$\text{Calories} \times \frac{(100\text{-air-drying loss})}{100} = \text{calories as received.}$$

Calculation from "air-dry" or as-received analysis to "dry coal"

A statement of analysis is referred to a moisture-free basis by calculation from the "air-dry" or "as-received" analysis in the following manner:

$$\text{Volatile matter} \times \frac{100}{100\text{-moisture}} = \text{volatile matter in dry coal.}$$

$$\text{Fixed carbon} \times \frac{100}{100\text{-moisture}} = \text{fixed carbon in dry coal.}$$

$$\text{Ash} \times \frac{100}{100\text{-moisture}} = \text{ash in dry coal.}$$

$$\text{Sulfur} \times \frac{100}{100\text{-moisture}} = \text{sulfur in dry coal.}$$

$$(\text{Hydrogen} - 1/9 \text{ moisture} \times \frac{100}{100\text{-moisture}} = \text{hydrogen in dry coal.}$$

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[13] All figures expressed in percent.

$$\text{Carbon} \times \frac{100}{100\text{-moisture}}$$
= carbon in dry coal.

$$\text{Nitrogen} \times \frac{100}{100\text{-moisture}}$$
= nitrogen in dry coal.

$$(\text{Oxygen} - 8/9\ \text{moisture}) \times \frac{100}{100\text{-moisture}}$$
= oxygen in dry coal.

$$\text{Calories} \times \frac{100}{100\text{-moisture}}$$
= calories in dry coal.

Calculation from air-dry, as-received, or moisture-free analysis to moisture and ash-free basis

For making comparisons coal analyses are sometimes referred to a "moisture- and ash-free" basis by calculation from the air-dry, as-received, or moisture-free analyses in the following manner:

$$\text{Volatile matter} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= volatile matter referred to moisture- and ash-free basis.

$$\text{Fixed carbon} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= fixed carbon referred to moisture- and ash-free basis.

$$\text{Sulfur} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= sulfur referred to moisture- and ash-free basis.

$$\frac{(\text{Hydrogen-}1/9\ \text{moisture}) \times 100}{100\text{-}(\text{moisture} + \text{ash})}$$
= hydrogen referred to moisture- and ash-free basis.

$$\text{Carbon} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= carbon referred to moisture- and ash-free basis.

$$\text{Nitrogen} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= nitrogen referred to moisture- and ash-free basis.

$$\frac{(\text{Oxygen-}8/9\ \text{moisture}) \times 100}{100\text{-}(\text{moisture} + \text{ash})}$$
= oxygen referred to moisture- and ash-free basis.

$$\text{Calories} \times \frac{100}{100\text{-}(\text{moisture} + \text{ash})}$$
= oxygen referred to moisture- and ash-free basis.

Calorific values in calories are converted to calorific values in British thermal units (Btu) by multiplying by 1.8.

METHODS OF PHYSICAL TESTS

Method of Test for Determination of Grindability of Coal

This method is used to determine the relative grindability or ease of pulverizing of coals, as compared with a coal chosen as 100 grindability. A prepared sample is subjected to a definite amount of grinding energy in a miniature pulverizer, and the new surface is determined by sieving.

Apparatus

The apparatus consists of:

(a) Hardgrove grindability machine shown in figure 13;

(b) these sieves: No. 4 (4.76 mm), No. 16 (1.19 mm), No. 30 (595μ), and No. 200 (74μ);

(c) a mechanical sieving machine;

(d) an adjustable plate coffee-mill type crusher; and

(e) a torsion balance having a sensitivity of 0.01 g.

Preparation of Sample

A representative coal sample collected according to Bureau of Mines sampling procedure is prepared by crushing to pass a No. 4 sieve.

Place approximately 1,000 grams of the air-dried coal sample on the No. 16 sieve nested with a No. 30 sieve and bottom pan. Shake the sieves with a mechanical sieving machine. Put the material remaining on the No. 16 sieve through the crusher for stage crushing. Close the plates of the crusher approximately $\frac{1}{16}$ inch after each pass until all the sample passes through the No. 16 sieve. The portion retained on the No. 30 sieve constitutes the sample to be tested.

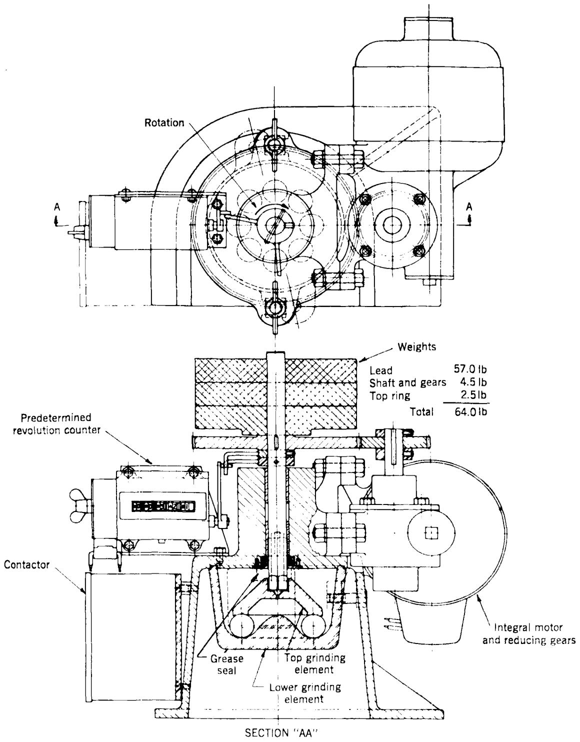

FIGURE 13.—Hardgrove Grindability Machine.

Procedure

Place a 50-gram sample of the material retained on the No. 30 sieve, and weighed to ± 0.1 gram, uniformly in the lower grinding element around the 8 evenly spaced balls. Set the upper part of the grinding element on top of the balls, and pull the whole assembly into place with the wing nuts. Care should be taken to draw the mill up evenly and completely so that the required weight ($64 \pm \frac{1}{2}$ pound) rests on the balls. Set revolution counter at zero, and start the mill. When the grinding cycle is completed, after 60 revolutions, the machine shuts off automatically. Transfer the sample immediately to the No. 200 sieve by brushing the grinding elements and balls thoroughly.

Shake the sieve mechanically for 10 minutes, remove it, and brush the dust on the bottom of the No. 200 sieve (using a soft brush) into the receiver pan. Reassemble the sieve and shake for a 5-minute period, followed by the brushing just described. Another 5-minute period of sieving and brushing completes the sieving.

Carefully transfer the material remaining on the sieve to the weighing pan, and weigh to the nearest 0.1 gram. Subtract this weight from 50.0 grams to determine the amount of material ground by the grinding machine to pass a No. 200 sieve. All sieving and weighing operations should be carried out without delay as high-moisture coals tend to lose moisture when finely pulverized.

The grindability index is calculated as follows:

$$\text{Hardgrove grindability index} = 13 + 6.93\,W,$$

Where

W = weight of material passing the No. 200 sieve.

The above equation is only correct if the apparatus gives 100 grindability index when a standard coal of 100 grindability index is run. To compensate for deviations due to differences of the mill and sieve, a factor must be determined to arrive at the correct results.

Using a standard 100 grindability coal and the equation above

$$100 = 13 + 6.93\,W_{st}, \text{ or}$$
$$6.93\,W_{st} = 87 \text{ if } 6.93 = \text{Factor}.$$

Then

$$\text{Factor} = \frac{87}{W_{st}},$$

where

W_{st} = Weight of material passing the No. 200 mesh sieve using standard coal of 100 grindability.

The equation then becomes (using the test sieve only):

$$\text{Hardgrove grindability index} = 13 + (\text{Factor} \times W),$$

where

W = Weight of material passing the No. 200 mesh sieve.

Factor = As determined above and may be used as long as there is no appreciable change in the sieve or machine.

Duplicability of Results

The permissible variation between two or more determinations shall not exceed the following:

	Percent
Same laboratory	2
Different laboratories	3

Method of Test for Determination of True Specific Gravity of Coal and Coke

This method of test is intended for determining the true specific gravity of coal and coke.

Apparatus

The Hogarth specific gravity bottle with side tubulure recommended by Blair[14] for the determination of specific gravity of iron ores is a convenient and accurate apparatus for determining the specific gravity of coal and coke. The specific-gravity bottle has a capacity of about 100 ml and is calibrated accurately in order that a table may be constructed giving the capacity of the bottle in grams of water at the temperature prevailing in the laboratory. This is conveniently done from data in the Bureau of Standards[15] tables of corrections for determining the true capacities of glass vessels from the weight of water in air.

Procedure

Introduce carefully a 10-gram portion of coke, ground to pass a No. 200 sieve, which has been previously dried for 1 hour at 105° C, into the specific-gravity bottle with enough distilled water to fill the bottle about half full. (For coal, a 10-gram portion is used, ground to pass a No. 60 sieve, and previously dried for 1 hour at 105° C.) Put the bottle on a hot plate, and keep the contents boiling for 1 hour;[16] during this time frequently shake the specific-gravity bottle to wash down any material adhering to the sides. If the contents froth on boiling, insert a straight-form, one-bulb, glass-drying tube in the mouth of the bottle through a small piece of pure-gum tubing to prevent loss of particles of the sample. After boiling for 1 hour, remove the bottle from the hot plate and fill to the tubulure with recently boiled and cooled distilled water, and cool the contents to room temperature. Then fill the specific-gravity bottle to slightly above the mark on the capillary of the stopper with recently boiled distilled water, which has been cooled to room temperature. Filling is conveniently done by inserting the end of the tubulure in a small beaker of the distilled water and applying a slight suction on the stopper. Adjust the water level to the mark on the capillary by touching a piece of filter paper to the end of the tubulure, and wipe dry and weigh the bottle. Immediately after the weighing, remove the stopper and measure the temperature of the contents.

The true specific gravity is calculated from the formula

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

in which

W = weight in grams of dry sample,
W^1 = weight in grams of bottle + dry sample + water required to fill the bottle, and
P = weight in grams of bottle + water required to fill the bottle.

Duplicability of Results

The difference in duplicate determination of true specific gravity shall be not more than the following:

Same analyst	0.01
Different analysts	0.02

Method of Test for Determination of Apparent Specific Gravity of Coal and Coke

This method of test is intended for determining the apparent specific gravity of coal and coke.

Apparatus

The apparatus used for determining the apparent specific gravity consists of a galvanized-iron cylinder shown in figure 14, which is filled with water to the water line indicated in the figure. A hydrometer made of brass is immersed in the cylinder. On top of the hydrometer are two pans; the upper one is used for weights and the lower for the sample. Below the air buoy is a brass cage perforated with holes to allow the air to escape when the instrument is immersed. The cage carries the sample when it is weighed under water.

Procedure

The method of determining the apparent specific gravity of coal is as follows: Place brass weights on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. Record the total weight required. Remove the weights and place about 500 grams of the sample in lump form (about 1½- to 2-inch

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[14] Blair, A. A. The Chemical Analysis of Iron. J. B. Lippincott Co., Philadelphia and London, 7th ed., 1908, p. 278.

[15] National Bureau of Standards. Standard Density and Volumetric Tables. Circ. 19, 1924, pp. 56–60.

[16] Selvig, W. A., and W. L. Parker. The Determination of the Specific Gravity of Coke. Chem. and Met. Eng., v. 28, 1923, pp. 547–550.

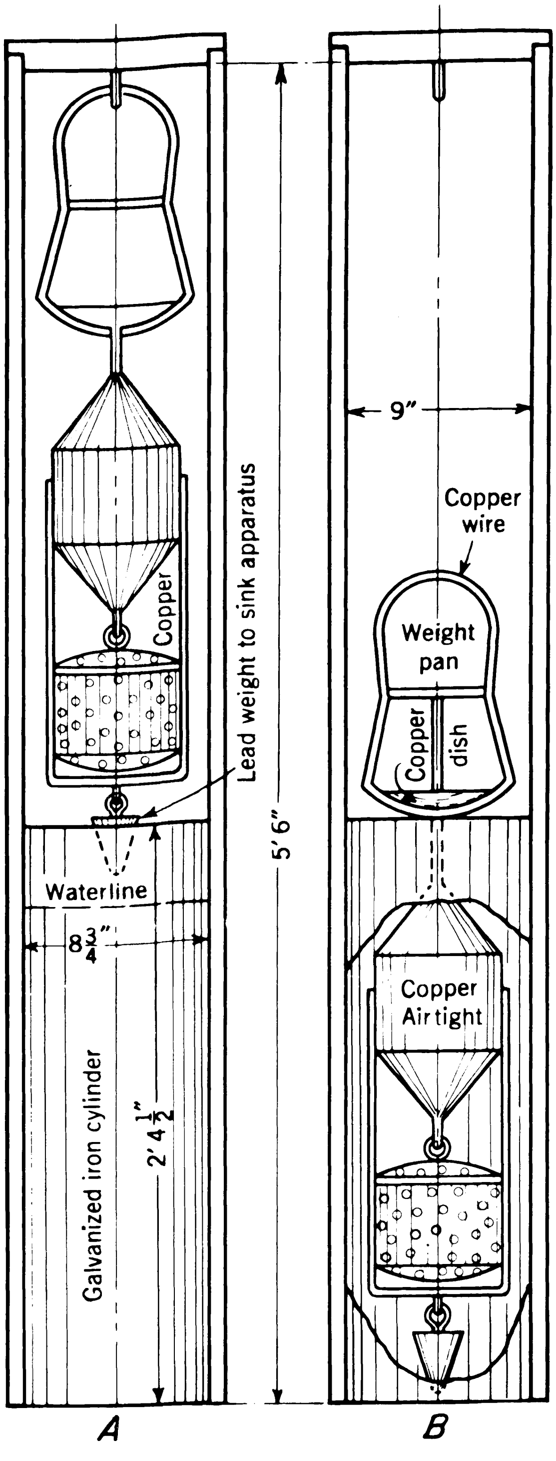

FIGURE 14.—Apparatus for Determining Apparent Specific Gravity.

cubes) in the copper dish. Add brass weights until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air.

Then carefully transfer the sample to the brass cage below the buoy. Immerse the cage with the coal and move the hydrometer rapidly up and down in the water several times to remove air bubbles. Adjust the weights on the upper pan until the instrument again sinks to the mark on the stem. The weight required to sink the hydrometer to the mark, with no sample on the upper pan or in the brass cage, minus the weight required to sink it to the mark, with the sample immersed in the cage, equals the weight of the coal in water. Then,

If the weight of the sample in air = x g, and the weight of the sample in water = y g, the apparent specific gravity =

$$\frac{x}{x - y}.$$

The method of determining the apparent specific gravity of coke is as follows: Use about 500 grams of the sample in lump form (about 1½- to 2-inch cubes) and dry the sample to constant weight at 105° to 200° C. As coke is porous, it takes up water rapidly,[17] so the method is modified to correct for the water absorbed by coke. Permit the coke to remain immersed in the water for 15 minutes, during which period the hydrometer occasionally is moved up and down to detach any air bubbles adhering to the surface of the pieces of coke. Then adjust the hydrometer to the mark on the stem in the usual manner, and at once remove the cage containing the sample from the water and allow it to drain for 1 minute. Transfer the wet coke to the copper dish of the hydrometer, and add weights until the hydrometer sinks to the mark on the stem. The difference in the weights used for the dry and wet coke gives the weight of water absorbed by the coke. Then,

If the weight of the sample in air = x g, and the weight of the sample in water = y g, and the weight of water absorbed = z g, the apparent specific gravity =

$$\frac{x}{(x - y) + z},$$

and

$$100 \times \frac{\text{apparent specific gravity}}{\text{true specific gravity}} = \text{percentage by volume of coke substance.}$$

Also,

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

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[17] Work cited in footnote 16.

Method of Test for Determination of Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30° C.

This method determines the equilibrium moisture of coal in an atmosphere over a saturated solution of potassium sulfate at 30° C. It affords a means of estimating the bed moisture of either coal that is wet and shows visible surface moisture, or coal that may have lost some moisture. It is a means to estimate the surface moisture of wet coal by subtracting the equilibrium moisture from the total moisture determined at 105° C.

Apparatus

The apparatus consists of the following:

(a) a small vacuum-type desiccator, shown in figure 15;

(b) a water bath to accommodate several desiccators equipped with a temperature controller to maintain a uniform temperature of 30° C;

(c) a moisture oven having a uniform temperature and a minimum of air space with provisions made for passing nitrogen through the oven at a rate that gives three volume changes per minute;

(d) mechanical vacuum pump;

(e) a coffee-mill type crusher;

(f) a manometer for measuring the pressure in the desiccator;

(g) a No. 16 (1.19 mm) sieve; and

(h) glass weighing bottles, low form, flat bottom, 70 mm in diameter, with ground glass cover.

Procedure

Stage-crush the sample of coal to pass a No. 16 sieve by means of the coffee-mill type crusher which produces a minimum amount of fine material.

Place 20 to 25 grams of the crushed coal into a 250-milliliter Erlenmeyer flask and add 100 milliliters of water. Shake the flask for ½ hour and then place it in a constant-temperature bath for 3 hours at 30° C. At the end of the wetting period, remove the excess water from the coal by filtering on a Buechner-type funnel using suction supplied by a water filter pump. Care should be taken to prevent drying of the coal. Mix the coal in the funnel by stirring with a spoon.

Spread about 5 grams of the wetted sample over the bottom of a weighing bottle of known weight. Place the uncovered weighing bottle in the small vacuum-type desiccator containing a saturated K_2SO_4 solution with excess salt (coarse crystals) projecting above the surface of the solution. Totally immerse the desiccator in the constant-temperature water bath and evacuate to an absolute pressure equivalent to about 30 mm of mercury with a mechanical vacuum pump. Keep the sample for 72 hours in the water bath at a temperature of 30° ± 0.2° C.

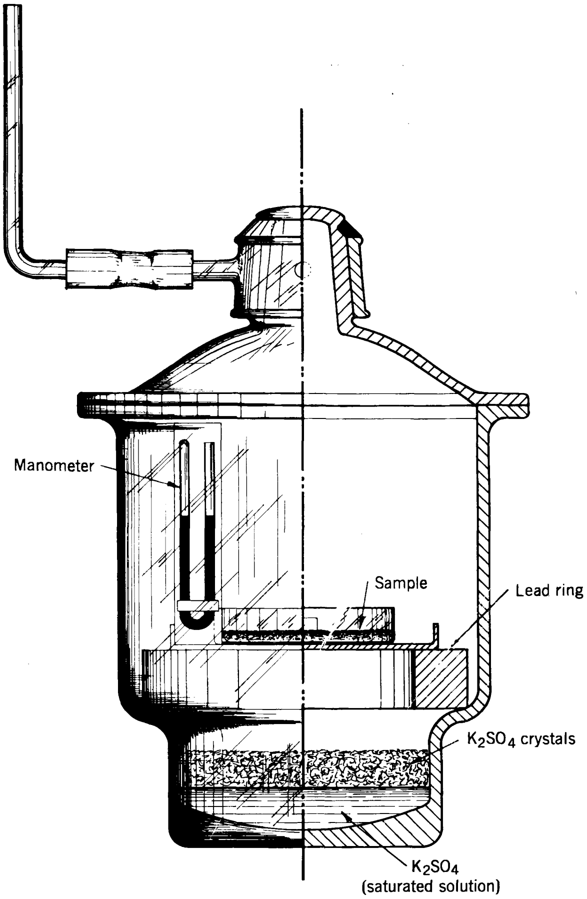

FIGURE 15.—Vacuum-Type Desiccator.

At the end of equilibration, restore atmospheric pressure in the desiccator, with the desiccator still in the bath, by slowly admitting dry air for a period of not less than 15 minutes. Admit the air to the inlet tube of the desiccator after passing it through a bubbler containing H_2SO_4 (sp gr 1.84), then a capillary tube for regulating the rate of air flow, and finally a coiled copper tube placed in the constant-temperature bath. Remove the desiccator from the bath and open immediately. Quickly close the weighing bottle, and weigh to the nearest 0.2 mg. Uncover the weighing bottle, place it in the moisture oven preheated to 105° C and heat for 1½ hours. At the end of the drying period remove the dish from the oven, cover, cool for 30 minutes in a desiccator over H_2SO_4 (sp gr 1.84), and then weigh. The loss in weight is designated as equilibrium moisture.

Samples of low-rank coals used for the determination of equilibrium moisture should contain nearly all their bed moisture.

Duplicability of Results

The permissible differences between two or more determinations shall not exceed the following values:

Equilibrium moisture, percent	Permissible differences	
	Same laboratory	Different laboratories
Under 5	0.3	0.5
5–15	.5	1.0
Over 15	1.0	1.5

Method of Test for Specific-Gravity Analysis of Coals

Most coal-washing processes effect a separation between coal and impurity on the basis of the difference in specific gravity of their components. Coals differ in the relative amount of material of different densities present, and it is this factor that determines to a large degree the amenability of a particular coal to upgrading by washing. In addition, the specific-gravity (float-and-sink) analysis of clean coal and refuse products resulting from a washing operation serves as the basic data for determining the sharpness of the separation achieved.

Preparation of Sample

The weight of a sample required depends to a great extent on the largest particle size to be tested. While sufficient data are not available to determine statistically the minimum sample weight required, the weights given below for testing various sizes of coal have been found by experience to give acceptable results.

Top size, inches, and sieve no.:	*Weight, pounds*
6	2,000
4	1,000
2	325
1	160
½	75
¼	35
No. 8	10
No. 16	3
No. 30	½

When salt solutions are used for the separations, the sample must be soaked in water for at least 12 hours before testing to insure that the coal is saturated; when organic solutions are used the sample must be air dried before testing.

Test Methods

There is no standard method of float-and-sink testing the total particle size range of coals. The methods employed by the various laboratories are selected on the basis of the amount of coal to be tested and the personal preference of the laboratory personnel.

The coarse coal retained on a No. 16 sieve may be tested either in salt or organic solutions. The particle sizes passing a No. 16 sieve may be separated in organic solutions or further sized into an intermediate size fraction passing a No. 16 and retained on a No. 200 sieve for testing in organic or salt solutions and an ultrafine size fraction passing a No. 200 sieze for centrifugation in organic solutions.

To determine the distribution of the various specific gravity components present in a coal, it is immersed in a series of heavy liquids ranging from about 1.30 to 2.00 specific gravity. The testing procedure is started in the bath that will eliminate the greatest amount of the sample as a finished product, generally the bath of lowest density. For clarity, the procedures are described starting with the lowest specific gravity solution; hence, the float material is a final product. The coal reporting to each of the specific gravity components then is washed when necessary, dried, weighed, and if washability data are desired, analyzed for ash, sulfur, and any other chemical characteristic desired.

The specific gravity of the solutions must be checked continually because of dilution, temperature variations, and evaporation. When separating fine-sized coals, ambient temperature around the separating vessel should not vary more than 1° or 2° F. Spindle hydrometers having an accuracy ± 0.001 specific-gravity units are adequate.

Salt Solution.—Aqueous solutions of zinc chloride are the most commonly used salt solutions for testing coals. Any specific gravity range from 1.00 to 1.93 can be obtained by adjusting the concentration of zinc chloride.

Zinc chloride is relatively cheap and does not produce toxic fumes. It is, however, acidic; hence, protective clothing must be worn by laboratory personnel, and suitable materials of construction must be used for the testing equipment. The high viscosity of zinc chloride, especially at gravities above 1.60 is a particular disadvantage in separating fine coal. Products separated in zinc chloride must be rinsed thoroughly to remove residual salt solution; this is simple for the coarse sizes but becomes increasingly difficult with decreasing particle size. Complete removal of the zinc chloride during rinsing is essential, as residual salt will produce erroneous chemical analyses.

Coarse coal (retained on a No. 16 sieve).—Figure 16 shows an overall view of the testing apparatus. The principal items of equipment are lead-lined steel tanks, 38 by 27 by 20 inches deep, for the baths, and the apparatus in which the float is separated from the sink. As shown in figure 17, this apparatus is a basket comprised of two parts. The lower part is provided with a reinforced screen bottom of No. 60 screen size. The bottom of the upper part is a grid which supports a flexible No. 30 sieve that can be inserted to divide the 2 parts of the basket. The two parts are clamped together when the apparatus is immersed in the float-and-sink bath, but can be separated for removal of the products after the basket has been hoisted from the bath. The apparatus and testing procedure have been described in detail by McMillan and Bird.[18]

FIGURE 16.—Coarse Coal Testing Apparatus Using Salt Solution.

Introduce the sample after the bath is adjusted to correct density and lower the basket into the tank. The weight of sample that can be put in the basket is limited by the danger of mechanical entrapment of particles in the wrong product and ranges usually from about 25 to 125 pounds depending on the size consist. After the sample has been put in the bath, stir the layers of float and sink to free trapped particles. Adjust the density, if necessary, and allow a few minutes for the particles to reach their proper stratum. Insert the sieve divider between the two halves of the basket to isolate the float from the sink. Finally hoist the basket from the bath and allow to drain for a few minutes before separating the two halves. Move the sink in the bottom part of the basket to the bath of next higher density and repeat the procedure.

When each final specific gravity fraction is obtained, place the portion of the basket containing it on a sloping sheet metal tray and rinse for a few minutes with hot water. Dump the fraction out of the basket and wash it into a rinsing pan, on the bottom of which has been placed a rinsing pipe. The pipe is connected by a hose to a manifold supplying hot rinsing water. The water rises through the coal in the pan, overflowing the lip at one end. When testing fine coal direct the overflow through a No. 200 sieve to prevent loss of coal. Continue rinsing until the addition of a drop of silver nitrate solution to the water in the pan shows no precipitate. Then drain, dry, cool to constant weight, and weigh the samples.

Fine coal (passing a No. 16 sieve).—Because of the viscosity of the high specific-gravity salt solutions, separating the particle sizes passing a No. 50 sieve is difficult. A centrifuge may be used to test this size fraction, but washing and recovery of the size fractions passing a No. 200 sieve is so difficult that the use of salt solutions is not recommended.

A satisfactory method for testing the size fraction passing the No. 16 and retained on the No. 200 sieve is to further size the sample by a No. 50 sieve. The size fractions passing a No. 16 and retained a No. 50 sieve are tested statically and those passing a No. 50 and retained on a No. 200 sieve are tested centrifugally.

The apparatus for testing the size fractions passing a No. 16 and retained on a No. 50 sieve consists of funnel-flask glass bottles having a 3-liter funnel joined by a standard ground glass taper joint to a 2- or 3-liter flask. A stopper on the end of a rod is used to separate the upper and lower portions of

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[18] McMillan, E. R., and B. M. Bird. Coal Washing Problems of the Pacific Northwest. Univ. Washington Eng. Exp. Sta. Bull. 28, 1924, 234 pp.

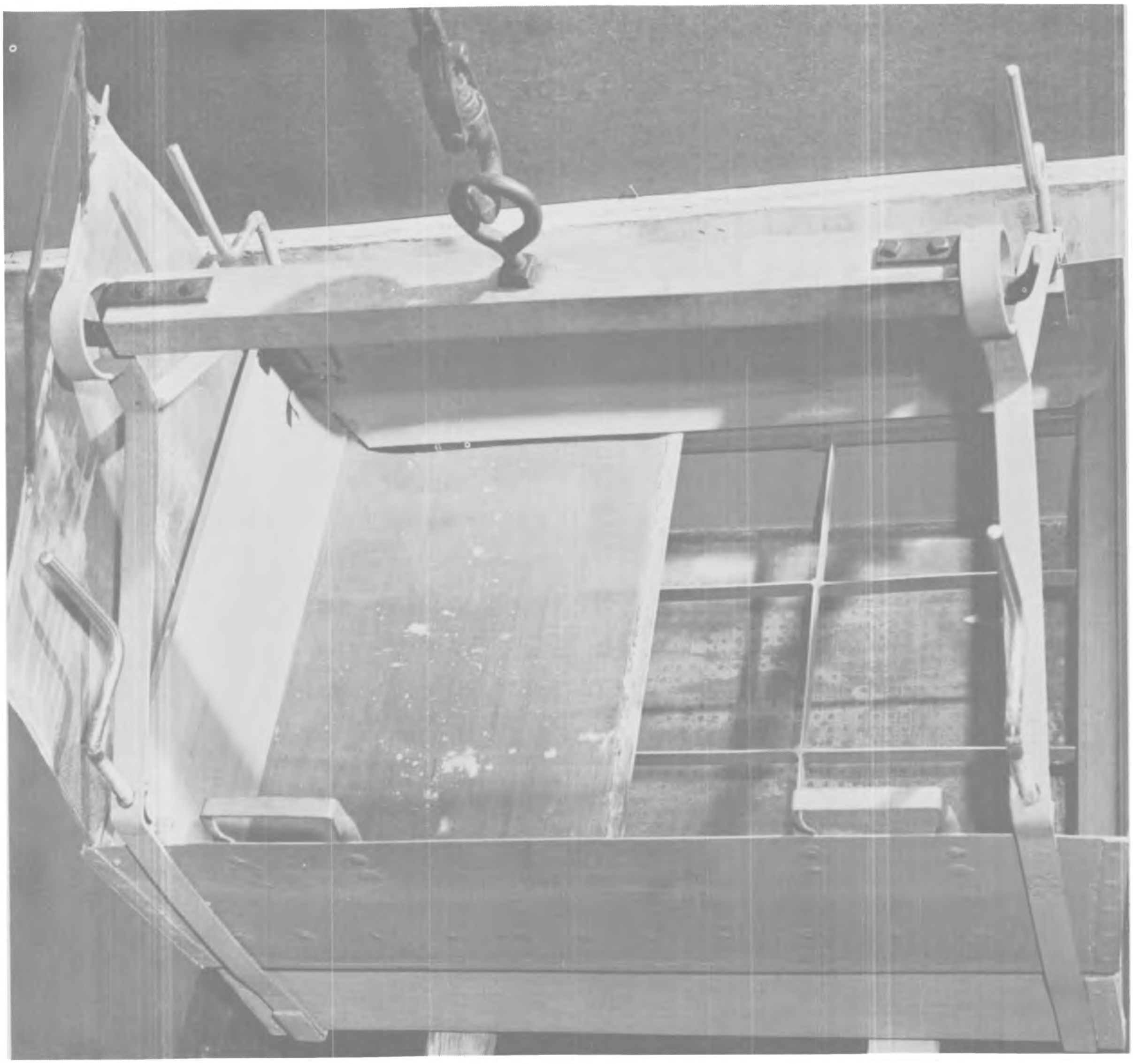

FIGURE 17.—Coarse Coal Separating Basket.

the bottle after the products are separated. Figure 18 shows a general view of the apparatus.

The apparatus for testing the size fractions passing the No. 50 and retained on a No. 200 sieve includes a centrifuge equipped with a four-place head having 600-milliliter capacity cups, four 500-milliliter capacity hourglass bottles, and a rubber stopper on the end of a rod. The centrifuge must be equipped with a brush release mechanism to prevent too rapid deceleration. Figure 19 shows an overall view of this apparatus; the analyst is pouring the float product into a filter funnel.

To make a separation of the size fraction passing a No. 16 and retained on a No. 50 sieve, fill a funnel-flask (fig. 18) approximately two-thirds full of solution and place the sample in the solution while being stirred. Add additional solution to raise the liquid level to within 1 inch of the top and agitate the sample. Check the specific gravity of the liquid and adjust if necessary; after which allow the sample to settle until the separation is complete.

When the separation is completed, move the rubber stopper gently through the float layer with a slight twisting motion and insert securely in the neck of the funnel. Separate

FIGURE 18.—Funnel-Flask Apparatus for Fine Coal Testing.

the vessel at the ground glass joint, the funnel containing the float and the flask containing the sink. Pour the float fraction into the washers shown in figure 20 and wash thoroughly with hot water. Dry and weigh the float product. Place the sink product in a vessel containing the next higher specific gravity liquid and repeat the above process.

A centrifuge is used to effect separations of the size fractions passing a No. 50 and retained on a No. 200 sieve. Riffle a 100-gram sample into four 25-gram samples which are prewetted and put into the four hourglass bottles containing about 400 milliliters of salt solution having the desired specific gravity. Check and adjust the specific gravity if necessary, place the bottles in the centrifuge cups, and centrifuge for 20 minutes at 1,500 revolutions per minute.

After the centrifuge has stopped, remove the bottles from the cups and separate the float and sink by inserting the stopper into the neck of the hourglass. Pour the liquid containing the float onto filter paper, remove the stopper, and pour the sink onto another filter paper. Rinse the float thoroughly with hot water, dry, and weigh; put the sink into the hourglass bottles containing a solution of the next higher specific gravity and repeat the above process.

ORGANIC SOLUTIONS.—Several organic solutions are used for testing coals. Carbon tetrachloride, having a specific gravity of 1.58 and perchlorethylene, having a specific gravity of 1.63, are commonly used, to which is added unleaded gasoline or bromoform or Stoddard's solution to decrease or increase the specific gravity within the usual specific gravity range from 1.3 to 2.0. Proprietary solutions such as Certigrav[19] are available.

Organic solutions are relatively expensive and produce toxic fumes which are heavier than air; therefore, all testing must be done in a downdraft hood. Because of their cumulative effect, protective clothing must be worn, and care must be exercised to prevent even minute quantities from entering the human body by inhalation, ingestion, and digestion. A distinct advantage of organic solutions is that the separated products air dry readily and require no washing.

Coarse coal (retained on a No. 16 sieve).—The apparatus for testing coarse coal in organic solutions consists essentially of tapered circular 10-gallon containers and inner tapered circular baskets slightly smaller having a screen bottom and a wide rimmed top. Figure 21 shows an overall view of the equipment inside a downdraft box.

Put the screen-bottomed basket into the separating bath and place small portions of the air-dried sample in the basket. Stir the coal to prevent entrapment and then allow it to settle for a few minutes. Remove the float portion with a screen-wire strainer. Lift the basket containing the sink portion out of the bath and allow to drain. Move the basket to the next bath where another increment of float coal is removed. Continue this process throughout the desired number of separations. Air dry the specific gravity components resulting from the separation in a downdraft hood, and weigh.

Fine coal (passing a No. 16 sieve).—The float-and-sink separation is made in a separatory funnel having a capacity of 3 liters mounted in a downdraft hood, as shown in figure 22.

Pour about 2 liters of solution of the desired specific gravity into the separatory funnel and add the sample of coal. Gently bubble air through a glass tube inserted into the layer of sink material to free trapped particles. Treat the layer of float in the same way. Allow the sample to stand for 1 hour or until the solution between the layers of float and sink becomes clear.

The separation is accomplished by withdrawing the bed of sink and about half the solution through the stopcock directly onto a filter paper in a funnel. Withdraw the float

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[19] Reference to specific brands is made for identification only, and does not imply endorsement by the Bureau of Mines.

FIGURE 19.—Equipment for Centrifugal Separation of Fine Coal.

product onto another filter; wash down particles of float adhering to the walls of the funnel with additional solution. Drain both products and then dry. Repeat the procedure with the sink in baths of successively higher density.

Because of the slow settling velocities of the very fine coal particles, the coal passing a No. 16 sieve may be screened by a No. 50 sieve; size fractions passing a No. 16 and retained on a No. 50 sieve are separated statically, and the size fractions passing a No. 50 sieve are separated centrifugally. Because no washing of the products is required, there is no limitation to the fineness of the coal that can be separated.

The apparatus used for separating the above mentioned size fractions in organic solutions is identical to that used for separating the respective size fractions in salt solutions, as shown in figures 18 and 19.

The procedure employed for separating the above mentioned size fractions is the same as that given earlier for separating the respective size fractions in salt solutions except that no rinsing of the products is required.

Report

The specific gravity fractions resulting from the specific gravity analysis are weighed and, if analyzed, for their ash and sulfur content, furnish the basic information for calculating washability data. The data may be plotted as washability curves shown in figure 23. An explanation of washability data and curves may be found in a paper by Coe.[20]

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[20] Coe, G. D. An Explanation of Washability Curves for the Interpretation of Float-and-Sink Data on Coal. BuMines Inf. Circ. 7045, 1938, 10 pp.

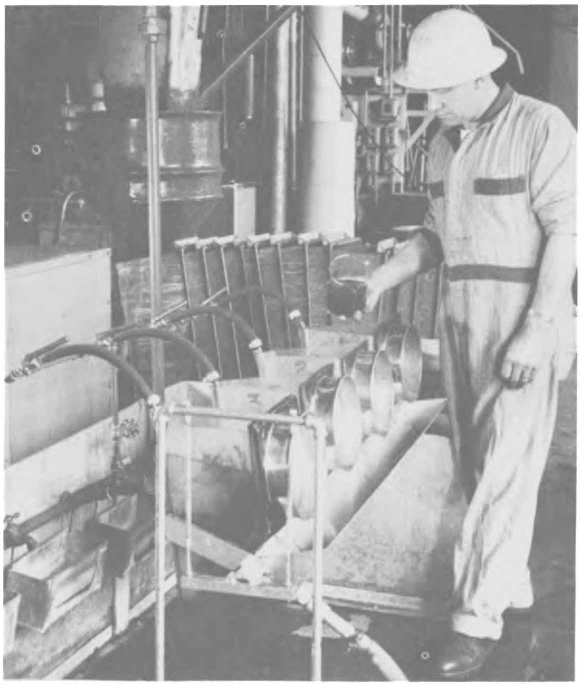


FIGURE 20.—Fine Coal Washing Devices.

FIGURE 21.—Coarse Coal Testing Apparatus Using Organic Solutions.

DUPLICABILITY OF RESULTS. — Sufficient data are not available to assess the accuracy of these test procedures under all operating conditions that may be encountered. Primarily, accuracy is a function of the density composition of the coal. If a higher percentage of the coal is concentrated near the specific gravity of a bath, the utmost care must be used in adjusting the specific gravity to avoid significant errors in the proportion of float and sink.

Evaluation of Froth Flotation Cleaning Potential of Fine Coal

Introduction

Froth flotation is a coal washing process for fine size coal, generally minus 28 mesh. The raw material in slurry form is introduced into a flotation vessel, called a cell; the clean coal product reports to the surface of the cell in a multitude of bubbles, called a froth and the impurity remains in the slurry and flows out of the cell as a tailings refuse product which is then disposed of.

Coal is a hydrophobic material; it resists being wetted by water but readily attaches itself to air at a liquid-solid-gas interface and is lifted out of the pulp into the clean coal froth product. The impurities are hydrophilic; that is, they are readily wetted at a liquid-solid-gas interface and remain in the pulp until discharged to the tailings product. The floatability of the various coal constituents decreases in the order vitrain, clarain, durain, and fusain.

Chemical reagents are added to flotation plant feed slurries to enhance flotation results. The two principal reagent types used for coal flotation are frothers and collectors. Frother reagents are used to produce stable froths and small size bubbles, both prime factors in successful flotation. Frothers, almost always needed, are used at the rate of 0.1 to 0.5 pounds per ton of feed. Collector reagents are used to impart a hydrohobic coating to desirable particles which, owing to oxidation or some other phenomena, do not display normal floatability. Collectors, when required, are used at the rate of 0.5 to 3.0 pounds per ton of feed.

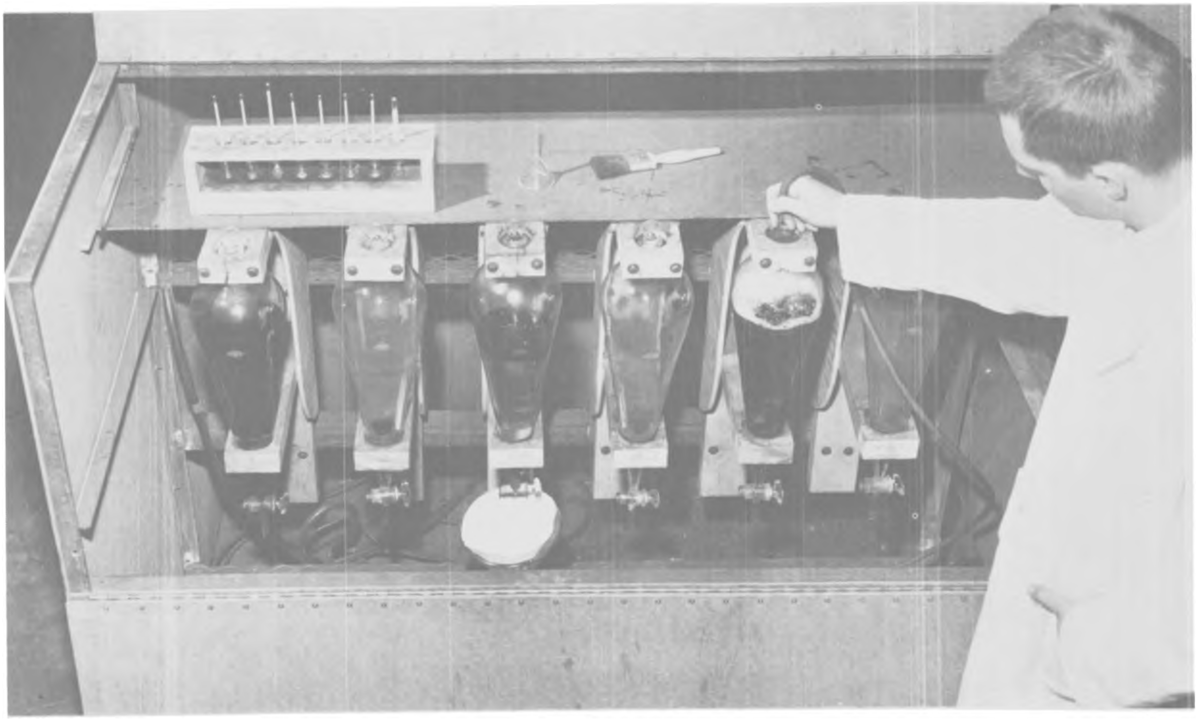


FIGURE 22.—Separatory Funnel for Testing Fine Coals in Organic Solutions.

Standard specific gravity analysis of fine coal is of limited value in determining the amenability of the coal to cleaning by froth flotation. Therefore, a timed release analysis technique has been developed to assess the amenability of fine coal to froth flotation cleaning. This technique is adaptable to any standard laboratory flotation cell; however, operating parameters, such as agitation, and air rate will vary for different cells.

Most American bituminous coals float quite readily, although an excessive amount of fine clay material or oxidized coal may adversely effect the flotation rate. Such factors, not discernible by standard density analysis, are of prime importance when designing a fine-coal cleaning plant.

Test Method

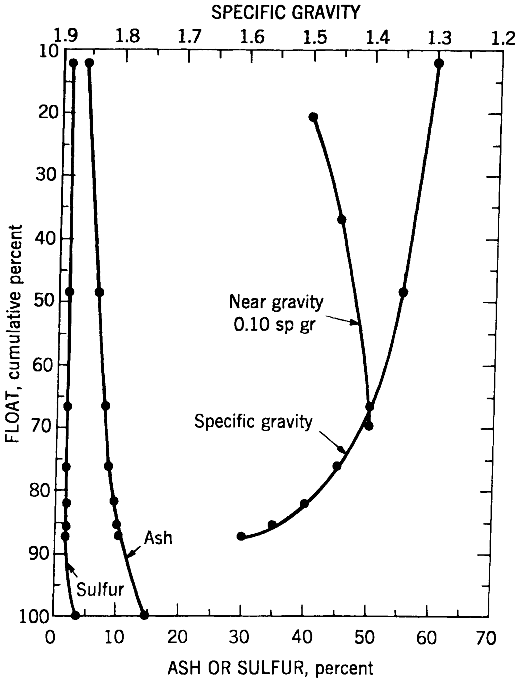
A coal and water slurry of approximately 8 percent solids is mixed in the flotation cell for ten minutes to assure thorough wetting of the material. Cell agitation and air rate are set at a minimum at the start of each float, using a tachometer and flowmeter respectively, to assure initial removal of the most readily floatable coal particles; sufficient reagent is added to assure a slight excess. As the float progresses, additional reagent is added, and the air and agitation rates are increased so that the final froth will contain everything that can possibly float under the most intense conditions. A diagram of the timed release analysis procedure is shown in figure 24. Operating conditions shown in table 1 are found to be applicable in the Bureau's flotation cell.

TABLE 1.—*Operating conditions for flotation tests using the timed release analysis*

Froth number	Frother drops [1]	Air, cfm	Agitation, rpm	Collection time, sec
1	3	0.23	1,500	15
2	2	0.24	1,600	30
3	2	0.26	1,700	30
4	2	0.28	1,800	30
5	2	0.30	1,900	60
6	2	0.54	2,000	180

[1] 28 drops per cm ^{3}.
10 drops equal 0.15 grams of methylisobutyl carbinol.

FLOAT 1.—After wetting 200 grams of coal in 2,300 ml of water for 10 minutes a predetermined amount of frother, from 0.5 to 1 pound per ton of solids, is added to the cell; air is introduced, and froth 1 is collected in basin 1 for a timed period, as shown in table 2. The air is turned off, and water is added to bring the pulp to its original level. More reagent is added, the air and agitation rates



Specific gravity fraction	Elementary data, percent			Computed data, cumulative percent			Near gravity ±0.10 specific gravity, percent
	Weight	Ash	Sulfur	Weight	Ash	Sulfur	
Float 1.30	12.0	3.9	1.51	12.0	3.9	1.51	-
1.30-1.35	36.5	7.3	1.66	48.5	6.5	1.62	-
1.35-1.40	18.2	11.3	1.93	66.7	7.8	1.71	69.8
1.40-1.45	9.4	15.2	2.33	76.1	8.7	1.78	36.9
1.45-1.50	5.7	19.6	2.54	81.8	9.5	1.84	20.5
1.50-1.55	3.6	23.5	3.44	85.4	10.0	1.90	-
1.55-1.60	1.8	27.1	3.34	87.2	10.4	1.93	-
1.60-Sink	12.8	42.2	13.53	100.0	14.5	3.42	-
Total	100.0	14.5	3.42	-	-	-	

FIGURE 23.—Illustration of Washability Data and Curves.

increased, and the second froth is collected. This procedure is repeated until six froths are collected. The tails are retained in a basin.

TABLE 2.—*Summary of float 1*

Froth number:	*Collection time, sec*
1	15
2	30
3	30
4	30
5	60
6	180

REFLOAT A.—The operating procedure shown in table 3 is repeated for the recleaning of the six froths.

Froth 1 from float 1 plus makeup water is added to the flotation cell. The initial portion of froth 1A is collected for 7½ seconds, air and agitation are discontinued, and froth 2 from float 1 is added to the cell. The refloat is then continued for 7½ seconds to complete froth 1A. With froth 1A removed, flotation is continued for 15 seconds before froth 3 from float 1 is added to the cell. The float is continued 15 seconds to complete froth 2A. Froth 2A is then removed and flotation is continued for 15 seconds. Froth 4 from float 1 is added to the cell and the float is continued for 15 seconds completing froth 3A. After removing froth 3A, an additional 15 seconds of refloating is required before adding froth 5 and continuing the refloat for 15 seconds to complete froth 4A. Froth 5A is collected for 30 seconds before the addition of froth 6 from float 1; froth 5A is then collected for another 30 seconds. After removing froth 5A, the final froth 6A is collected by continuing the refloat for 3 minutes.

TABLE 3.—*Summary of refloat A*

Froth number from float 1	Froth collection time, sec	Total froth collection time, sec	Refloat A froth number
1	7½	15	1A
2	7½		
2	15	30	2A
3	15		
3	15	30	3A
4	15		
4	15	30	4A
5	15		
5	30	60	5A
6	30		
6	180	180	6A

REFLOAT B.—For refloat B the operating procedure shown in table 2 is again repeated. The procedure for recleaning of the products from the succeeding froth is modified so that the products from refloat A are not added to the cell until the froth collection time has progressed two-thirds of the way through the collection time of the preceding froth, as shown in table 4.

Some difficulty may be experienced because of the excessive volume of froth in the basins during refloating, which causes the cell to overflow when air and agitation are turned on. To remedy this, the collecting basins may be allowed to settle until clean liquid can be decanted off into the tails collecting basin.

The six froths thus collected and the three tailings products combined as one are then filtered, dried, weighed, and analyzed for ash and sulfur.

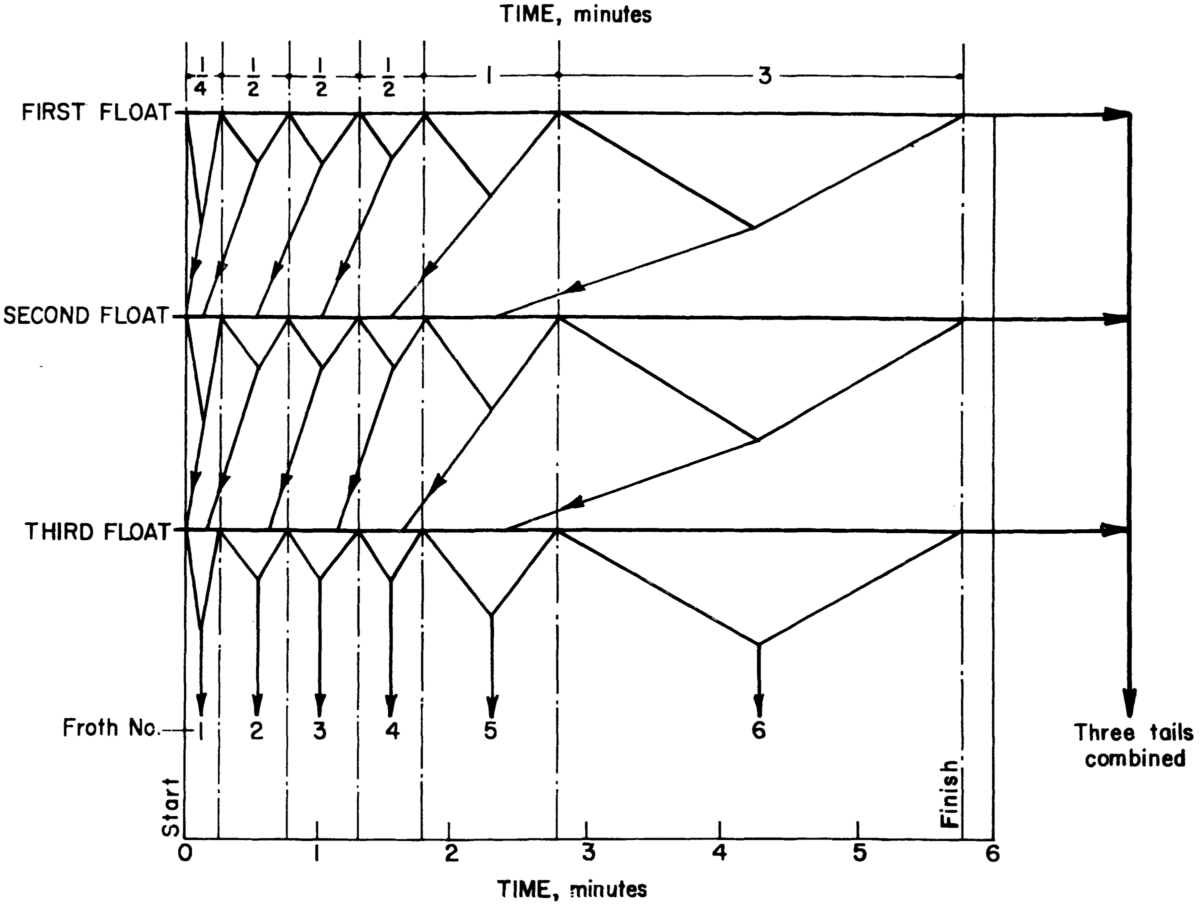


FIGURE 24.—Diagram of the Timed Release Analysis Procedure.

TABLE 4.—*Summary of refloat B*

Refloat A froth number	Froth collection time, sec	Total froth collection time, sec	Refloat B froth number
1A	10 5	15	1B
2A	20 10	30	2B
3A	20 10	30	3B
4A	20 10	30	4B
5A	40 20	60	5B
6A	180	180	6B

The timed release analysis technique was developed to provide washability data from which product yields and qualities may be estimated. Yield-ash curves for 3 coals shown in figure 25 were drawn from typical timed release analysis data. From the curves, predictions of product yield at a given ash may be made.

The flotation data obtained may also be used as shown in figure 26 to provide flotation rate data which show the effect of retention time in the cell on yield of salable product.

METHODS FOR DETERMINATION OF PLASTIC PROPERTIES OF COALS

Method of Test for Agglomerating Index of Coal

The agglomerating index is a measure of the caking properties of coal.

The procedure determines the agglomerating index of coal by examination of the residue in the platinum crucible incident to the standard volatile matter determination.[21]

Table 5 gives the method of designating the degrees of caking from coals that give a noncoherent residue to coals that give buttons showing strong swelling and pronounced cell structure. Buttons corresponding to these grades of caking are shown in figure 27.

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[21] Gilmore, R. E., G. P. Connell, and J. H. H. Nicolls. Agglomerating and Agglutinating Tests for Classifying Weakly Caking Coals. Trans. AIME Coal Div., v. 108, 1934, pp. 255–265.

TABLE 5.—*Agglomerating and caking properties of coals based on examination of residue incident to the volatile-matter determination*

Designation		Appearance of residue from standard method for determination of volatile matter in coal
Class	Group	
Nonagglomerating [1]—button shows no swelling or cell structure and will not support a 500-gram weight without pulverizing.	NA (nonagglomerate)	NAa—noncoherent residue. NAb—coke button shows no swelling or cell structure and after careful removal from the crucible will pulverize under a weight of 500 grams carefully lowered on button.
Agglomerating [1]—button shows swelling or cell structure or will support a 500-gram weight without pulverizing.	A (agglomerate)—button dull black and sintered; shows no swelling or cell structure; will support a 500-gram weight without pulverizing.	Aw (weak agglomerate)—buttons come out of crucible in more than, one piece. Af (firm agglomerate)—buttons come out of crucible in one piece.
	C (caking)—button shows swelling or cell structure.	Cp (poor caking)—button shows slight swelling with small cells, has slight gray luster. Cf (fair caking)—button shows medium swelling and good cell structure, has characteristic metallic luster. Cg (good caking)—button shows strong swelling and pronounced cell structure, with numerous large cells and cavities, has characteristic metallic luster.

[1] Agglomerating index—coals which in the volatile-matter determination produce either an agglomerate button that will support a 500-gram weight without pulverizing or a button showing swelling or cell structure are classified as agglomerating.

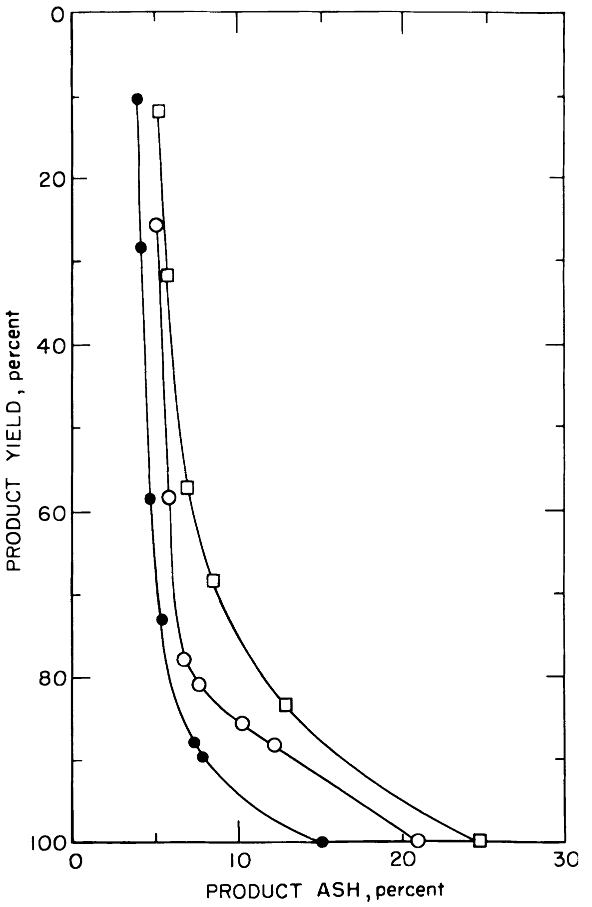

FIGURE 25.—Typical Froth Flotation Washability Data.

Method of Test for Determination of Free-Swelling Index of Coal

This test is used to obtain information on the free-swelling properties of bituminous coal and serves as an approximate measure of the caking and coking characteristics.[22] It is not recommended for determining the expansion properties of coals in coke ovens. The test is made by heating, at a specified rate over a gas burner, a 1-gram sample of freshly prepared coal in a special silica crucible. The residue or button resulting from the carbonization is compared for size and shape with standard profiles.

Apparatus

The apparatus consists of:

(a) Low-form crucibles of translucent silica, with silica ring-handle lids, according to the following specifications:

Weight	grams	11.0 to 12.75
External height	millimeters	26 ± 0.5
External diameter at top	do	41 ± 0.75
Internal diameter at base, minimum	do	11
Capacity (approximate)	milliliters	17

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[22] Ostborg, H. N., H. R. Limbacher, and Ralph A. Sherman. An Experimental Investigation of the British Standard Method for the Crucible Swelling Test for Coal. Proc. ASTM, v. 42, 1942, pp. 851–864.

Selvig, W. A., and W. H. Ode. An Investigation of a Laboratory Test for Determination of the Free-Swelling Index of Coal. BuMines Rept. of Inv. 4238, 1948, 11 pp.

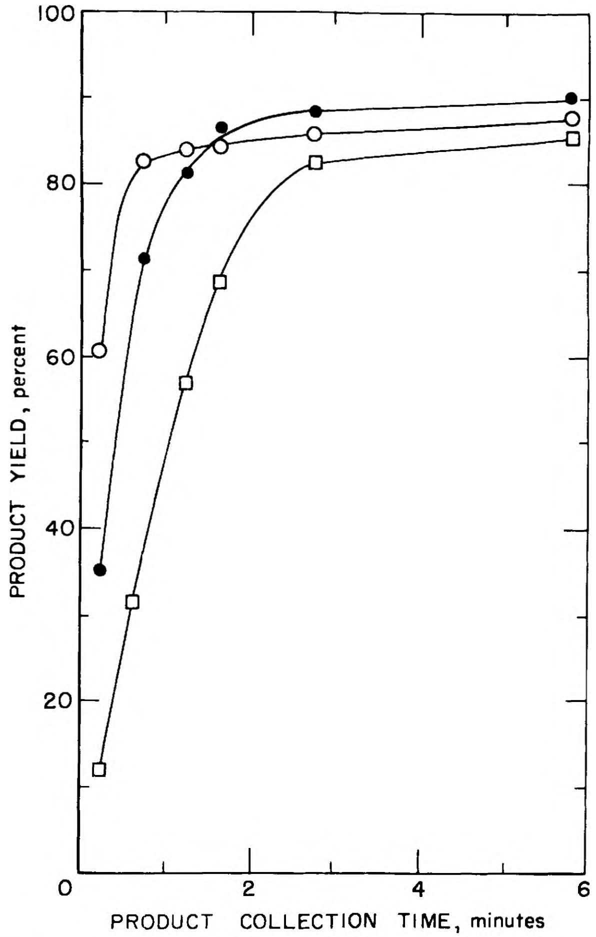


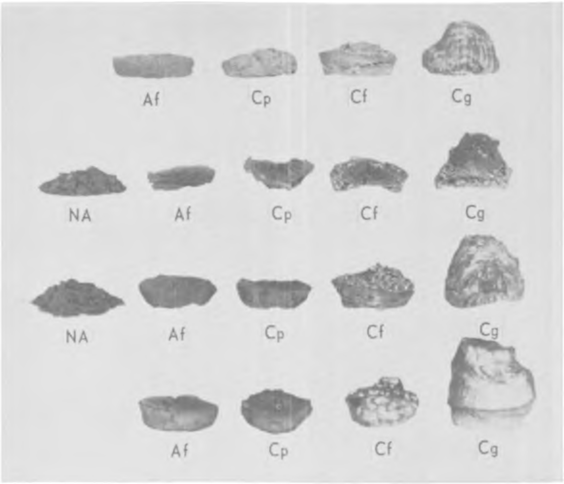
FIGURE 26.—Typical Froth Flotation Rate Curves.

One of the lids has a hole near the center large enough to accommodate the thermocouple used in determining the temperature in the crucible.

(b) A sight tube, shown in figure 28, is used to view the coke buttons so that the effect of parallax is eliminated. The brass tube is supported on a ring stand.

(c) A capillary flowmeter with water manometer is placed in the gas line before the burner as a guide to the control of the rate of flow shown in figure 29. A booster pump equipped with a diaphragm-valve pressure controller is installed to provide a constant gas pressure to the burner sufficient to attain the required temperature.

(d) A natural gas burner with a large grid (33 millimeters), a draft shield, and a silica triangle are shown in figure 29. The draft shield is made from asbestos cement pipe. At the top of the shield three slots, 3 millimeters wide and 25 millimeters deep, are cut at points 120° apart. These slots serve to hold the triangular crucible support in place. The shield is supported on a ring stand so that the distance between the base of the crucible and the top of the burner grid is approximately 3/8 inch. A triangular crucible support is made of three pieces of translucent silica tubing, 6 millimeters in external diameter and 63 millimeters long, mounted on chromium nickel wire. The



KEY

NA Nonagglomerate	Cf Fair caking
Af Firm agglomerate	Cg Good caking
Cp Poor caking	

The buttons in the second row have been cut in half to show the internal structure of the caked materials.

FIGURE 27.—Residues From Volatile Matter Determination, Showing Various Degrees of Agglomeration and Caking.

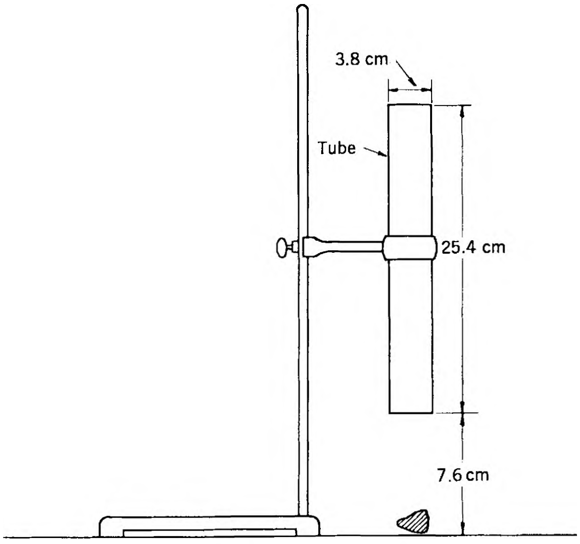


FIGURE 28.—Sight Tube.

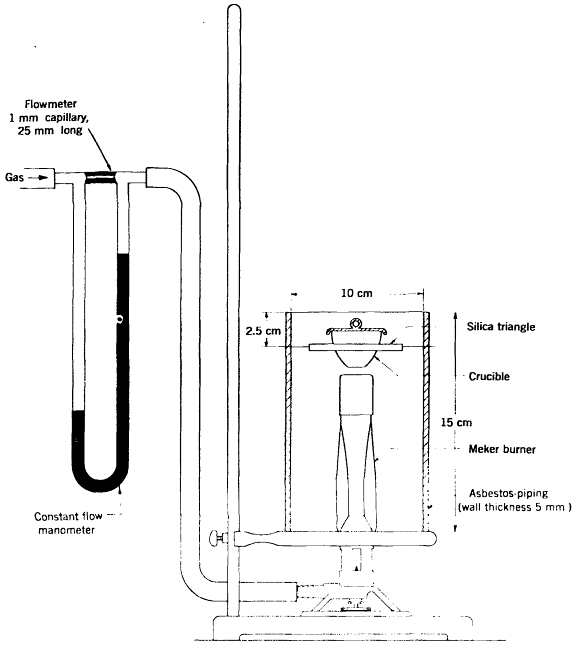


FIGURE 29.—Details of Burner Assembly.

diameter of the circle inscribed in the triangle is 32 millimeters. Ends of the twisted wires are used as handles to remove the hot crucible.

Calibration of Burner

With the burner assembly arranged as shown in figure 29, and with an empty crucible and special lid in position, the burner is lighted for 15 minutes to allow the assembly to come to an equilibrium temperature. The temperature of the inner surface of the bottom of the crucible is measured with a No. 28 gage base metal thermocouple and potentiometer. Care is taken to place the junction of the thermocouple and portions of each wire on the bottom of the crucible. By adjustment of the burner, distance between the burner and the bottom of the crucible, and gas pressure, the temperature of 800° ± 10° C is obtained in 1½ minutes, and 820° ± 5° C is obtained in 2½ minutes after placing the crucible in position.

Procedure

The sample of coal is freshly ground to pass a No. 60 sieve and is prepared in accordance with the procedure described in this report under "Preparation of Laboratory Sample with Preliminary Drying."

Place 1 gram of the freshly pulverized coal weighed to the nearest milligram in the cold crucible. Tap the crucible lightly 12 times on a block of wood and rotate between taps to level the coal, cover with the lid, and place on the silica triangle over the burner. Heat until the flame of burning gases dies out, and in no case heat less than 2½ minutes. Make three buttons for each sample which are viewed through the sight tube, rotating the button around the vertical axis to get the maximum cross-sectional area of the button. Place the standard profile as shown in figure 30 in the center of the field of vision as viewed from the top of the sight tube. Record the number of the standard profile most nearly matching the maximum cross-sectional area of the button as the free-swelling index. If any button differs more than 1 unit from the other two results, another button is made and tested.

Buttons from some coals do not closely resemble the standard profiles. The cross-sectional areas of these odd-shaped buttons are measured by tracing the shadow cast on millimeter graph paper placed immediately below the button. Force a steel wire through the button along the vertical axis, and then fasten in a horizontal position just above the graph paper. A point source ceiling light or an incandescent light in a hood several feet above the button will cast a sharp shadow on the graph paper. Count the number of square millimeters within the tracing and compare them with the profile having the same area, as shown in table 6.

Report

Report the average swelling index of the series of three buttons, expressed to the nearest one-half unit.

TABLE 6.—*Areas of standard profiles*

Standard profile	Area, square millimeters	Standard profile	Area, square millimeters
1	95	5½	322
1½	112	6	355
2	133	6½	385
2½	155	7	415
3	181	7½	455
3½	205	8	487
4	230	8½	515
4½	260	9	546
5	289		

If the residue is a powder, or if the button pulverizes under a weight of 500 grams carefully lowered on it, the coal is designated as "nonagglomerating." Buttons that break into two or three hard coherent pieces under the 500 gram weight are reported as number one.

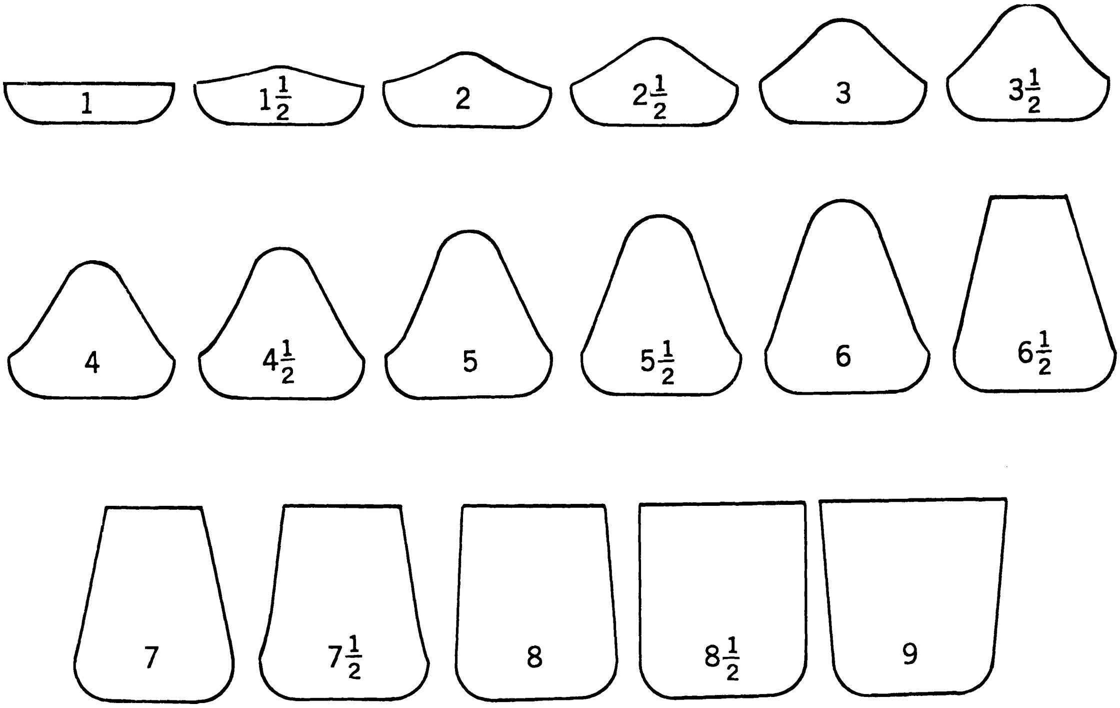


FIGURE 30.—Full-Scale Standard Profiles and Corresponding Swelling Index Numbers.

Method of Test for Agglutinating Value of Coal

The agglutinating-value test[23] is a small-scale laboratory test intended to give information regarding the coking and caking properties of bituminous coal. It is an approximate measure of the material in coal that fuses and becomes plastic on heating. The test consists in heating a mixture of 15 parts of closely sized silicon carbide with 1 part of coal ground to pass a No. 200 sieve in a cylindrical porcelain crucible of prescribed dimensions in a vertical electric tube furnace for 20 minutes at temperatures increasing to 950° C. The crushing strength in kilograms of the resulting carbonized button is recorded as the agglutinating value of the coal.

Apparatus

The apparatus consists of:

(a) An electric furnace of the vertical type as used for determining volatile matter in coal is suitable. It is equipped with a nickel-chromium wire stirrup, shown in figure 31, for supporting the crucible, and a controller to maintain the required temperature.

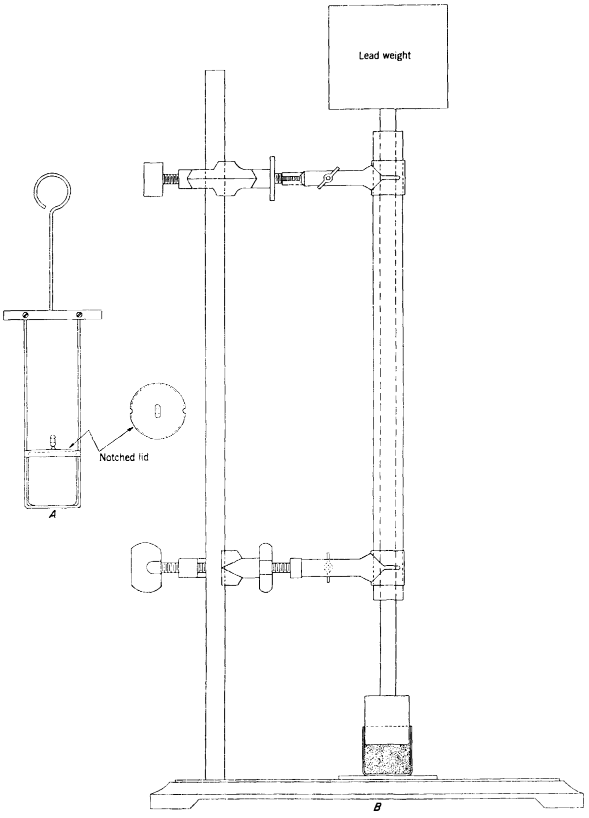


FIGURE 31.—Equipment for Agglutinating Value Test. *A*, Crucible stirrup. *B*, Charge compressor.

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[23] Selvig, W. A., B. B. Beattie, and J. B. Clelland. Agglutinating Value Test for Coal. Proc. ASTM, v. 33, pt. 2, 1933, pp. 741–757.

(b) The apparatus shown in figure 31 is used to compress the mixture of coal and silicon carbide in the carbonizing crucible. The lower end of the compressor is made to fit snugly into the crucible without binding, so that the load of 3,500 grams is applied to the mixture.

(c) A Riehle compression testing machine equipped with a constant speed motor is used for crushing the carbonized buttons. It can apply the load to the test specimen at a continuous rate of approximately 20 kg per minute. The indicating dial, in metric units, is graduated by tenths up to 25 kg. Periodically, the spring scale is calibrated by using standard weights. Rubber pads 3/8-inch thick, cut from the small end of a soft rubber stopper, are cemented on to the steel plates of the compression cage to equalize the pressure over the top and bottom surfaces of the button.

(d) High-form porcelain mixing crucible having a capacity of approximately 55 milliliters.

(e) Cylindrical porcelain carbonizing crucible according to the following specifications:

Inside diameter	millimeters	28
Inside height	do	30
Capacity (approximate	milliliters	18

Selected stock free from irregularities of shape.

(f) Ring-handle porcelain lid having an inside diameter of 32 millimeters. Two notches are ground in opposite sides of the cover to accommodate the side wires of the crucible support as shown in figure 29.

(g) Silicon carbide which is carefully graded by removing for use the portion passing through a No. 45 sieve and retained on a No. 60 sieve. The selected portion is washed by shaking vigorously with water in a bottle and decanting; this operation is repeated five times. It is thoroughly dried and stored for use in a covered container.

The Bureau of Mines investigated various materials for use as inert in the agglutinating-value test.[24] These included silica sand, electrode carbon, fused bauxite, fused aluminum oxide, kaolin grog, and silicon carbide. Of these, silicon carbide appeared to be the most suitable with respect to uniformity of different shipments. However, experience has shown that different lots have given erratic results, making it necessary to set aside one lot as a standard, and to test each lot received to determine whether it checks with the standard. If a new lot does not check with the standard, enough coals of various ranks are tested to obtain a factor for converting results obtained by the new lot to those of the standard.

Calibration of Furnace

The thermocouple actuating the temperature controller is installed permanently in the furnace through the bottom so that the junction is just below the bottom of the carbonizing crucible. A carbonizing crucible is filled with the silicon carbide and placed in the center of the heating zone of the furnace by adjusting the supporting stirrup. A standard thermocouple is placed in the crucible containing the silicon carbide so that the tip of the well touches the bottom. The temperature controller is adjusted to get a constant temperature of 950° C by the standard thermocouple. A higher temperature is registered by the permanent thermocouple, but corresponds to a temperature of 950° C in the crucible. This temperature is recorded and the controller is adjusted to operate at this temperature. In starting a series of tests, the controller is set to operate at this predetermined temperature and a crucible filled with crushed carbonized residue from a previous test is inserted in the furnace.

Preparation of Sample

The coal for the test is prepared by further crushing a portion of the laboratory sample prepared in accordance with the procedure described in this report under "Preparation of Laboratory Sample with Preliminary Drying." About 25 grams of the laboratory sample is sieved on a No. 200 (74-micron) sieve. The oversize portion is crushed lightly on a bucking board so that it will just pass through the sieve. An excessive amount of fines is undesirable. Since the stage crushing segregates the sample, it must be thoroughly mixed after the several screenings are combined. The test should be made immediately after the preparation of the sample.

Procedure

Make the test on a mixture of 18.750 grams of silicon carbide and 1.250 grams of the freshly prepared coal.

Place the silicon carbide in the mixing crucible, and wet it with one drop (0.07 gram) of glycerin, which is delivered from a suitable burette. After adding the glycerin, stir the carbide for 1 minute; then add the

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[24] Selvig, W. A., and W. H. Ode. Inert Material for Agglutinating-Value Test of Coals. Fuel, v. 21, 1942, pp. 46–51.

coal and stir for 2 minutes. It is important that the mixing operations be done in a thorough and uniform manner as follows: Turn the crucible, resting on a table, with the left hand in a counterclockwise direction. Draw a small spatula held in the right hand in a nearly vertical position repeatedly from the bottom of the crucible toward the top and simultaneously move it horizontally in a clockwise direction around the side of the crucible.

Carefully transfer the mixture to the carbonizing crucible and level the top by means of a square-end spatula. Take care not to tap the crucible, since this would change the bulk density and affect the determination appreciably. Compress the mixture in the crucible by carefully lowering and resting the 3,500-gram load of the charge compressor on it for 30 seconds. Fill the space at the top of the crucible with crushed carbonized buttons from previous tests. Cover the crucible with the lid, put it in the stirrup, and place the assembly in the furnace heated to 950° ± 10° C in the crucible.

The thermo-couple will register a 40° to 80° C drop in about one minute and then will gradually rise. Adjust the temperature controller so that a temperature corresponding to 950° ± 10° C in the crucible zone is reached in 15 minutes and maintained at this temperature for the remaining 5 minutes of the carbonization period.

After carbonizing for exactly 20 minutes, remove the assembly from the furnace and suspend it in air until it has cooled to room temperature. Remove the crucible from the stirrup, and pour off the uncarbonized material on top without removing the button from the crucible. Invert the crucible over a sheet of No. 00 sandpaper and gently rub the button to remove any irregularities on the top surface. Remove the button from the crucible and place the sanded surface in the center of the lower rubber pad on the cage of the compression machine and crush. Record the crushing strength as registered on the dial of the machine to the nearest 0.1 kg.

Report

Six buttons are carbonized and crushed for each sample. The average agglutinating value of the six buttons is calculated, and the variation of the individual buttons from this average is computed. If all six buttons are within 10 percent of the average value, this value is taken as the agglutinating value. If one button shows a difference greater than 10 percent of the average, the value for this button is discarded, and the average of the five remaining buttons is taken as the agglutinating value. If more than one button shows variations exceeding 10 percent of the average value, the test is considered unsatisfactory, the results are discarded, and another test is made on six buttons.

The agglutinating value of a coal is reported to the nearest tenth of a kilogram as follows:

	Agglutinating value, kilograms
Ratio, silicon carbide to coal:	
15:1	

Method of Test for the Measurement of Plastic Properties of Coal by the Gieseler Plastometer

This method of test covers a semiquantitative procedure for determining the relative plastic behavior of coal when heated under prescribed conditions in the absence of air.[25] The test is used when studying coals and blends used in carbonization and in other situations where plastic properties are of practical importance.

Apparatus

A convenient form of the Gieseler plastometer is shown schematically in figure 32. The apparatus consists of the following:

(a) A steel retort consisting of four parts as shown in figure 3 is provided:

(1) Retort crucible, cylindrical, 0.844 ± 0.003 inch in inside diameter and 1.375 inch in depth, with exterior threads for joining the crucible to the barrel.

(2) Barrel, at least 5.5 inches long including collar, and having an inside diameter of 0.375 ± 0.003 inch except at the crucible end, where it has an inside diameter of 0.844 ± 0.003 inch to a height of 0.375 inch. The top end of the barrel is 0.625 inch inside diameter to a depth sufficient to allow clearance for the axle of the plastometer head when the apparatus is assembled. A hole, fitted with a tube 0.1875 inch inside diameter is provided at a point 3.125 inch above the crucible so as to afford exit for the volatile products during a test. The barrel has two holes, for observation and ventilation, located on the side opposite the off-take tube. One hole 0.25 inch in diameter is

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[25] Brewer, R. E., and J. E. Triff. Measurement of Plastic Properties of Bituminous Coals. Ind. and Eng. Chem., anal. ed., v. 11, No. 3, May 1939, pp. 242–247.

Soth, G. C., and C. C. Russell. The Gieseler Method for Measurement of the Plastic Characteristics of Coal. Proc. ASTM, v. 43, 1943, pp. 1176–1193.

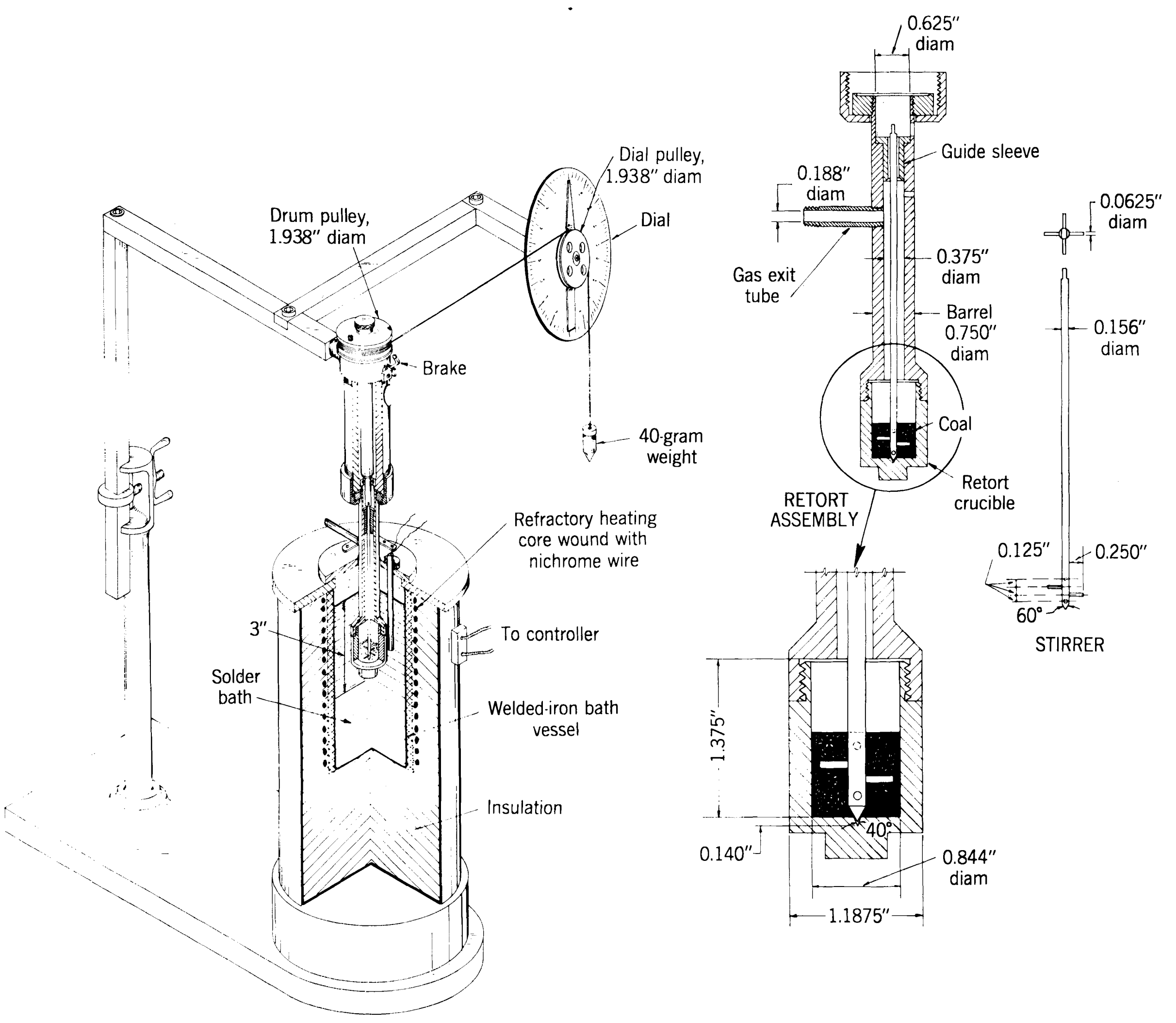

FIGURE 32.—Gieseler-Type Plastometer.

centered 0.125 inch below the collar; the other hole is 0.12 inch in diameter and centered 0.50 inch above the offtake tube.

(3) Steel stirrer, as shown in figure 32, provided with a straight shaft of 0.156 ± 0.001 inch in diameter and equipped with four rabble arms. The lower end of the stirrer is tapered to a point having an included angle at least 10 degrees greater than that of the notch in the bottom of the crucible. The rabble arms on the stirrer are 0.0625 ± 0.001 inch in diameter, 0.250 ± 0.002 inch in length, and are placed perpendicular to the shaft at 90° intervals around the shaft and 0.125 ± 0.001 inch apart center to center along the shaft. The middle two rabble arms are set at 180 degrees to each other, and likewise the remaining two arms 180 degrees to each other. The lowest rabble arm is set in the shaft to give a $\frac{1}{16}$-inch clearance between it and the bottom of the crucible when the stirrer is in place. The upper end of the stirrer is cut to fit into the slot on the lower end of the axle in the plastometer head.

(4) Guide sleeve, provided near the upper end of the stirrer to guide the latter within the barrel, with a clearance of at least 0.002 inch.

(b) The plastometer head, shown in figure 32, contains an axle mounted in ball-bearing races with the lower end of the axle slotted to receive the upper end of the stirrer. A 1.938-inch diameter drum pulley is attached to the upper end of the axle in such a manner that it can be quickly loosened during a test for rewinding of the weight cord. A suitable brake is provided to stop and release the pulley during a test. A cord[26] approximately 6 feet long is wound around the drum pulley and is passed as shown over a second, vertically mounted, slotted dial pulley of the same diameter as the drum pulley. The dial pulley has ball bearings and a counterbalanced pointer to indicate movement on a concentrically mounted round dial divided into 100 divisions for the 360 degrees. The end of the cord is loaded with a total weight of 40 g.

(c) An electrically heated furnace with suitable manual or automatic controls is provided so that a heating rate of 3.0° ± 0.1° C per minute on an overall basis with not more than 3.0° ± 1.0° C per any 1 minute can be maintained over the range of 300° to 550° C. The furnace contains a molten solder bath of approximately 50 percent lead and 50 percent tin composition or equivalent. Temperatures in the bath are measured with a suitable thermocouple in a ¼-inch outside diameter protection tube immersed in the bath so that the tube touches the outside wall of the crucible and the hot junction of the couple is at the same height as the center of the coal charge. A suitable furnace is illustrated in figure 32.

(d) The loading device is provided so that the coal is packed uniformly around the stirrer in the crucible, sufficiently tight to permit transfer to the plastometer head and to withstand a torque of 40 gram-inches until it reaches the softening temperature. A suitable device is shown in figure 33. It consists of a rack with a sliding piston, a cylindrical weight holder and a two-part weight. The combined weight of the cylinder and static weight are 9 kilograms, and the drop weight is 1 kilogram. The drop weight can be raised 4½ inches.

Preparation of Sample

Take a representative sample (50 grams) of the air-dried coal ground to pass a No. 20 sieve, and reduce it in size to pass a No. 40 sieve. Test the coal for plastic properties as soon as possible after preparing the sample.

Preparation of Apparatus for Test

(a) Friction Determination. Make a static test of the friction of the apparatus at room temperature by assembling the plastometer as for a test, except that the crucible is empty. Remove the weight from the end of the cord and substitute a tared light pan.

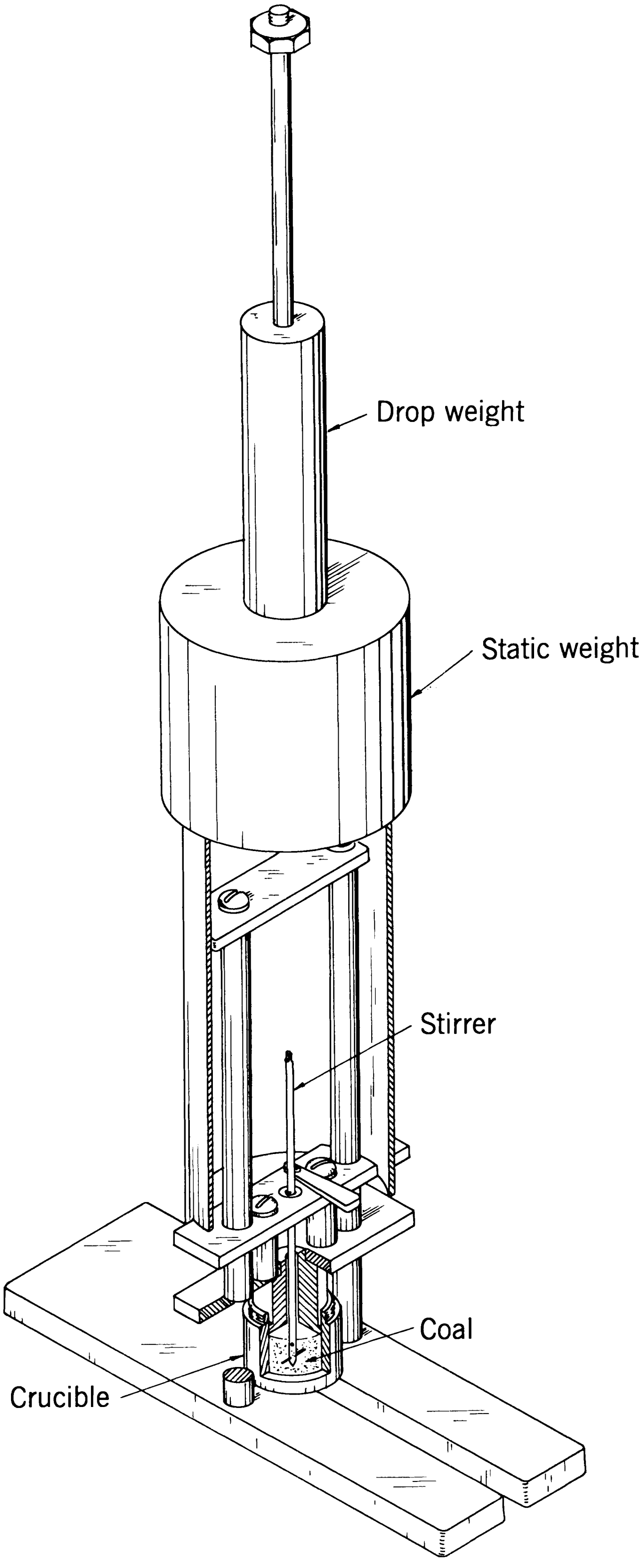

FIGURE 33.—Loading Device.

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[26] 12 Thread Linen Fisherman's Line has been found satisfactory for this purpose.

Add analytical weights to the pan until the pointer just moves at an even rate. With the best bearings in the plastometer head, this weight is less than 0.5 gram. This test is made prior to the first test of the day.

(b) Packing Procedure. Mount the crucible, with the stirrer in place, in the loading device with the piston raised (fig. 33) and place 4.5 grams of coal in the crucible. Remove the voids in the coal by stirring with a stiff wire. Lower the piston and put on the weight holder and weights. Let the drop-weight fall three times and then let the assembly stand for 15 minutes with the 10 kilograms pressing on the coal. Remove the crucible and screw the barrel on the crucible without disturbing the stirrer. Put the sleeve guide in place and attach the barrel to the plastometer head, making sure the top end of the stirrer fits in the slotted end of the axle.

Procedure

The test is carried out as follows:

(a) Lower the assembled apparatus into the furnace until the bottom of the crucible is immersed to a depth of 3 inches in the molten solder bath maintained at a temperature of 300° C. For low volatile coals with an initial softening temperature of over 400° C, it is permissible to maintain a temperature of 350° C in the solder bath. Place the thermocouple in the bath as previously described and cover the bath with a piece of transite. Adjust the heating control so that the bath will regain the initial temperature in 10 ± 2 minutes after immersion of the retort. Thereafter, heat the retort at a rate of 3.0° ± 0.1° C per minute on the overall basis.

(b) When the retort has attained the initial bath temperature, release the brake on the drum pulley, set the dial pointer at zero, and start the clock. At the first detectable continuous movement of the pointer, record the corresponding temperature as the "initial softening temperature." Thereafter, take the readings of time, temperature, and pointer movement at 1-minute intervals. If the rate of turning of the pointer becomes such that the length of cord on the drum pulley will not permit completion of the determination, apply the brake and rewind the cord on the pulley. Release the brake at 1-minute intervals, and determine the rate of pointer movement by means of a stopwatch. Take care to allow the pointer to reach a uniform movement before timing, and to obtain a time interval as long as is conveniently possible in order to increase the accuracy. Make these periodic readings until the point movement becomes such that after releasing the brake the length of cord remaining on the drum pulley will permit the completion of the determination. Continue readings until the pointer shows no further movement. When it is necessary during the test to rewind the cord on the drum pulley, take care not to disturb the stirrer in the coal sample.

All tests are made in duplicate and the average values are reported.

Care of Plastometer

To obtain satisfactory results the apparatus is maintained in good working condition as follows:

(a) It is most important that the dimensions of the rabble arms on the stirrer meet the specifications as previously described. In addition to thorough cleaning of the stirrer and crucible between tests, it is important that the dimensions of the rabble arms be checked at frequent intervals. The total surface are of the four rabble arms, when new, is approximately 0.21 square inch. When, after use, it is found by accurate measurement that the area is reduced to 0.18 square inch or less, the rabble arms are replaced or the entire stirrer is discarded.

(b) The ball bearings are thoroughly cleaned in a light solvent at frequent intervals. Before reassembly they are lubricated with a high-temperature, low-viscosity, silicone oil. Three drops of oil are used per bearing, and the oil is distributed uniformly over the balls.

Report

The schedule for reporting results is as follows:

(a) The corresponding movement of the pointer in dial divisions per minute is calculated from the observed times and dial readings. All values over 15,000 are reported as "greater than 15,000 divisions per minute."

(b) The following information is included in the report:

(1) Initial softening temperature.—The temperature of the first detectable continuous movement of the dial pointer. It is permissible to characterize this temperature by other dial divisions per minute, but in these cases they are reported as such.

(2) Fusion temperature.—The temperature at which the rate of dial pointer movement reaches 5 dial divisions per minute.

(3) Temperature of maximum fluidity.—The temperature at which the dial pointer movement reaches the maximum rate.

(4) Maximum fluidity.—The maximum rate of dial pointer movement in dial divisions per minute.

(5) Solidification temperature.—The temperature at which the dial pointer movement stops.

(c) Certain coals have the tendency to swell up into the barrel during the determination. Upon completion of the test and after cooling, the retort is carefully disassembled, and the height of the material in the barrel is recorded in inches.

Duplicability of Results

All characteristic temperature points for duplicate tests have to agree within 5° C. Maximum rate of pointer movement has to agree within 20 percent of the average.

Method of Test for the Measurement of Dilatation of Coal by the Audibert-Arnu Dilatometer

This test is used to determine the coking properties [27] of coal or coal blends. It is not designed, nor can it be used, to indicate the pressures exerted by coals on the walls of industrial carbonization ovens. The results of the test are not comparable with the free-swelling index or with expansion in the sole-heated oven.

The method is somewhat similar in principle to the Hoffmann dilatometer test,[28] which had some use by the Bureau of Mines in studies of coal plasticity.

A pencil made of powdered coal is inserted in a narrow tube and topped by a steel rod (piston) which slides in the bore of the tube. The whole is heated at a constant and definite rate in a vertical furnace. By recording the displacement of the piston as a function of temperature and expressing the displacements as percentages of the original length of the pencil, a curve of the type shown in figure 34 is obtained.

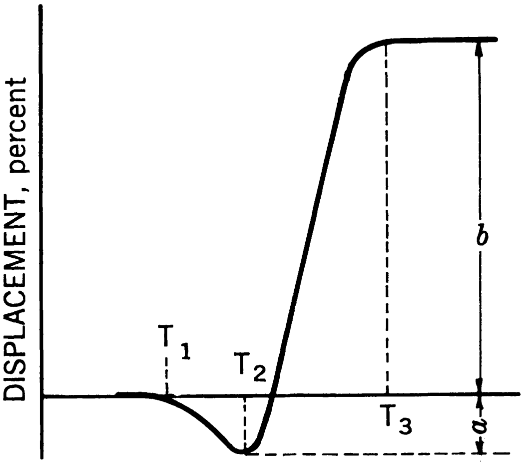

FIGURE 34.—Audibert-Arnu Dilatometer Test for Coal.

The following items are characteristic:

T_1—Temperature at which the piston has moved down 1 percent: initial softening temperature.

T_2—Temperature at which the piston reaches its lowest point: temperature of maximum contraction.

T_3—Temperature at which the piston reaches its highest point: temperature of maximum dilatation.

a—Maximum contraction in percent.

b—Maximum dilatation in percent.

Apparatus

The apparatus consists of the following:

(a) The dilatometer illustrated in figure 35 consists of an electric furnace composed of an aluminum-bronze block held vertically 400 mm high and 65 mm in diameter. It is bored with three holes 350 mm deep and 15 mm in diameter to accommodate three dilatometer tubes; one tube is used for the thermocouple. The block is heated by a wire winding suitably insulated; all is enclosed in a metal case. The instrument is equipped with a recording device consisting of a spring-powered drum carrying a double chart on which the dilatation of two coal samples is recorded simultaneously as the furnace is heated at three degrees per minute in the range of 330° to 550° C. The chart is printed with vertical and horizontal lines corresponding to elapsed time and percent dilatation.

A program controller with a base metal thermocouple is used to control and indicate the temperature.

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[27] This method is recommended by the International Organization for Standardization for determination of coking properties of coals for classification purposes. International Organization for Standardization, ISO/TC 27—Document 664.

[28] Berg, H. Contribution to Dilametric Technique in the Study of Bituminous Coal. Boletin Informativo del Instituto Nacional del Carbon, v. 5, 1956, pp. 151–161.

Hoffmann, H. Die Bestimmung der Bildsamkeit von Steinkohlen nach der Dilatometermethode. (The Determination of Plasticity of Coals by the Dilatometer Method). Oel und Kohle, v. 40, 1944, pp. 531–581.

Hoffmann, H., and K. Hoehne. Über das plastische Verhalten von Steinkohlen. (Pasticity of Coals). Brennstoff-Chem., v. 35, 1954, No. 13/14, pp. 201–211; No. 15/16, pp. 236–246; No. 17/18, pp. 269/275; No. 19/20, pp. 298–304.

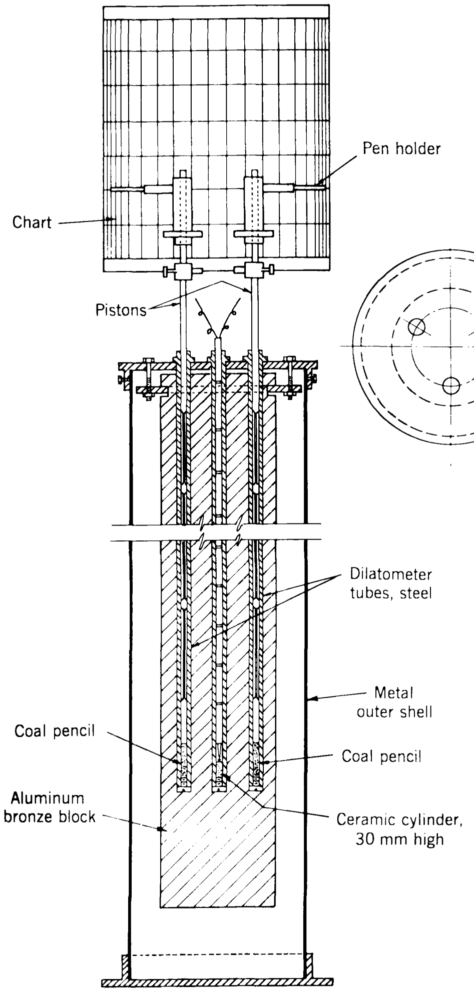


FIGURE 35.—Dilatometer Furnace Assembly With Recording Device.

(b) Dilatometer tubes and pistons are shown in figure 36. At least three dilatometer tubes are required (one is used for the thermocouple). The weight of the piston assembly which includes the pen holder and arm is adjusted to 150 ± 5 grams.

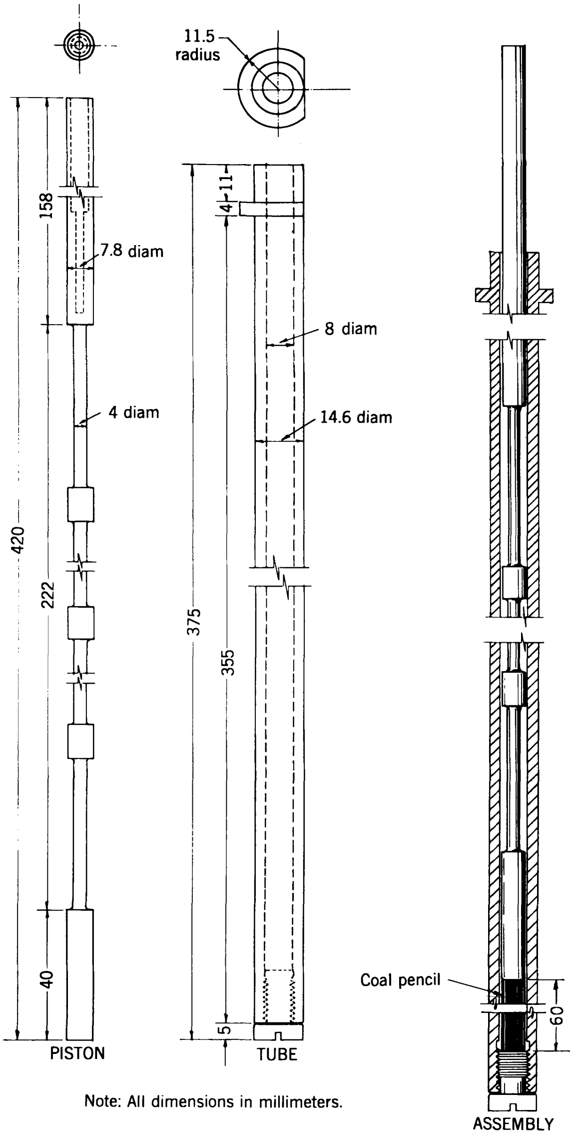
(c) Cleaning instruments for the dilatometer tubes consisting of:

(1) An auger, diameter 7.8 mm ($\frac{5}{16}$ inches).

(2) A reamer consisting of a steel bar of semicircular section, 7.95 mm in diameter.

(3) Rifle ramrod with 30 caliber wire brush.

(d) Apparatus for preparing the coal pencils is shown in figures 37, 38, and 39 and consists of: Mold and accessories, ram, and press.



Note: All dimensions in millimeters.

FIGURE 36.—Dilatometer Tube and Piston.

Calibration and Inspection of the Apparatus

(a) The furnace is constructed so that the temperature conditions are uniform in the dilatometer tubes placed in their normal positions in the holes. To verify this, the furnace is heated at a rate of 5° C per minute. When the temperature reaches about 450° C, an exploration is made of the lower 180 mm of a dilatometer tube placed in the furnace by comparing the temperature shown on the controller with that shown by a probe in the tube. The difference between the probe temperature and the regulator temperature has to be less than:

± 2° C in the lower 120 mm
± 5° C from 120 to 180 mm

The furnace is calibrated by comparing the temperature of the regulator tube with that in each of the other tubes as the furnace is heated from 330° C at the rate of 3° C per minute. The regulating thermocouple is placed in its tube with the junction touching the wall 3 cm above the bottom; a piece of ceramic thermocouple protection tubing 7 mm in diameter and 3 cm long is placed in the bottom of the tube to support the thermocouple. Thermocouples are placed in the other tubes in the same way. The temperatures observed during tests are corrected by the differences found during this calibration.

(b) The dilatometer tubes are inspected for wear after 100 determinations made with any one tube. Results of the next four determinations are compared with those obtained in a new tube. The results are then examined.

If b_0 = dilatation in the old tube,
b_n = dilatation in the new tube.

Calculate the ratio:

$$X = \frac{b_0 - b_n}{1 + \frac{b_n}{100}}.$$

Then, if the average value of X for the four coals, taking into account the sign, is greater than 3.5, the old tube is rejected. Tubes that are found satisfactory are retested after 25 additional determinations.

(c) The mold is periodically checked with the gage, which also is used to check new molds.

If, when the gage is inserted in the larger orifice of the mold,

(1) Two lines can be seen, the mold is too small and has to be reamed out;

(2) One line can be seen, the mold is satisfactory;

(3) No line can be seen, the mold is worn and has to be replaced.

Preparation of Coal Pencil

A representative sample of 50 grams of air-dried coal previously ground to pass a No. 20 sieve is reduced in size to pass a No. 100 sieve. Immediately after preparation, weigh 10 grams of sample and place it in a glass mortar; add exactly 1 ml water and mix with the pestle until all of the coal is uniformly wetted. Place the mold (fig. 37) in its support with the larger orifice upward and set the funnel on the mold. Place a small amount of coal in the funnel and tamp with tamping pin without removing the funnel. Place the mold assembly under the ram (fig. 38) in order to tamp the sample by dropping the plunger four times. Repeat this until the mold is filled. Take increments of sufficient size so that the mold will be filled with four increments.

To remove the pencil from the mold, remove the support and the funnel, place the ejector guide at the end of the mold with the small orifice, and place the guide tube at the other end with the receptacle in the guide tube. Insert the ejector piston in the guide and push the pencil onto the receptacle by means of the press (fig. 39). Adjust the length of the pencil to 60 ± 0.25 mm by cutting away as much as necessary of the thick end with a razor blade.

Procedure

Carefully insert the pencil, thick end first, in the dilatometer tube and push it gently into position with the piston. Place the tubes into the furnace when the temperature is 330° C. Where, in exceptional cases, T_1 is less than 350° C, charge the furnace when the temperature is 20° C below T_1. As soon as the tubes are in place, attach the arms and recorder pens and set the pens on the zero line. When the temperature returns to the starting temperature, start the recorder, the clock, and the program controller, which has been set to increase the temperature at the rate of 3° C per minute. The temperature returns to 330° C in 7 to 10 minutes. Although the dilatation is recorded on the chart, read and record the temperature shown on the controller every two minutes throughout the test. Continue the heating for 5 minutes after the maximum dilatation is reached. Remove the tubes from the furnace and take the pistons from the tubes.

Duplicate determinations are carried out in a separate run.

Cleaning of Tube and Piston

Remove as much of the coke as possible with the auger. Soak in benzene; then use the reamer. Finish cleaning with benzene and a brass wire brush. Clean the piston with very fine emery paper, taking care not to round the edges, and check to ensure that the piston slides freely in the tube.

For coals that are difficult to remove from the mold, it is recommended that the ejector piston and inside of mold be cleaned from time to time.

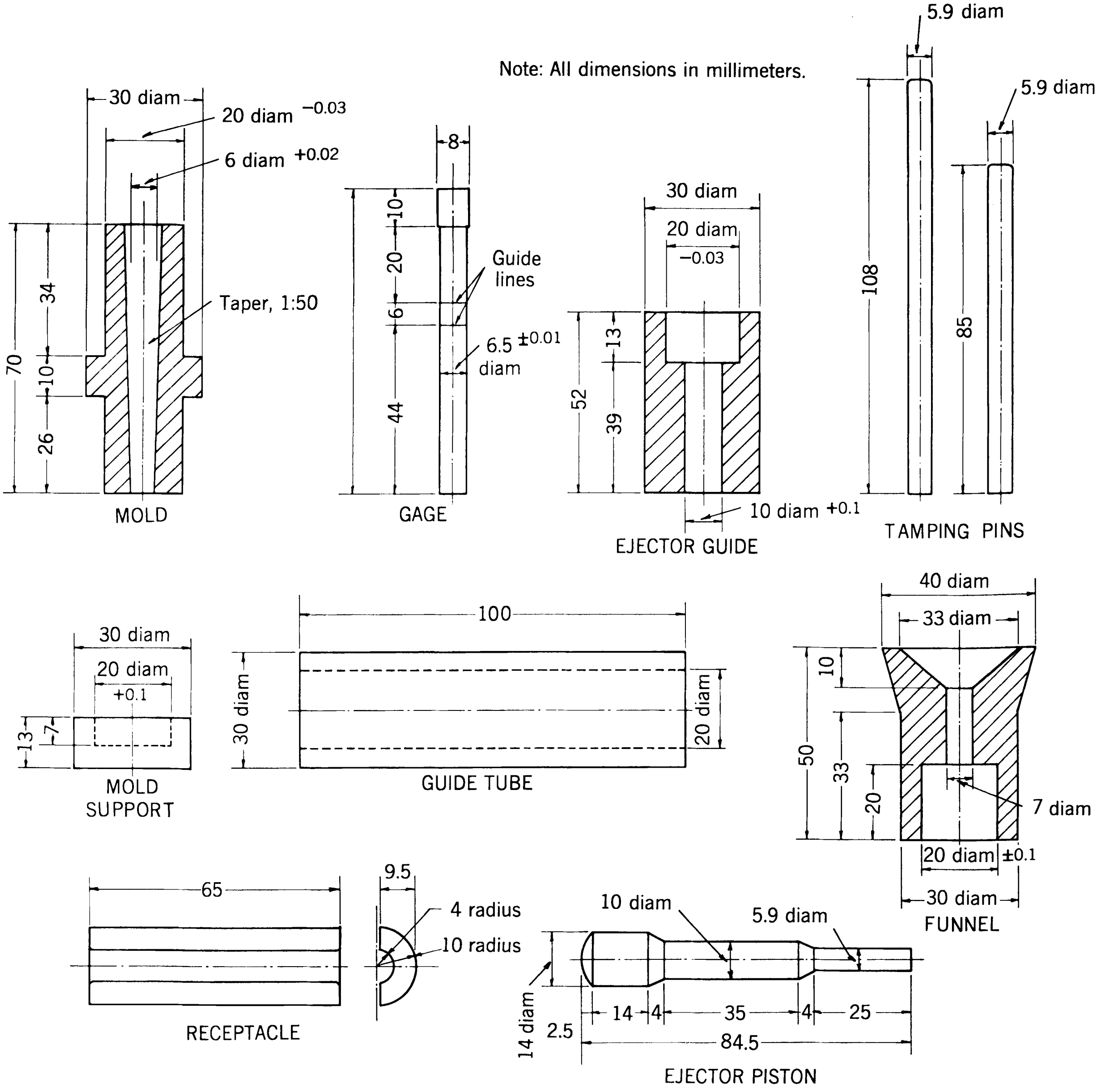


FIGURE 37.—Mold and Accessories.

Report

Record the following information:

T_1—Initial softening temperature.

T_2—Temperature of maximum contraction.

T_3—Temperature of maximum dilatation.

Percent maximum contraction: to nearest whole number.

Percent maximum dilatation: to nearest whole number for negative dilatation; to nearest 5 for dilatation up to 100; to nearest 10 for dilatation over 100.

Duplicability of Results

The results of duplicate determinations carried out at different times on the same sample in the same laboratory by the same operator using the same apparatus should not differ by more than $7\ \frac{(1 + b)}{100}$ percent where b = maximum dilatation in percent.

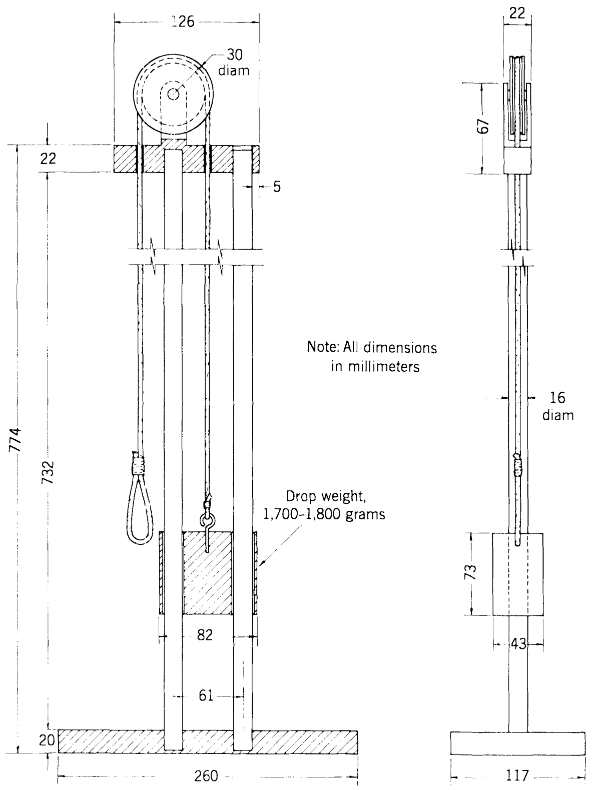


FIGURE 38.—Ram.

Most coals show a slight swelling of the pencil before contraction; when this occurs after the recorder has been started the pen is returned to the zero line.

If a coal has a dilatation greater than 300 percent, repeat the test using pencils of 30 mm length made by cutting the usual pencil in half. Calculate the percent contraction and dilatation for each half and report the average.

COAL CHARACTERIZATION BY ASSAY METHODS

Fischer-Schrader Low-Temperature Carbonization Assay of Coal

The procedure for making low-temperature carbonization assays is a modification of the method developed by Fischer and Schrader [29] at the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr, Germany. The method is used by fuel laboratories in many countries.

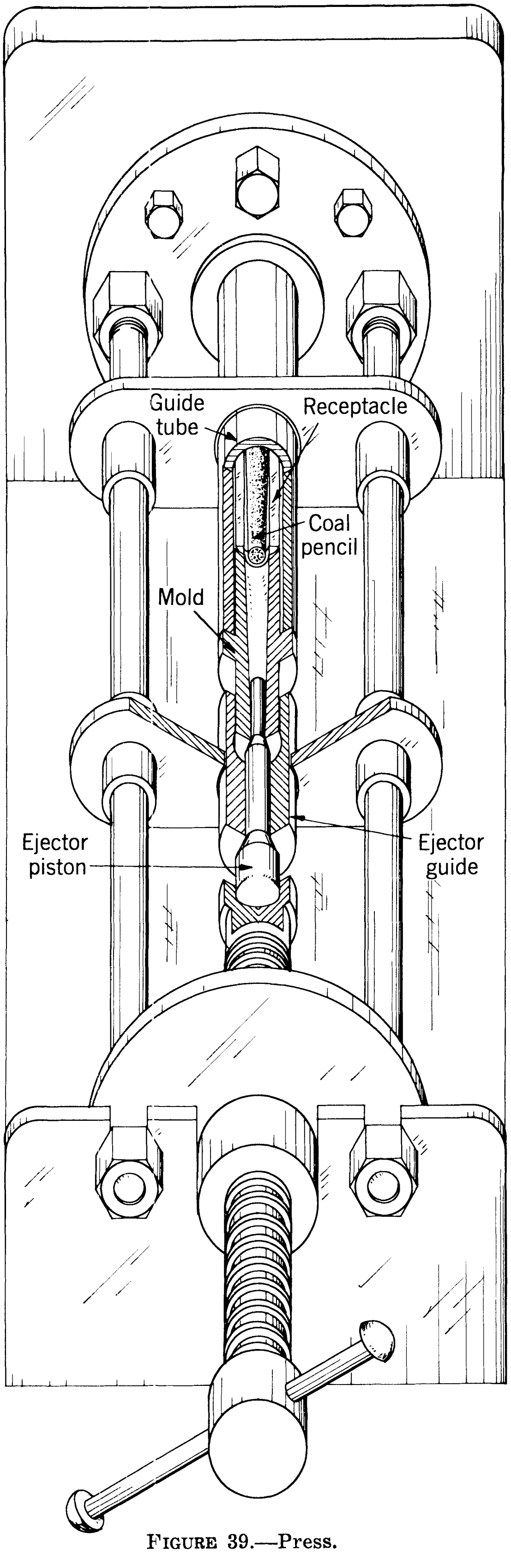


FIGURE 39.—Press.

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[29] Fischer, F., and H. Schrader. (Crude-Tar Determination With an Aluminum Distillation Apparatus). Ztschr. angew. Chem., v. 33, No. 1, 1920, pp. 172–175.

In the assay as originally developed, no provision was made for collecting and measuring the light oil and gas. Since that time the method has been modified to provide for measurement of these products.[30]

Apparatus

The apparatus shown in figure 40 consists of the following:

(a) The retort[31] is designed to carbonize a 50-gram charge of coal. With cover in place, its volume is approximately 200 ml; it is approximately 55 mm in inside diameter, and 95 mm in height below the lid. The retort is a heavy-walled, machined aluminum casting with a triangular side projection or nose through which a brass outlet tube extends downward at an angle of 45°. The large heat capacity of the nose prevents condensation of the heavy fraction of the tar in the outlet tube. The cover is an aluminum plug that fits into the top of the retort in a precision-ground taper joint. A well in the wall of the retort provides for measurement of the temperature either with a high-temperature mercury thermometer or with a thermocouple. The retort is clamped to a support by a steel rod permanently fitted into the side of the retort. During the carbonization an asbestos-cement shield, open at the bottom, is placed around the retort to reduce heat losses. A Meker-type gas burner with grid diameter of 1 inch is used to heat the retort; the temperature is regulated by adjusting the gas flow.

(b) The tar-water receiver is a 200-ml Erlenmeyer flask with a side tube 50 mm long and a 4 mm bore. During the test it is immersed in an ice-water bath for rapid cooling of the vapors. A 100-mm glass-stoppered U-tube containing anhydrous $CaCl_2$, connected to the side arm of the tar-water receiver, removes any water that may have escaped condensation in the receiver. A slight modification of the tar-water receiver is necessary for subbituminous coals and lignites, since tars from these coals are somewhat more difficult to condense than are tars from coals of higher rank. In this modification a weighed glass U-tube is inserted in the recovery system between the regular tar-water receiver and the calcium chloride drying tube. The U-tube is partly filled with a loose packing of absorbent cotton and is immersed in an ice-water bath.

(c) A freezing tube is used to remove the light oil from the gas. It is of similar design but smaller than that used for light-oil recovery in the United States Steel Corp. dry distillation test for coal.[32] During the assay the freezing tube is kept cold (—78° C) by immersion in a wide-mouthed Dewar flask filled with a thick slush of Dry Ice and acetone.

(d) The gas is collected in a calibrated 5-liter gasometer containing a 20-percent solution of anhydrous sodium sulfate and 5

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[30] Selvig, W. A., and W. H. Ode. Determination of Gas, Coke, and By-Products of Coal. Evaluation of Laboratory Assay Tests. Ind. Eng. Chem., anal. ed., v. 7, No. 2, 1935, pp. 88–93.
Selvig, W. A., and W. H. Ode. Low-Temperature Carbonization Assays of North American Coals. BuMines Bull. 571, 1957, 56 pp.

[31] Detailed drawings of the 50-gram retort (Drawing B–1129) may be obtained on request from the Graphic Services Section, Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pa., 15213.

[32] United States Steel Corp., Chemists' Committee. Methods of the Chemists of the United States Steel Corp. for the Sampling and Analysis of Coal, Coke, and Byproducts. Carnegie Steel Co., Bureau of Technical Instructions, 3d ed., 1929, pp. 134–136.

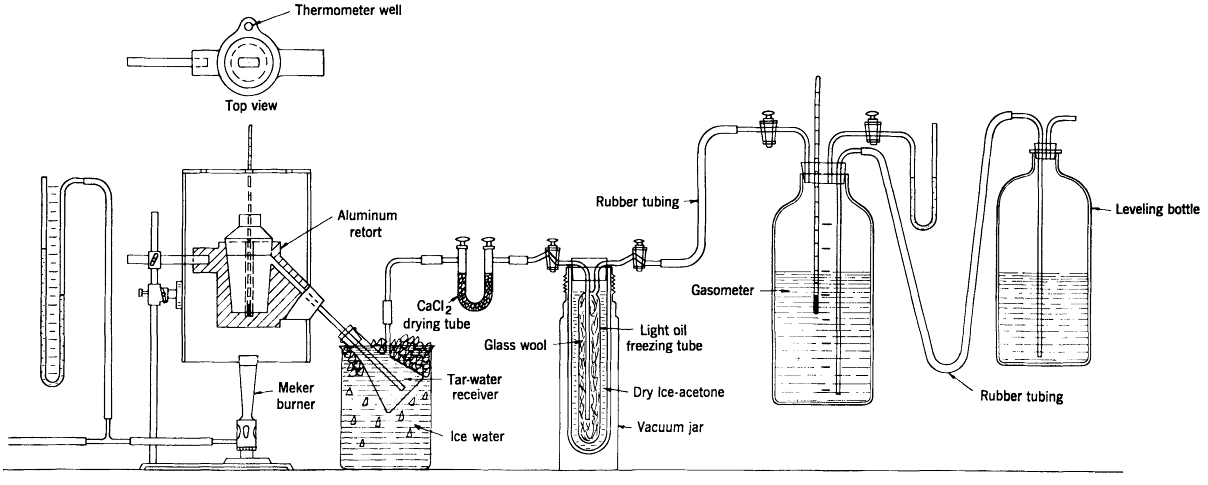

FIGURE 40.—Apparatus for Fischer-Schrader Low-Temperature Carbonization Assay.

percent, by volume, of sulfuric acid. The gasometer is provided with a thermometer and manometer and is connected to a leveling bottle for controlling the gas pressure.

Procedure

Charge 50 grams of air-dried coal crushed to pass a No. 20 sieve to the aluminum retort. For very strongly swelling coals reduce the weight of the sample to 30 to 40 grams. It has been reported that successful assays of a full 50-gram charge of even the highest swelling material may be made if the top of the retort is filled with a loose plug of glass wool that extends downward below the retort outlet.[33] After the coal has been charged into the retort, seat the retort plug tightly into place with a thin film of flake graphite-mineral oil paste. Insert the thermometer or thermocouple in the well, and put the retort shield in place.

Weigh the tar-water receiver to the nearest 0.01 gram and attach it by a well-fitting cork to the outlet tube of the retort. The outlet tube extends 11.5 cm into the flask. To keep the cork from charring and to make a gastight joint with the outlet tube, coat the top of the cork with glycerin-litharge cement. Attach the drying tube to the tar-water receiver by a glass-to-glass connection and immerse the receiver to its neck in the ice-water bath.

Insert the light-oil freezing tube with stopcocks open in the freezing mixture. After temperature equilibrium is reached, close the stopcocks, remove the freezing tube, bring to room temperature, and dry. Weigh the tube to the nearest 0.001 gram and replace in the freezing mixture. After temperature equilibrium is reached, attach it to the U-drying tube.

Connect the gasometer filled with the confining liquid to the system through the freezing tube.

Open the stopcocks on the freezing tube and gasometer and test the system for leaks by putting it under reduced pressure by lowering the leveling bottle attached to the gasometer. If any leakage occurs, remove the plug on the retort and reseat. Normally, no trouble is experienced with leakage if the joint between the plug and retort is well ground.

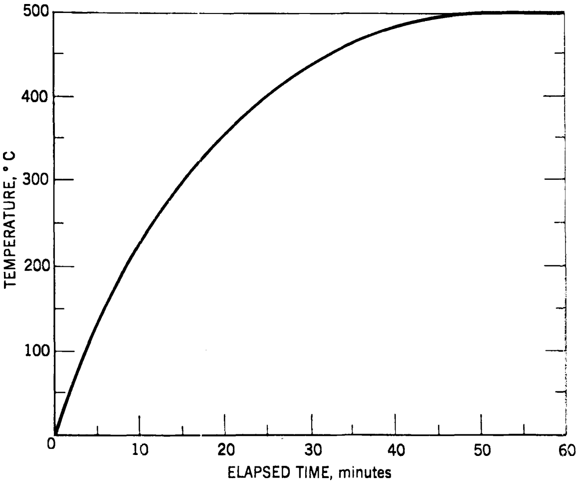

FIGURE 41.—Time-Temperature Curve for Fischer-Schrader Low-Temperature Carbonization Assay.

Carbonize the coal at a rate conforming to the time-temperature curve shown in figure 41. Adjust the primary-air ports on the Meker burner to give a long flame that envelops the bottom and sides of the retort. With a little practice, no difficulty will be experienced in regulating the temperature. Raise the temperature of the retort to a maximum of 500° C in about 50 minutes. Continue the heating at 500° C (± 3°) until the gas evolution is not more than 25 ml in 10 minutes. The total time of carbonization generally is about 3 hours, the exact time depending on the weight of charge and the rank of coal. Maintain the pressure in the system at atmospheric during the test.[34]

After carbonization is completed, turn off the gas burner and close the stopcocks. Record the volume of gas, its temperature, and the barometric pressure. Disconnect the tar-water receiver from the system, and stopper the outlet of the retort. Disconnect the freezing tube from the gasometer, but keep it in the freezing mixture.

Weigh the tar-water receiver; the increase in weight represents the total tar plus water. Determine the water content of the tar-water mixture by the ASTM Standard Method of Test for Water in Petroleum Products and Other Bituminous Materials

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[33] Hensel, R. P. Prevention of Frothing in Fischer Assay Method. Anal. Chem., v. 26, 1954, p. 1393.

[34] For a more careful investigation of the gas obtained from the assay, the contents of the train at the end of the test are mixed with that in the holder by recirculation. By means of a small pump the gas is recirculated through a water trap, flowmeter, and drying tube into a second side-arm on the tar flask and on through the train. This is continued for 10 minutes, with the temperature of the retort maintained at 500° C, at a rate of about 1000 ml per minute, which is sufficient to change the gas in the gasometer about three times.

(D 95–62),[35] except that toluene is used as the solvent. After the side arm has been stoppered, use the tar-water receiver as a distilling flask for the water determination. Add about 75 ml of toluene to the flask, attach a Stark-Dean moisture tube and reflux condenser, and boil the contents of the flask until all of the water is collected in the moisture tube. Convert the volume of water directly into grams by assuming a specific gravity of 1.00. Determine the weight of tar by deducting the weight of water from the weight of the tar-water mixture.

Purge the light-oil freezing tube in the Dry Ice-acetone mixture with dry air to remove any residual gas. Close the stopcocks and remove the freezing tube from the freezing mixture and allow it to come to room temperature. Weigh the tube immediately, since the light oil is extremely volatile and will escape; the increase in weight represents the light oil.

After the retort has cooled, remove and weigh the coke or char, and record its appearance after considering the following physical properties:

Degree of fusion—complete, partial, slight, none.
Swelling—much, some, slight, none.
Cells—large, medium, small, none.
Color—silver gray, black.
Luster—bright, medium bright, dull.

Take the weight of gas as the difference between the weight of the original sample and the sum of the weights of the coke or char, tar, water, light oil, and hydrogen sulfide. Correct the volume of gas, measured in ml, to standard conditions of 60° F and 30 inches of mercury, saturated with water vapor. This volume may be converted to cubic feet per ton of coal by multiplying by the factor 0.641.[36]

Collect a sample of gas from the gasometer and analyze it in a Bureau of Mines-type Orsat apparatus.[37] The following constituents are determined: Carbon dioxide and hydrogen sulfide, illuminants, oxygen, hydrogen, carbon monoxide, methane, and ethane; nitrogen is obtained by difference.

To determine the hydrogen sulfide, bubble a known volume of the gas, which usually is 1,000 ml, through about 10 ml of a 1:1 potassium hydroxide solution in an absorption bulb. Remove the solution from the bulb and wash the bulb with several portions of water; dilute the solution to 100 ml in a volumetric flask, add a 25-ml aliquot slowly with constant stirring to a beaker containing about 100 ml of water, 10 ml of standardized 0.1 *N* iodine solution, and 6 to 7 ml of concentrated hydrochloric acid. Titrate back the excess iodine with standard 0.1 *N* sodium thiosulfate, using starch as indicator.

Correct the gas analysis to an air- and hydrogen sulfide-free basis for reporting purposes.[38] Calculate the heating value and specific gravity of the gas from the analysis of the gas and the heating values and specific gravities of the constituents.[39]

Calculate the percentage yields of the carbonization products from their weights and the original weight of the air-dried coal. Yields in gallons per ton of coal are calculated by assuming a specific gravity of 1.00 for the tar and 0.76 for the light oil.[40] Specific gravities of tar and light oil from individual coals may vary slightly from the figures given; they are, however, an average selected from data obtained in low-temperature carbonization tests at 500° C by the BM–AGA method.

The yields obtained on an air-dried coal basis are calculated to the as-received and dry-coal basis.

Duplicability of Results

No difficulty is experienced in checking duplicate determinations within the following limits:

Coke or char	percent	0.4
Tar	do.	.4
Water	do.	.2
Light oil	do.	.10
Gas	do.	.5
Gas	cu ft per ton of coal	100
Gross heating value of gas	Btu per lb of coal	40

Bureau of Mines Low-Temperature Carbonization Assay of Coal

The assay was developed to eliminate the criticisms leveled at the early methods by which certain of the more important prod-

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[35] American Society for Testing and Materials. Specification for Determination of Water in Petroleum and Other Bituminous Materials. D 95–62 in 1965 Book of ASTM Standards: Part 17, Petroleum Products—Fuels; Solvents; Lubricating Oils; Cutting Oils; Grease; pp. 44–47 and Part 18, Petroleum Products—Measurement and Sampling—LPG; Light Hydrocarbons; Plant Spray Oils; Sulfonates; Crude Petroleum; Petrolatum; Wax; Graphite; pp. 4–7, Philadelphia, Pa. 1965.

[36] Page 143 of work cited in footnote 32.

[37] Fieldner, A. C., G. W. Jones, and W. F. Holbrook. The Bureau of Mines Orsat Apparatus for Gas Analyses. BuMines Tech. Paper 320, 1925, 18 pp.

[38] "Air free" for this test is considered to be free of oxygen + equivalent nitrogen.

[39] The illuminants obtained in this test are considered to be equal parts of ethylene, propylene, and butylene.

[40] To convert percent of coal to gallons per ton, multiply by 2.3965 for tar and by 3.156 for light oil.

ucts were determined by difference. In the present procedure all products are directly weighed or determined volumetrically and converted to equivalent mass. The development of the assay has been reported in detail in prior publications.[41] This assay has been found to be a convenient and reliable method for establishing carbonization yields of both noncoking and coking coals at 500° C.

Apparatus

Apparatus shown schematically in figure 42 and assembled in figure 43 consists of:

(a) The carbonization retort proper is made from 13-gage mild-steel boiler tubing, 2 inches OD by 7 inches in length, with a welded 16-gage top and bottom. The gas - offtake tube is constructed from a 7-inch piece of $\frac{7}{16}$ inch ID thin-wall seamless steel tubing, welded to the retort top. The side gas - offtake line is made from the same type tubing. This latter offtake is approximately 12-inches long and is welded to the vertical gas - offtake tube 1 inch from the top, at an angle of 45° with reference to the vertical gas - offtake and charging tube. At the top of the vertical section of the offtake tube, a standard ¼-inch I.P.T. ground, bronze-seat pipe union is welded. To the top half of the union is brazed a ¼-inch OD by 0.199-inch ID type 306 stainless steel thermocouple well, which extends into the retort chamber to a point 1 inch above the retort bottom at its midsection. Closure of the ground seat union effectively prevents any leakage from the retort.

(b) The furnace cylinder is made from a piece of 3½-inch steel shafting, 9-inches long, bored out to receive the 2-inch OD retort. The boring is about $\frac{1}{32}$-inch greater to

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[41] Gomez, Manuel, and John B. Goodman. Distillation Assays of Missouri River Basin Coals. BuMines Rept. of Inv. 5009, 1953, 9 pp.

Goodman, John B., Manuel Gomez, V. F. Parry, and W. S. Landers. Low-Temperature Carbonization Assay of Coal in a Precision Laboratory Apparatus. BuMines Bull. 530, 1953, 24 pp.

Goodman, John B., Manuel Gomez, and V. F. Parry. Laboratory Carbonization Assay of Low-Rank Coals at Low, Medium, and High Temperatures. BuMines Rept. of Inv. 5383, 1958, 49 pp.

Landers, W. S., J. B. Goodman, and D. J. Donaven. Low-Temperature Carbonization Assays of Coals and Relation of Yields to Analyses. BuMines Rept. of Inv. 5904, 1961, 41 pp.

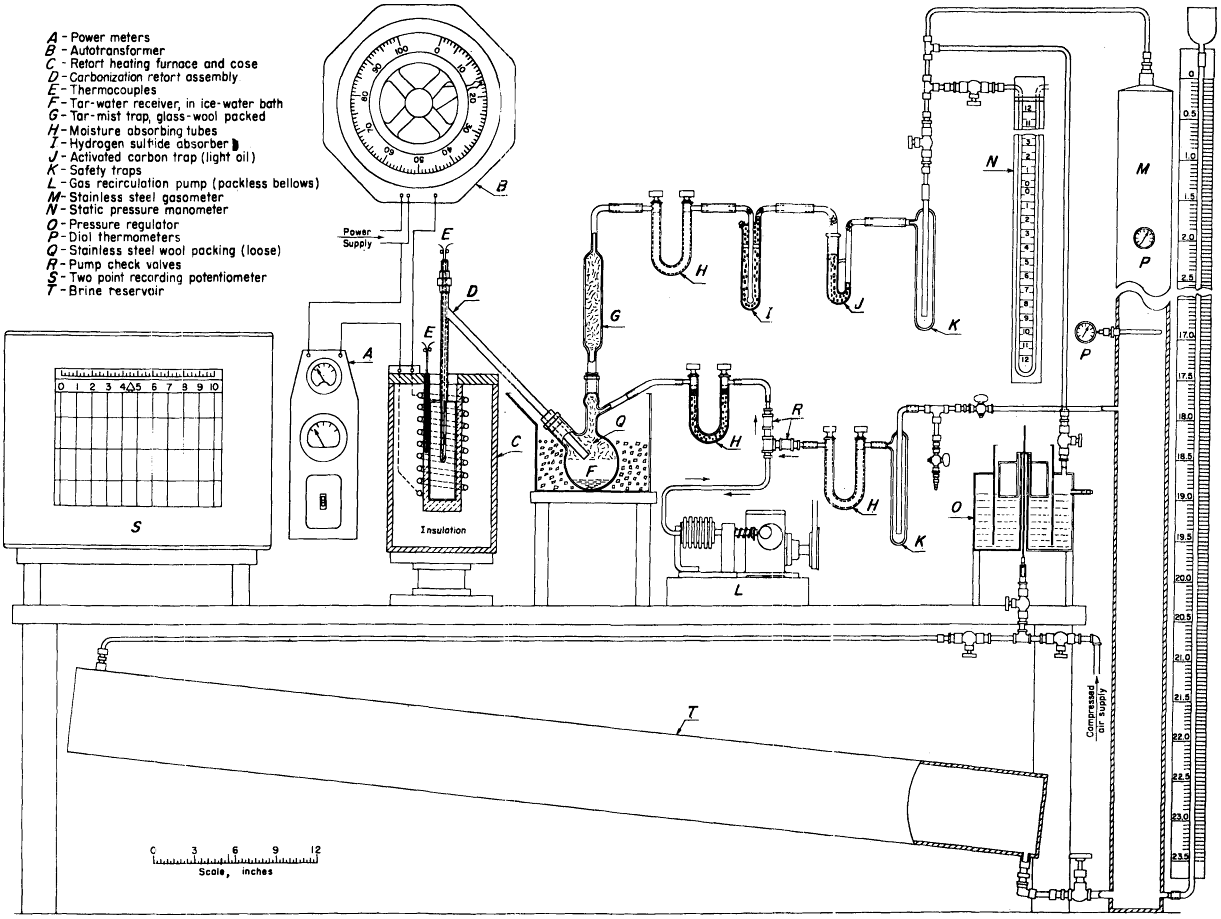

FIGURE 42.—Bureau of Mines Low-Temperature Carbonization Assay Apparatus.

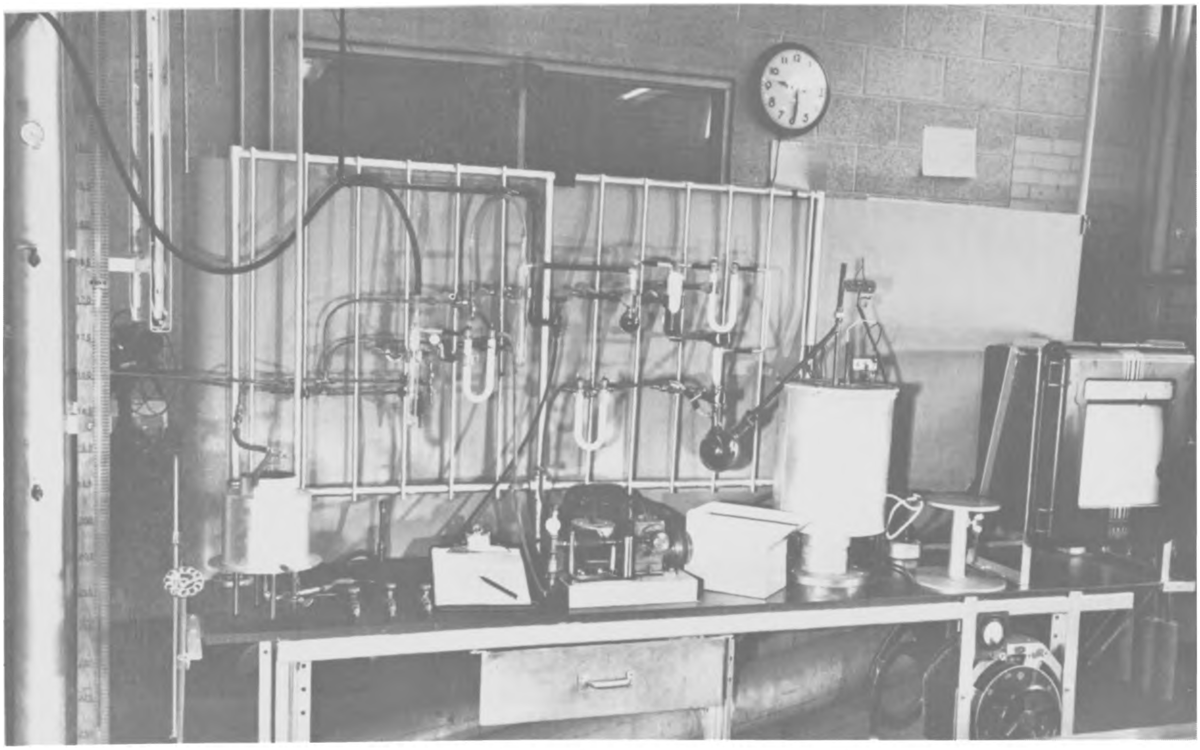

FIGURE 43.—Assembly of Bureau of Mines Low-Temperature Carbonization Assay Apparatus.

allow easy removal if a little scale or dirt wedges between the walls. Three 750-watt band type or magnesia insulated tubular type electric heaters tightly encircle the cylinder. The 2,250 watt potential heat input exceeds that required for any carbonization assay up to 500° C, but this reserve allows the heater elements to operate at a lower current level and prolongs their life. Loose diatomite thermal insulation is poured around the furnace cylinder and heater units. The amount of current entering the heater units is controlled by a variable autotransformer of 0- to 135-volt range and requisite wattage. A pair of panel mounted indicating ac voltage and current meters is used to establish heating conditions.

The inside, or center thermocouple, measures the temperature of the coal charge and indicates when carbonization is complete at a specific temperature. The outer thermocouple is a bare-end type, and is inserted in the thermostat steel. In boring this outer well, a minimum wall thickness is provided on the side adjacent to the retort, since it is intended to measure, as nearly as possible, the outside shell temperature of the retort. Both couples are constructed from matched 22-gage base metal wires.

(c) As shown in figure 42, the tar- and water-receiver is a 500 ml, round bottom, short-ring-necked flask with a standard taper 24/40 female ground-joint tube attached at a 45° angle to the ring neck and loosely packed with stainless steel wool turnings. The ground joint section is about 3 to 4 inches long. It accommodates the glass-wool-packed tar-mist trap in the tapered ground-joint tube and the small side gas-recirculation outlet, which is fused to the tube just below the ground joint section. The recirculation outlet is, in turn, connected to a packless bellows-type gas pump equipped with check valves, or if this is unavailable, to an 85 ml rubber gas-aspirating bulb on the exhaust-valve side. The function of the pump or gas bulb is to enable the operator to circulate a large volume of the fixed gases derived from the assay through the assay train and gasometer system. The mixing insures homogeneous gas composition for analysis. A sulfur-free rubber stopper connects the side gas offtake of the retort with the tar-water receiver. Any water carried through as vapor in the gas stream during the course of an assay run is absorbed in the Schwartz-type calcium chloride tube following the tar-mist trap.

(d) The hydrogen sulfide trap shown in figure 44 is constructed from 1½-inch-diameter glass tubing 6 inches in length, and provided with inlet and outlet tubes through ring seals at the top. A standard taper 9/14 joint closed with a pennyhead stopper is provided at the top for charging the absorber with copper sulfate-impregnated siliceous absorbent to about 5 inches of its length. The remaining top 1 inch of the trap is filled with anhydrous calcium chloride; a thin layer of glass wool or cotton separates the impregnated diatomite from the calcium chloride. One charge of copper sulfate reagent lasts about three to five gas determinations and often more, depending upon the sulfur content of the coals. The degree of copper sulfate exhaustion is indicated by the formation of a dark brown-black copper sulfide deposit in the absorber tube.

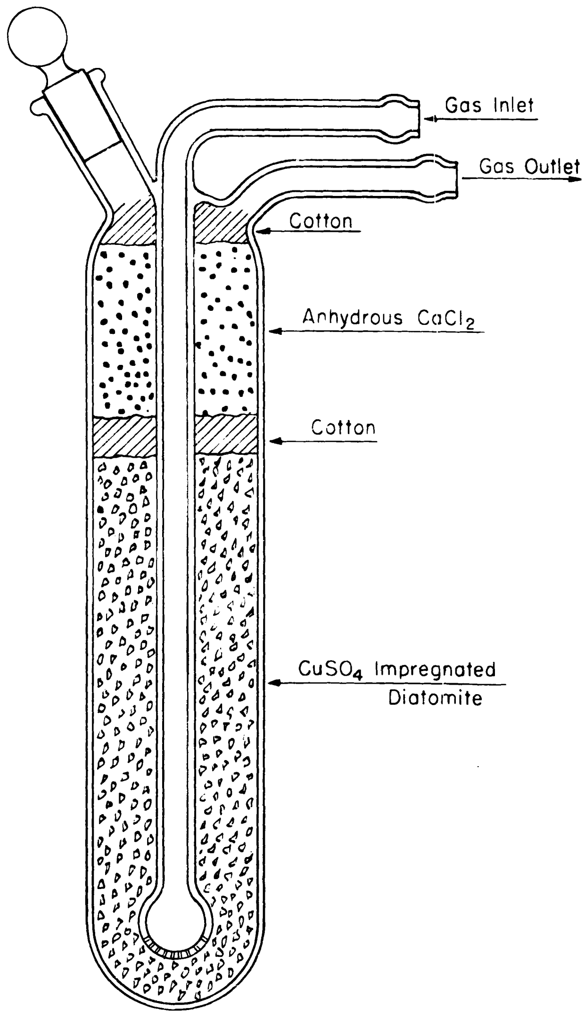

FIGURE 44.—Hydrogen Sulfide Absorber.

(e) The light-oil trap is fabricated from the male and female halves of a standard 24/40 tapered ground-glass joint, and has an overall length of 7 inches. This trap has a capacity of approximately 30 ml of 8 x 14 mesh activated carbon and 15 ml of 8 mesh anhydrous calcium chloride. The gas stream carrying the light oil vapor enters the top of the trap and travels down through the carbon and up through the drying charge of calcium chloride.

(f) To prevent corrosion caused by the saturated brine used for the gas-confining liquid, the gasometer or gas holder, as indicated schematically in figure 42 (items *M* and *T*), is constructed from a 12-foot length of 4-inch OD stainless-steel tubing (3⅝-inch ID) with provision made for a domed head and a flat-mounting base. The slightly inclined reservoir section of the gasometer is of the same material and size. All connecting tubing and valves are of brass or stainless steel, and all welds are made with stainless-steel welding rod. The total gasometer capacity as indicated on figure 42 is 23.5 liters, and the smallest division shown in the side scale is 50 ml. Dial type thermometers inserted in copper wells are placed at the 2- and 8-foot levels of the gasometer to show gas temperature. Stainless-steel petcocks are placed at various levels to permit the attachment of a gas-recirculation line at the optimum point indicated by the volume of the gas collected.

Through tubing and a needle-type by-pass valve, the bottom outlet of the gasometer is connected to the lower end of the brine reservoir. A valving manifold provides all connections necessary for operation. One connection is made to the compressed-air supply; a second connection is made to the automatic pressure regulator, and a third connection vents the gas to the atmosphere.

Procedure

Depending on its gas yield, fluidity, and swelling properties, charge 125 to 200 grams of coal previously crushed to ⅛-inch by 0 size to the retort. Lower rank coals, if not air-dried, yield higher total water at the expense of the true coal substance, and thus may reduce the test precision. The permissible maximum moisture content of the charge is 10 percent.

Introduce the coal charge into the assay retort through the $\frac{7}{16}$-inch gas-offtake tube, *D*, figure 42. Maintain a free volume of not less than one inch below the outlet of the gas-offtake tube in order to prevent plugging due to expansion of the charge which may occur with coking coals. Weigh the retort and contained coal charge on a pulp balance sensitive to 0.05 gram. Seal the retort by inserting the center thermocouple well and tightening the welded union nut. Attach the dry, tared, tar-and-water receiver flask, *F*, figure 42, to the 45° retort side gas-offtake tube; connect the gas-recirculation line to the side tube of the tar-and-water flask; and place the entire assembly in a crushed ice-water bath. Attach the glass-wool-packed tar-mist trap to the tar-and-water receiver by way of a ground joint. Connect a weighed, Schwartz-type, 150 mm U-tube filled with 8-mesh anhydrous calcium chloride desiccant to the outlet tube of the tar-mist trap. Connect a previously prepared and weighed hydrogen sulfide absorber to the open arm of the calcium chloride U-tube and then to a freshly activated carbon adsorption trap for light oil collection. Fit all traps and adsorbers used in the assay train with protective plug seals on the inlet and outlet tubes when they are weighed on the analytical balance. The activated carbon sized to pass a No. 6 sieve and retained on a No. 16 sieve is freshly reactivated before use by heating in a rotating tubular retort at about 300° C for one-half hour, during which time dry steam is passed through the charge. After steaming, and while still hot, the activated carbon is subjected to an absolute pressure of about 100 mm of mercury for about 30 minutes, and is then rapidly removed from the retort and stored in stoppered bottles for current use.

Place two safety traps, *K*, figure 42, in the gas circuits from the carbon trap to the gasometer and from the gasometer to the recirculating gas pump, *L*, figure 42, to prevent the saturated brine in the gasometer from accidentally contaminating the carbon trap or the tar-and-water receiver during recirculation of the carbonization gas at the conclusion of the assay. Water vapor carried over from the gasometer during recirculation of the gas is removed by a second calcium chloride U-tube located between the pump and the brine safety trap. Small amounts of water taken up by the dry gases entering the tar-water receiver during recirculation are absorbed and accounted for in the calcium chloride tube in the main collection train.

Control the rate of heating by a variable autotransformer of 0- to 135-volt range and requisite wattage. The heating schedule chosen for most lignites and higher rank coals is one that reaches 500° C in about one hour using a heating rate of 7° to 8° C per minute. Continue the heating at the final carbonization temperature for one additional hour. Measure the temperature in the center of the coal charge and at the wall of the retort by automatically compensated thermocouples in the center well of the retort and in the wall of the furnace, *E*, figure 42, and recorded by a two-point temperature indicating-recording potentiometer. By means of an automatic pressure regulator, *O*, figure 42, hold the entire system at zero pressure or at a slight vacuum the greater part of the assay run to prevent leakage into or out of the system.

At the termination of an assay, isolate the gasometer from the lower brine reservoir. To obtain a homogeneous gas sample representative of the entire determination, recirculate the gas in the gasometer through the train by means of a bellows-pump for at least three minutes. Read the gas volumes to 50 ml and estimate to one-half of a division or 25 ml. Collect a gas sample from the gasometer and analyze for carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen in an Orsat-type precision gas analyzer.

Reweigh the calcium chloride U-tube, the hydrogen sulfide trap, and the activated-carbon trap on an analytical balance. Weigh the tar-and-water receiver, together with the tar-mist trap, on a 2-kilogram capacity pulp balance with a sensitivity of ± 0.1 gram. The differences in weights determined before and after the assay test give the yields directly of water in the gas, hydrogen sulfide, light oil, and tar-and water, respectively. The water phase is separated from the tar-water mixture by distillation with xylene.[42] Attach to the tar-and water receiver by ground glass joints a Stark-Dean type moisture tube connected to a water condenser; add xylene to the receiver and reflux the mixture for about one hour. Alternatively, when it is desired to recover the tar for ultimate analysis, decant the major portion of the water and dry the remaining tar for three to four days over concentrated sulfuric acid.

Allow the retort to cool and then reweigh to obtain the yield of char or coke. During cooling, close the angled gas-offtake tube with a small stopper to prevent access of air to the hot char or coke residue. When cool, pour the char out of the retort through the vertical gas-offtake tube, *D*, figure 42, if lignites or weakly caking coals are assayed.

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[42] Work cited in footnote 3.

If a strongly coking coal has been carbonized, remove the bottom from the retort using a thin hacksaw starting cut, then peeling the bottom off and extracting the coke. Gas-weld a new bottom plate onto the retort for subsequent usage, thus extending its life almost indefinitely.

Report

As shown on the sample worksheets 1 and 2, the yields of all solid and liquid products are directly calculated from weight determinations while gas yields are obtained by the actual measurement of gas volumes corrected for specific temperature and pressure conditions prevailing in various parts of the assay equipment and converted to weight percent from the composition of the gas.

To complete the material balance, calculate the assay-distillation gas as a percentage of the moisture- and ash-free coal according to the following procedure. The total volume of the carbonization assay system, exclusive of that volume occupied by the adsorbents and desiccants, is found by direct calibration to be 1,620 ml for the apparatus used in the sample worksheet 1. This volume is different for another apparatus because of changes in construction and layout. As shown in sample

Sample Worksheet 1.—Low-temperature carbonization assay data

Carbonization temperature:	
°C	500
°F	932
Weight grams:	
Retort and coal	1,082.9
Retort, tare	883.9
Coal carbonized	199.0
Tar, water, and flask	346.2
Flask	302.9
Tar and water	43.3
Total water, by xylol	18.1
Tar residue	25.2
Dryer and moisture	64.0752
Dryer ($CaCl_2$)	63.9898
Moisture in gas	.0854
H_2S tube and H_2S	176.7058
H_2S tube, tare	176.2102
H_2S in gas	.4956
Light oil, trap, and carbon	81.8205
Trap and Carbon, tare	79.2276
Light oil	2.5929
Char residue and pan	1,026.8
Pan, tare	883.9
Net char	142.9

Gas analysis	Percent		Btu per cu ft calc
	Total	O_2- and N_2-free	
H_2S			
CO_2	14.7	16.1	
Illuminants	2.3	2.5	55.4
O_2	2.5		
CO	9.5	10.4	33.5
H_2	9.9	10.9	35.4
CH_4	49.3	54.0	548.1
C_2H_6	5.6	6.1	109.3
N_2	6.2		
Total	100.0	100.0	781.7

Material balance:	*Grams*	*Percent*
Coal charged	199.0	100.0
Free water	9.2	4.6
Water formed	9.0	4.5
Tar	25.2	12.7
Light oil	2.6	1.3
Char	142.9	71.8
Gas	9.9	5.0
H_2S	.5	.3
Total	199.3	100.2

Proximate, percent:
H_2O, as received 4.6, H_2O, air dried
Volatile matter....41.2
Fixed carb............46.8
Ash, as received .. 7.4, Ash, air dried
Total....................100.0

Btu, as received		12,590
Btu, moisture and ash free		14,310
Observed gas volume	ml	13,500
Temperature, gasometer, 69°F	°C	20.5
Net gas, O_2- and N_2-free (as carbonized), STP[1] ml/g		54.0
Net gas, O_2- and N_2-free (as carbonized) STP[1] cu ft/lb		0.865
Retort temperature, gas correction	°C	485
Observed barometer	in Hg	24.80
Correction	in Hg	0.12
Corrected barometer	in Hg	24.68
Calculated sp gr gas		0.748
Volumes of system components for assay unit, ml;		
Retort		325
Tar-water receiver		575
Train and traps		720
Total		1,620

Sample Worksheet 2.—Low-temperature carbonization assay: Assay gas calculations

A. Gas in gasometer (STP × gas-saturation factor at 69° F)

$$13{,}500 \times \frac{24.68}{30} \times \frac{520}{529} \times 0.9764 = 10{,}659 \text{ ml}$$

B. Gas in system after test: (V train) + (V trap) + (V retort)

$$\left(720 \times \frac{24.68}{30} \times \frac{520}{529}\right) + \left[\left(575 - 43.3\right) \times \frac{24.68}{30} \times \frac{520}{492}\right] + \left[\left(325 - \frac{142.9}{1.6}\right) \times \frac{24.68}{30} \times \frac{520}{1365}\right]$$

$$582 + 462 + 74 = 1{,}118 \text{ ml}$$

C. Total gas in system: Gas (gasometer) + gas (system after test) = A + B

$$10{,}659 + 1{,}118 = 11{,}777 \text{ ml}$$

D. Net yield (O_2- N_2-free) $= 11{,}777 \text{ ml} \times \left(1.00 - \frac{8.7}{100}\right) = 10{,}752$ ml (STP, dry)

E. Net gas, ml per g: $\frac{10{,}752}{199.0} = 54.0$ ml per g[(STP, dry) (O_2- and N_2-free, as carbonized)]

F. Net gas, cu ft per lb: 54.0 ml per g $\times \frac{453.6}{28{,}316} = 0.865$ cu ft per lb [(STP, dry) (O_2- and N_2-free, as carbonized)]

The yield of gas, expressed as weight-percent, is calculated from the molecular distribution of elements in the carbon dioxide, illuminants, carbon monoxide, hydrogen, methane, and ethane, all gases referred to an oxygen- and nitrogen-free, dry, total gas. The volume-percent of the individual gases, as determined by the Orsat gas analyzer, provides the starting point for gas yield calculations. From the volume-percent is obtained the elemental mole (carbon, hydrogen, and oxygen) volume.

Gas, O_2- and N_2-free	Percent	Mole volume per 100 moles		
		Carbon	Hydrogen	Oxygen
CO_2	16.1	16.1	......	16.1
Illuminants	2.5	7.0	7.0	......
CO	10.4	10.4	......	5.2
H_2	10.9	......	10.9	......
CH_4	54.0	54.0	108.0	......
C_2H_6	6.1	12.2	18.3	......
Total	100.0	99.7	144.2	21.3

The sum of the elemental mole volumes, when divided by the calculated average volume (378 cu ft per lb mole), for all gases mentioned, taken at 60° F and 30 inches of mercury, will yield the moles of the calculated elemental gas (carbon, hydrogen, and oxygen) per 100 cu ft of total gas yield.

Moles per cu ft of gas, O_2— and N_2— free

Carbon $\frac{99.7}{378} = 0.264$

Hydrogen $\frac{144.2}{378} = 0.381$

Oxygen $\frac{21.3}{378} = .056$

The moles of each elemental gas, when multiplied by their respective molecular weight expressed as pounds, will give the pounds of that gas per 100 cu ft of the total assay-gas yield.

Lb per 100 cu ft of gas, O_2- and N_2-free

Carbon $0.264 \times 12.01 = 3.171$

Hydrogen $.381 \times 2.016 = .768$

Oxygen $.056 \times 32.000 = 1.792$

Total $.701$ 5.731

The sum of the pound weights of the elemental gases, when multiplied by the observed assay gas yield, expressed as cubic feet of gas produced per pound of coal carbonized, will give the pounds of gas made per 100 pounds of coal carbonized or the percent of gas.

5.731 lb/100 cu ft × 0.865 cu ft per lb = 4.96 lb gas per 100 lb coal.
= 5.0 percent gas yield (as carbonized coal basis).

To obtain the specific gravity of the assay gas, the weight of that gas expressed as pounds per cubic foot is divided by the weight of 1 cu ft of air at standard conditions of 60° F and 30 inches of mercury. This figure is taken to be 0.07657.

$$\frac{0.05731 \text{ lb per cu ft}}{0.07657 \text{ lb per cu ft}} = 0.748$$

worksheet 1, the total volume of the system is composed of the volume of the retort, the volume of the tar-water receiver flask, and the volume of the assay train. The gas volume remaining in the train at the conclusion of a test is obtained by calculating the three component volumes in the particular system as shown in the sample worksheet 2.

(1) Reduce to standard gas conditions the combined volumes of the calcium chloride U-tubes, hydrogen sulfide trap, light-oil (activated carbon adsorber) trap, brine safety traps, and connecting tubing (720 ml).

(2) Correct the volume of the gas in the tar-water receiver flask for the volume occupied by the stainless-steel packing and the volume of condensed water and tar collected at 32° F.

(3) Calculate the volume of the gas remaining in the retort by subtracting the volume of residual char from the volume of the retort, at the temperature indicated by the center retort thermocouple, read at approximately the same time recirculation of the gas has been completed. The assumption is made that the char contained in the retort has a true specific gravity of 1.6. Small differences in specific gravity do not significantly affect the computed gas volumes.

The total gas volume obtained from carbonization of the coal charge is the sum of the gas volumes in the gasometer and the system. The observed gasometer volume is reduced to standard gas conditions of 60° F and 30 inches mercury pressure and further correction for water saturation. For reporting purposes recalculate the total gas volume to an oxygen- and nitrogen-free basis. This step gives the final net volume of gas.

PETROGRAPHIC ANALYSIS OF COAL

Coal is composed of various physical components, some of which are visible to the unaided eye while others may be seen only under a microscope. There are a number of systems of description and classification of these components. Those used in describing the appearance of coal under the microscope may be combined into two major groups, depending on whether the coal is observed by transmitted or reflected light. For the former observations sections of coal thin enough to transmit considerable light are required; the latter studies are made on polished surfaces. Thin section methods were pioneered in the United States by Dr. Reinhardt Thiessen of the Bureau of Mines, and have been used by the Bureau for many years.[43] Studies of polished surfaces of coal were developed mainly in Europe, but have been used extensively in this country in recent years. In fact, there has been very recent agreement among American coal petrographers that a method involving measurement of reflectance of the various recognizable components is the most promising for correlation with utilization of coal.

Thin Section Analysis by Transmitted Light

The most recent complete description of the Bureau of Mines method of petrographic analysis of coal using thin sections was published in 1948.[44] In this method components termed anthraxylon, translucent attritus, opaque attritus, and fusain are determined, in addition to mineral matter. The term anthraxylon is applied to orange-to-red bands or lenses wider than 0.014 mm in the direction perpendicular to the bedding, fairly homogeneous in appearance but often showing evidences of cell structure. Translucent attritus consists of anthraxylous material less than 0.014 mm and yelow spores, pollen, and cuticles of characteristic shape. Opaque attritus consists of irregularly-shaped black masses, sometimes having a granular structure. Fusain also consists of irregular opaque masses, but it has a characteristic fibrous, cellular structure. However, fusain less than 0.037 mm in the direction perpendicular to the bedding is classed with the opaque attritus.

Petrographic thin section analysis is usually made on specimens obtained from column samples cut out of a coal bed from top to bottom. The specimens are small blocks measuring approximately 1 x 0.8 x 0.5 inches. The 0.8-inch dimension is in the vertical direction of the column or bed, so that the total of the 1 x 0.8-inch faces represents a ribbon area over the entire height of the bed, excluding the material lost in cutting between the blocks. One such face of each block is ground flat on a silicon carbide lap, further smoothed on a fine Belgian hone, and finally polished on a cloth lap using alumina powder. This face is cemented to a glass microscope slide with a mixture of Canada balsam and marine glue. The opposite face is then ground on laps and the hone until the coal begins to transmit light. The section is finally ground to the desired uniform thickness by grinding on the hone with localized finger pressure on areas appearing to be relatively thick when the section is held up to a strong light. Final steps in this process and polishing of the surface are performed with a piece of cork dipped in a fine polishing powder. All of these grinding and polishing steps are conducted under running water or with wet materials. The final thickness of the coal section is between 5 and 10 microns. A microscope cover glass is cemented over the finished section for protection.

Microscopic analysis of thin coal sections is conducted with a biological microscope equipped with 15X binocular eyepieces, with 16 and 32 mm objectives to attain magnifications of 60X and 150X. Anthraxylon is measured at 150X and opaque attritus, fusain, and mineral matter at 60X. Translucent attritus is determined by difference. Measurements are made by means of a Whipple micrometer disk inserted in one of the eyepieces. This is a glass disk on which is centered a 7 mm square field divided into one hundred 0.7 mm squares with the central one subdivided into twenty-five 0.14 mm squares. The effective sizes of these squares under different magnification conditions are determined by comparison with a stage micrometer.

To begin the analysis, an area of the section near the center of the left half and at the top or bottom of the section is observed in the eyepiece containing the Whipple disk. In particular the ribbon of the section covered by the central vertical tier of squares is observed. The remaining squares are masked for convenience. The number of squares or fractions of squares occupied by each component is estimated and recorded. The stage is then moved the length of the tier of squares, and the components in this field are estimated. This procedure is continued until the opposite edge of the section is reached. Measurements are next made by a similar traverse near the center of the right half of the section. Proportions of each component determined in the two traverses are averaged. A detailed study[45] of the errors involved in this type of thin section analysis showed that the percentages of components present in a column sample of a coal bed as

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[43] Parks, B. C., and H. J. O'Donnell. Petrography of American Coals. BuMines Bull. 550, 1957, 193 pp.

[44] ———. Determination of Petrographic Components of Coal by Examination of Thin Sections. Trans. AIME, Coal Div., v. 177, 1948, pp. 535–551; AIME, Coal Technol., Tech. Pub. 2492, November 1948, 17 pp.

[45] Work cited in footnote 44.

determined by the above described technique should not usually be in error by more than 2 percent.

Polished Surface Analysis by Reflected Light

In petrographic analysis of coal by reflected light microscopy, various investigators have made determinations of components or assemblages of components defined or described by different methods. There has been a greater diversity of techniques of polished surface analysis than of thin section analysis. In the method usually used at the Bureau of Mines the proportions of the so-called macerals (analogous to minerals in rocks), termed vitrinite, exinite, micrinite, fusinite and semifusinite, are determined, together with the amount of recognizable mineral matter. Vitrinite, the principal maceral of bright coal, is dark to light gray in appearance and may or may not show cell structure. It is nearly analogous to anthraxylon. Exinite is composed of the remains of spores, pollen, and cuticles. It is usually recognized by morphology and very low reflectance. It is an ingredient of translucent attritus. Micrinite is completely structureless, has a high reflectance, and occurs in granular or massive form. It is the major part of the opaque attritus. Fusinite always shows a characteristic fibrous, cellular structure and has high reflectance. The fusain of the thin section classification consists almost entirely of fusinite; fusinite less than 0.037 mm is classed with opaque attritus. Semifusinite, representing the transition stage from vitrinite to fusinite, also has the fibrous, cellular structure but a lower reflectance than fusinite. In thin section analysis it may be classed with translucent attritus, opaque attritus or fusain depending on its relative translucency and size.

Petrographic analysis by reflected light may be conducted on blocks similar to those cut out of a column sample for thin-section analysis. They must, of course, be well polished on one face perpendicular to the bedding. However, the reflected light method is especially suited to analysis of broken or granular coal. For this purpose, the received sample of broken coal is reduced in amount and particle size by successive breakage and riffling steps until two equivalent 10-gram samples passing a No. 20 sieve are obtained. From each of these, 4½ gram portions are taken with a spatula for incorporation into a briquet using a thermoplastic binder. Several thermoplastics having a low melting point and hardness similar to that of coal have proved satisfactory. A 5-gram quantity of the plastic is melted and the coal sample stirred in until well dispersed. The hot mixture is poured into a mold of aluminum foil shaped into a 1-inch cube. When the mixture has set at room temperature the foil is stripped away. One face of the resulting briquet is then ground and polished by a technique similar to that used in preparing thin sections. However, more care is taken in the final polishing on the cloth lap so that a well-polished surface nearly free of scratches is obtained. The briquet is then mounted and leveled on a microscope slide by being pressed into modeling clay with a hand press.

Petrographic analysis in reflected light is made using a metallographic binocular microscope. A 25X oil immersion objective is used together with pairs of 10X or 15X oculars to give magnifications of 250X or 375X. Glycerin or cedar oil may be used as an immersion medium, the former for convenience in removal with water and to obviate minor repolishing for later use, the latter for better optical conditions or for photomicrography. The same Whipple disk as used in thin section analysis is also used in this technique, and the procedure of estimation of proportions of components is similar. Of course the components determined in the two methods are different and only partly analogous, as described previously. Five equally-spaced traverses are usually made on each of the two equivalent briquets, and the final results are averages of ten traverses.

Because briquets of a common coal sample usually contain a heterogeneous assortment of components, the precision of the above determination is not much better than 5 percent. This could be improved, if desired, by making more traverses. The apparent greater precision of the thin section method mentioned earlier (2 percent) was the result of twenty traverses over ten thin sections. A more detailed study of the two methods would be necessary for a better comparison.

CLASSIFICATION OF COALS

Because of the worldwide occurrence of coal deposits, the numerous varieties which are available, and the diversity of uses, efforts have been made in this country and abroad to develop systems for classifying coal according to characteristic properties

TABLE 7.—*Classification of coals by rank*[1]

Class	Group	Fixed carbon limits, per cent (dry, mineral-matter-free basis)		Volatile matter limits, percent (dry, mineral-matter-free basis)		Calorific value limits, Btu per pound (moist,[2] mineral-matter-free basis)		Agglomerating character
		Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	
I. Anthracitic	1. Metaanthracite	98	......	......	2	......	......	......
	2. Anthracite	92	98	2	8	......	......	......
	3. Semianthracite	86	92	8	14	......	......	Nonagglomerating[3]
II. Bituminous	1. Low-volatile bituminous coal	78	86	14	22	......	......	Commonly agglomerating[5]
	2. Medium-volatile bituminous coal	69	78	22	31	......	......	
	3. High-volatile *A* bituminous coal	......	69	31	......	[4] 14,000	......	
	4. High-volatile *B* bituminous coal	......	......	......	......	[4] 13,000	14,000	
	5. High-volatile *C* bituminous coal	......	......	......	......	11,500 10,500	13,000 11,500	 Agglomerating
III. Subbituminous	1. Subbituminous *A* coal	......	......	......	......	10,500	11,500	Nonagglomerating
	2. Subbituminous *B* coal	......	......	......	......	9,500	10,500	......
	3. Subbituminous *C* coal	......	......	......	......	8,300	9,500	......
IV. Lignitic	1. Lignite *A*	......	......	......	......	6,300	8,300	......
	2. Lignite *B*	......	......	......	......	......	6,300	......

[1] This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties, and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound.

[2] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[3] If agglomerating, classify in low-volatile group of the bituminous class.

[4] Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

[5] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high-volatile *C* bituminous group.

determined by laboratory methods.

As can be expected, many national classification systems have been developed in accordance with characteristics of domestic coals without reference to coals of other countries. Terms for describing similar or identical coals differed in each nation. Because of increased trade among various nations after World War II, efforts were made to develop an international system for classifying coal to eliminate confusion in international trade and to facilitate exchange of technical and scientific information on problems of coal research and utilization.

Information on the American and International systems of coal classification is presented in this section of the publication.

American System

The Bureau of Mines cooperated in the development of a system for classifying American coals, which later became the ASTM (American Society for Testing and Materials) system for classification of coals by rank according to their degree of metamorphism or progressive alteration in the natural coalification series from lignite to anthracite. Recently, the system has been revised and published as Tentative Specification (ASTM Designation D 388–64T) for Classification of Coals by Rank.[46]

With the permission of ASTM, the classification system is shown in table 7. It is based on the parameters of fixed carbon and calorific value (expressed in Btu per pound) calculated to the mineral-matter-free basis. The higher-rank coals are classified according to fixed carbon on the dry basis; the lower-rank coals according to calorific value on the moist basis. Agglomerating character is used to differentiate between certain adjacent groups.

Because the mineral matter in coal cannot be analytically determined, the following method of calculating to the mineral-matter-free basis from the determined ash content is used: Parr formulas:[47]

Dry, Mm-free FC =

$$\frac{\text{Btu} - 0.15\text{S}}{100 - (\text{M} + 1.08\text{A} + 0.55\text{S})} \times 100 \qquad (1)$$

Dry, Mm-free VM =

$$100 - \text{Dry, Mm-free FC} \qquad (2)$$

Moist, Mm-free Btu =

$$\frac{\text{Btu} - 50\text{S}}{100 - (1.08\text{A}) + 0.55\text{S}} \qquad (3)$$

where:

Mm = mineral matter,

Btu = British thermal units per pound (calorific value),

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[46] American Society for Testing and Materials. Tentative Specification for Classification of Coals by Rank. D 388–64T in 1965 Book of ASTM Standards: Part 19, Gaseous Fuels: Coal and Coke. Philadelphia, Pa., 1965, pp. 73–78.

[47] Parr, S. W. The Classification of Coal. Eng. Exp. Sta., Univ. Illinois, Bull. 180, 1928, 62 pp.

FC = percentage of fixed carbon,
VM = percentage of volatile matter,
M = percentage of moisture,
A = percentage of ash, and
S = percentage of sulfur.

"Moist" refers to coal containing its natural inherent or bed moisture, but not including water adhering to the surface of the coal.

If it is impossible to sample the coal without including visible surface moisture, or if there may be other reason to question the accuracy of inherent moisture content determinable from the sample, and the coal is likely to be classified on the "moist" basis, the sample shall include the following statement in the description: "Moisture questionable." Samples so marked shall not be used for classification on a moist basis unless the equilibrium moisture of the particular coal is determined according to "Method of Test for Equilibrium Moisture of Coal at 96–97 Percent Relative Humidity and 30° C as described in this publication.

International Systems

Whereas the ASTM system provides for classification of all ranks of coal, international classification is based on two systems, one for the hard coals and the other mainly for brown coals and lignites. The borderline between the two international systems is placed at 10,260 Btu per pound (5,700 kcal per kilogram) moist and ash-free.

International Classification of Hard Coals by Type

As a result of an exchange of information on existing national systems of coal classification and extensive laboratory work by a working group in which the Bureau of Mines participated, a paper was published by the Economic Commission for Europe as a United Nations document in December 1956.[48]

The Bureau has published information on this classification system and its application to American coals.[49] The following discussion has been prepared from this publication.

Figure 45 shows the international classification of hard coals by type. The term "hard coal" is defined as coal with a gross calorific value of more than 10,260 Btu per pound (5700 kcal per kg) on the moist ash-free basis. Coals classified in the American Society for Testing and Materials system as anthracite, bituminous, and higher rank subbituminous are included in the international system according to this definition. While names are used in the ASTM system, a numbering system is used in the international classification. Moreover, in the ASTM system, coals are classified on the mineral-matter-free basis and in the international system on the ash-free basis.

In the international system the hard coals are separated into nine classes according to their volatile-matter content, calculated on a dry, ash-free basis. The first five classes include coals with a volatile-matter content to 33 percent, while the gross calorific value on the moist, ash-free basis is used to separate coals containing more than 33 percent volatile matter into classes six to nine.

The nine classes of coal, based on volatile-matter content and calorific value are divided into groups (0–3) according to their caking properties when heated rapidly. Either of two methods—the free-swelling test or Roga test—may be used to measure caking properties.

The coal groups are further divided into subgroups (0–5) according to coking properties, as measured by tests in which the coal is heated slowly. The coking properties are measured either by maximum dilatation, using the Audibert-Arnu method or by Gray-King coke type.

The numerical values obtained from the respective tests are combined into a three-figure code number to arrive at the proper classification of the coal. The first figure indicates the class of coal, the second figure, the group, and the third figure, the subgroup.

In figure 46 are compared the class numbers and group boundaries of the international system with those of the ASTM classification. As the figure shows, the group boundaries in the two schemes are quite similar; thus class numbers in the international system are nearly equivalent to group names in the ASTM Classification.

International Classification of Brown Coals and Lignites

According to a proposal of the Classification Working Party with which the Bureau of Mines cooperated by having representatives at meetings and by performing laboratory research, coals with less than 10,260 Btu per pound (5,700 kcal per kg), moist, and ash

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[48] United Nations' Economic Commission for Europe. International Classification of Hard Coals by Type. E/ECE/247, E/ECE/COAL/110. U.N. Pub. Sales No. 1956 II E. 4, 1956, 52 pp.

[49] Ode, W. H., and W. H. Frederic. The International Systems of Hard-Coal Classification and Their Applications to American Coals. BuMines Rept. of Inv. 5435, 1958, 19 pp.

GROUPS (determined by caking properties)			CODE NUMBERS										SUBGROUPS (determined by coking properties)		
GROUP NUMBER	ALTERNATIVE GROUP PARAMETERS		The first figure of the code number indicates the class of the coal, determined by volatile-matter content up to 33 pct volatile matter and by calorific parameter above 33 pct volatile matter The second figure indicates the group of coal, determined by caking properties. The third figure indicates the subgroup, determined by coking properties.										SUBGROUP NUMBER	ALTERNATIVE SUBGROUP PARAMETERS	
	Free-swelling index (crucible-swelling number)	Roga index												Dilatometer	Gray-King
3	>4	>45	▨	▨	▨	▨	435	535	635	▨	▨	▨	5	> 140	$> G_8$
			▨	▨	▨	334	434	534	634	▨	▨	▨	4	>50-140	G_5-G_8
			▨	▨	▨	333	433	533	633	733	▨	▨	3	>0-50	G_1-G_4
			▨	▨	▨	332 a 332 b	432	532	632	732	832	▨	2	≤0	E-G
2	$2\frac{1}{2}$-4	>20-45	▨	▨	▨	323	423	523	623	723	823	▨	3	>0-50	G_1-G_4
			▨	▨	▨	322	422	522	622	722	822	▨	2	≤0	E-G
			▨	▨	▨	321	421	521	621	721	821	▨	1	Contraction only	B-D
1	1-2	>5-20	▨	▨	212	312	412	512	612	712	812	▨	2	≤0	E-G
			▨	▨	211	311	411	511	611	711	811	▨	1	Contraction only	B-D
0	0-$\frac{1}{2}$	0-5	▨	100 A' B	200	300	400	500	600	700	800	900	0	Nonsoftening	A
CLASS NUMBER →			0	1	2	3	4	5	6	7	8	9	As an indication, the following classes have an approximate volatile-matter content of: Class 6 33-41 pct volatile matter 7 33-44 pct do 8 35-50 pct do 9 42-50 pct do		
CLASS PARAMETERS	Volatile matter (dry, ash-free) →		0-3	>3-10 >3-6.5 >6.5-10	>10-14	>14-20	>20-28	>28-33	>33	>33	>33	>33			
	Calorific parameter[1] →		—	—	—	—	—	—	>13,950	>12,960-13,950	>10,980-12,960	>10,260-10,980			

CLASSES

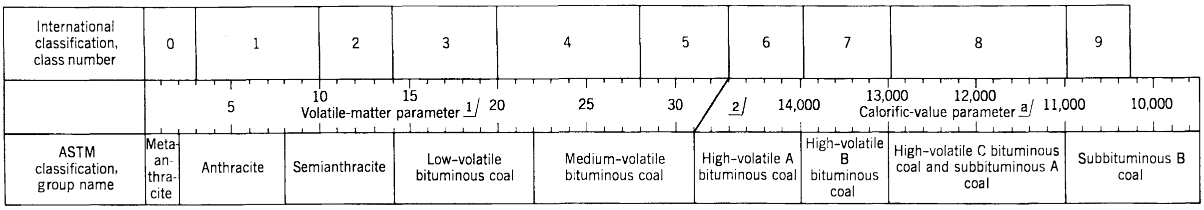
(Determined by volatile matter up to 33 pct volatile matter and by calorific parameter above 33 pct volatile matter.)

Note: (1) Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink method (or any other appropriate means). The specific gravity selected for flotation should allow a maximum yield of coal with 5 to 10 percent of ash.

(2) 332a . . . >14-16 pct volatile matter
332b . . . >16-20 pct volatile matter

[1] Gross calorific value on moist, ash-free basis (30° C, 96 pct relative humidity) Btu/lb

FIGURE 45.—International Classification of Hard Coals by Type.



1/ Parameters in international system are on ash-free basis; in ASTM system, they are on mineral-matter-free basis.

2/ No upper limit of calorific value for class 6 and high-volatile A bituminous coals.

FIGURE 46.—Comparison of Class Numbers and Boundary Lines of International System With Group Names and Boundary Lines of ASTM System.

free should be classified as brown coals and lignites.[50]

The parameters chosen for classifying the lower rank coals were total moisture and yield of low-temperature tar. As a correlation exists between the total moisture and calorific values of the lower rank coals, the moisture parameter indicates the value of the coal as a fuel; the yield of tar indicates the value of the coal for chemical processing.

Low-rank coal refers to the relative position in the scale of rank classification, that is, according to the degree of metamorphism, or progressive alteration, in the natural series from lignitic coals to anthracite. It does not refer to the quality or grade of coal.

The Bureau has interpreted the international system and discussed its application to American low-rank coals.[51] The following information has been adapted from this publication.

The coals are first classified according to their total moisture content as ash-free coals. Total moisture is that contained in freshly mined coal. The class numbers and corresponding range of moisture values are:

Class No.:	*Total moisture ash-free, percent*
10	20 and less
11	>20–30
12	>30–40
13	>40–50
14	>50–60
15	>60–70

The coals divided into classes according to total moisture are subdivided into groups by yield of low-temperature tar, calculated dry and ash free.

Group numbers with corresponding range of tar yields are:

Group No.:	*Tar dry, ash-free, percent*
00	10 and less
10	>10–15
20	>15–20
30	>20–25
40	>25

The classification of brown coals and lignite as shown in table 8 is indicated by a four-figure code number. The first two figures identify the class and the last two, the group.

Data on total moisture and tar yield of 73 American coals ranging from subbituminous B coals to lignite indicated that these coals can be classified by the international system.

TABLE 8.—*International classification of coals with gross calorific value below 10,260 Btu/lb (5,700 kcal/kg (Statistical Grouping)*

Group No.	Group parameter: Tar yield (dry, ash-free), percent	Class parameter: Total moisture, ash-free, percent					
		0–20, class 10	>20–30, class 11	>30–40, class 12	>40–50, class 13	>50–60, class 14	>60–70, class 15
40	>25	1040	1140	1240	1340	1440	1540
30	>20–25	1030	1130	1230	1330	1430	1530
20	>15–20	1020	1120	1220	1320	1420	1520
10	>10–15	1010	1110	1210	1310	1410	1510
00	<10–10	1000	1100	1200	1300	1400	1500

[1] Moist, ash-free basis (30°C/96 percent relative humidity).

[2] Total moisture content refers to freshly mined coal. For internal purposes, coals with a gross calorific value over 5,700 kcal/kg (maf), considered in the country of origin as brown coals but classified as hard coals for international purposes, may be classified under this system, to ascertain, in particular, their suitability for processing. When total moisture content is over 30 percent, gross calorific value is always below 5,700 kcal/kg.

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[50] United Nations' Economic Commission for Europe. Mining and Upgrading of Brown Coal in Europe—Developments and Prospects. E/ECE/297, E/ECE/Coal/1248. U.N. Pub. Sales No. 1957. II E. Mim. 20, October 1957; Internal Documents Service, Columbia Univ. Press, New York, 1957.

[51] Ode, W. H., and F. H. Gibson. International System for Classifying Brown Coals and Lignites and Its Application To American Coals. BuMines Rept. of Inv. 5695, 1960, 20 pp.

METHODS OF ANALYZING AND TESTING COKE

PREPARATION OF LABORATORY SAMPLE

Most coke samples analyzed in the Bureau of Mines laboratory are prepared without air-drying, but, if the coke sample is wet, it is air-dried in the same manner as a coal sample (See "Preparation of Laboratory Sample With Preliminary Air-Drying.").

If the dry (or air-dried) sample is larger than ¼ inch, it is crushed mechanically with a jaw crusher or by hand on a chilled iron or hard-steel plate by impact of a hard bar or sledge, avoiding all rubbing action; otherwise, the ash content will be increased materially by the addition of iron from the sampling apparatus, even though hardened iron or steel is used. Crushing is continued until all the sample is finer than ¼ inch; the sample is then mixed and reduced on a large riffle sampler to approximately 5 pounds. The 5-pound sample is crushed further by means of a hard-steel roll crusher to pass a No. 20 sieve, mixed, and reduced on a ¼-inch riffle sampler (fig. 2) to 200 grams. The 200-gram portion is put in the porcelain jar (1 gallon capacity) of a ball mill and ground to pass a No. 60 sieve. The jar is slightly more than half-full of well-rounded flint pebbles, which are about ¾ inch in diameter, and it makes 45 to 50 revolutions per minute. The wear of the pebbles and the interior of the mill do not increase the ash content appreciably.

Coke requires ½ to 1 hour of grinding to be pulverized to pass a No. 60 sieve. When pulverization is completed the contents of the jar are poured on a ½-inch square-mesh screen, the sample is separated from the pebbles by shaking the screen over a rubber mixing cloth, and the pebbles and the inside of the jar are brushed carefully to remove any adhering pulverized coke. The sample is then passed quickly through a No. 60 sieve. Some coarse particles may remain on the sieve, and these are reduced in size to pass a No. 60 sieve by impact in a hard-steel, diamond mortar. The sample is mixed quickly and then passed through a small riffle sampler to obtain a 50-gram sample, which is put in a rubber-stoppered, wide-mouthed, 4-ounce bottle and constitutes the laboratory sample. To minimize change in the moisture, the mixing and reducing of the pulverized sample after removal from the ball mill are done with utmost dispatch. The total time elapsing from the opening of the porcelain jar to the stoppering of the laboratory sample bottle does not exceed 3 minutes.

Before portions for the various analytical determinations are weighed, the sample is mixed thoroughly. The bottle containing the sample is placed in the mixing wheel shown in figure 3 and rotated for 20 minutes. The wheel is 30 inches in diameter and revolves 25 times in a minute. The sample bottles are held by spring clips on the periphery of the wheel at an angle of 45° with the axis. The bottles should not be more than three-fourths full, and the speed of rotation should be slow enough to prevent centrifugal action from hindering the thorough mixing of the powdered coal.

METHODS OF ANALYSIS

The methods of analysis for coke are identical to the tests for coal except for the nitrogen determination.

In the nitrogen determination the only difference is that approximately 0.1 gram of chromic oxide (CrO_3) is added to the mixture of coke, K_2SO_4, H_2SO_4, and mercury before digesting. The total digestion time, including the two hours after the solution has reached the gray-colored stage, is approximately eight hours.

METHODS OF PHYSICAL TESTS

The true specific gravity and apparent specific gravity of coke are determined according to "Method of Test for Determination of True Specific Gravity of Coal and Coke" and "Method of Test for Determination of Apparent Specific Gravity of Coal and Coke" as described in a previous section of this publication.

Method of Test for Determination of Apparent Specific Gravity of Coke Using a Large Sample

This method of test is intended for determining the apparent specific gravity of coke on a large sample weighing approximately 25 pounds according to ASTM Designation D 167–24 Standard Method of Test for Volume of Cell Space of Lump Coke.[52] This method has the advantage that the large sample (about 25 pounds) is more representative than much smaller samples.

Apparatus

The apparatus consists of a suitable container, such as a wash boiler, not smaller than approximately 13 inches high, 22 inches long, and 11 inches wide, or its equivalent in size, provided with a spout consisting of a short ½-inch nipple extending horizontally from the container to about 2½ inches below the top. A wire cage for holding the sample is made of about ½-inch square-mesh screen-wire cloth; it is provided with a cover of the same material and with two long handles. The wire cage is made so that it fits inside the container below the spout.

Procedure

Select about 25 pounds of coke representative in size, shape, and general appearance of the coke under consideration. Dry this sample to constant weight at a temperature of 105° to 200° C, allow to cool, and weigh after any adhering dust has been shaken and brushed off. Put a cork in the spout of the container, and place the container on a level and rigid base or floor. Put the empty cage inside the container, and add water at room temperature until the water level is above the spout. After the water has come to rest, remove the cork from the spout, and permit the excess water to drain out for 1 minute after the overflow stream starts to discharge drop by drop. Replace the cork in the spout, and remove the cage from the water, care being taken to shake all adhering water back into the container. Place the weighed and dried coke sample in the cage, and, after the cover is fastened, lower the cage containing the coke into the water. If the container is not large enough to retain the displaced water, draw some of the water into a weighed bucket by removing the cork from the spout while the coke is being lowered.

Permit the cage with the coke to remain in the water for 15 minutes; shake it occasionally to detach any air bubbles adhering to the surface of the coke, care being taken not to disturb the position of the container. Keep the coke completely submerged at all times. At the end of the 15-minute period, after the water has come to rest, remove the cork, and allow the displaced water to drain into a weighed bucket for 1 minute after the overflow stream starts to discharge drop by drop. Replace the cork, remove at once the cage containing the coke from the water, and let it drain for 1 minute. Finally, remove the wet coke from the cage and weigh; determine the weight of the displaced water, which has been caught in the bucket. Calculate the apparent specific gravity as follows:

$$\text{Apparent specific gravity} = \frac{A}{B + (C - A)},$$

in which

A = weight of dry coke,
B = weight of water displaced by wet coke, and
C = weight of wet coke.

Method of Drop Shatter Test for Coke

This method of test affords a measure of the relative resistance of coke to breakage when subjected to handling and during transit to the consumer.

Apparatus

The shatter-test machine shown in figure 47 consists of a box 18 inches wide, 28 inches long, and approximately 15 inches deep, supported above a rigidly mounted cast-iron or steel plate not less than ½ inch thick, 38 inches wide, and 48 inches long. The inside of the bottom of the box is 6 feet above the plate. The bottom of the box consists of two doors hinged lengthwise and latched so that they swing open freely and do not impede the fall of the coke. Boards about 8 inches high are placed around the plate so that no coke may be lost. To prevent breakage of coke while the sample is being put in the box, pulleys and a counterweight are provided to permit lowering of the box to a convenient level.

Procedure

Place about 50 pounds of the coke pieces, none of which will in any position pass a

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[52] American Society for Testing and Materials. Standard Method of Test for Volume of Cell Space of Lump Coal. D 167–24 in 1965 Book of ASTM Standards: Part 19, Gaseous Fuels: Coal and Coke. Philadelphia, Pa., 1965, pp. 8–11.

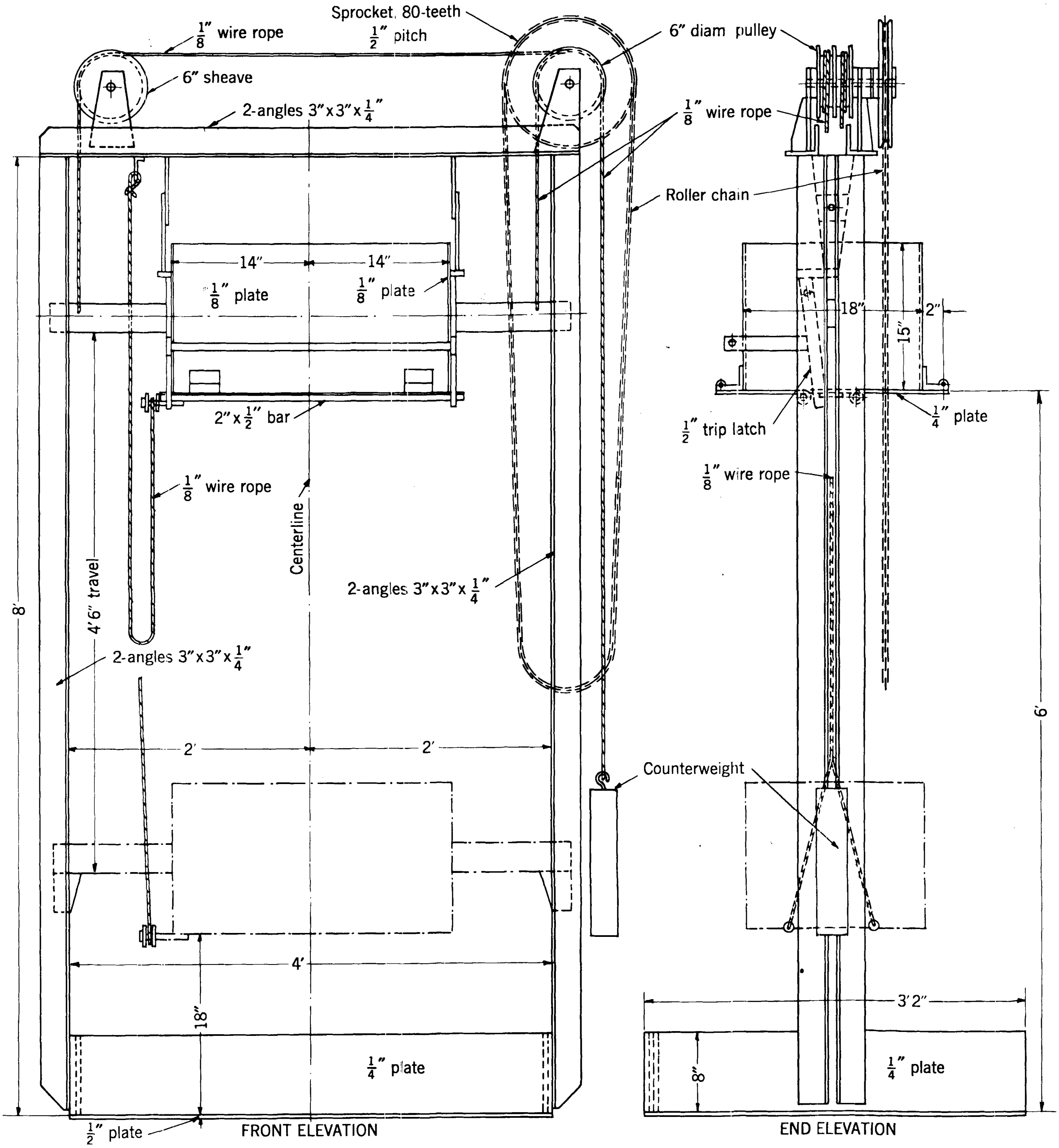

FIGURE 47.—Shatter-Test Machine.

2-inch square-mesh sieve, in the box of the shatter-test machine, level the coke, and raise the box to such a height that the inside of its bottom is 6 feet above the iron or steel plate. Release the hinged bottom to allow the coke to fall on the plate. Drop the coke four times on the plate, and return all small pieces each time to the box with the large coke. To prevent possible breakage of the coke by handling, lower the box to a convenient height each time the coke is being transferred to it. After the fourth drop, screen the coke successively through square-mesh sieves with 2-inch, 1½-inch, 1-inch, and ½-inch openings. Circular sieves 2 feet in diameter are convenient to use. In sieving take care to prevent breakage of the coke pieces. Sieve the coke in such increments to allow all pieces to be in direct contact with the sieve openings, and shake the sieve gently to avoid breakage. Weigh separately the pieces remaining on each sieve and those passing the ½-inch sieve. If the sum of these weights shows a loss of more than 1 percent, reject the test and make another one. Since the average probable error of a single shatter-test determination is approximately 2 percent, it is advisable to make several tests and report the average result.

Report

The results of the test are reported as follows:

Passing	Retained on	Percent
	2-inch sieve	
2-inch sieve	1½-inch sieve	
1½-inch sieve	1-inch sieve	
1-inch sieve	½-inch sieve	
½-inch sieve		

Method of Tumbler Test for Coke

This test is a relative measure of the resistance of the coke to degradation by abrasion. The results obtained, however, are also influenced by the effect of impact.

A somewhat similar test is the Micum drum method used principally in some European countries.[53]

Apparatus

The tumbler machine consists of a motor-driven circular steel drum 36 inches in inside diameter and 18 inches in inside length, made of steel plate at least ¼ inch in thickness. Two equally spaced 2- by 2- by ¼-inch angles are riveted longitudinally inside the drum. These angles are riveted to the shell so that the attached legs point away from the direction of rotation and thus give a clear unobstructed shelf for lifting the coke. To provide for rotating, the drum is mounted on a horizontal steel shaft 1½ inches in diameter passing through the drum. An opening is provided in the shell for introducing and removing the sample. During the test the steel cover is fastened rigidly to the shell and is constructed to fit into the shell and give a smooth inner surface.

SIEVES.—For sizing the sample for the test square-mesh sieves having 2-inch and 3-inch openings between the wires are used. For sieving the coke after the tumbler test square-mesh sieves having 1.00-inch and 0.250-inch openings between the wires are used. Sieves of heavy double-crimped wire with circular frames about 24 inches in diameter are suitable.

BALANCE.—A balance for weighing the coke, sensitive to 1 gram, is satisfactory.

Procedure

Size the coke before testing by sieving on 3-inch and 2-inch square-mesh sieves, without crushing the larger pieces, to obtain a sample that will pass the 3-inch and be retained on the 2-inch sieve. In sizing the sample upend each piece on the sieve by hand to determine whether in any position it passes the sieve. If a large proportion of the pieces is larger than 3 inches, break out representative smaller pieces of the desired size. Accomplish this without shattering the coke pieces with a heavy screw driver or similar tool by prying apart at fracture cracks.

Dry the sized coke sample at 104° to 200° C, weigh accurately approximately 22 pounds (10 kg) of the dried coke and place in the drum of the tumbler machine. Fasten the cover rigidly and rotate the drum at 24 ± 1 rpm for a total of 1,400 revolutions. Remove all of the coke from the drum and sieve on the one-inch and 0.250-inch sieves. Weigh separately pieces retained on each sieve and those passing the smallest sieve. Make the weighings to the nearest 1 gram.

Report

Report the sieve analysis after the tumbler test in cumulative percentages to the nearest 0.1 percent as follows:

	Percent cumulative	
Total retained on:		
1.00-inch sieve		(stability factor)
0.250-inch sieve		(hardness factor)

The coke industry has generally adopted the practice of designating the percentage of coke retained on the one-inch sieve as the stability factor and the percentage retained on the 0.250-inch sieve as the hardness factor.

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[53] Walters, J. G., G. W. Birge, and D. E. Wolfson. Correlation of ASTM and Micum Coke Test Methods. BuMines Rept. of Inv. 6482, 1964, 48 pp.

METHODS OF ANALYZING AND TESTING ASH AND SLAG

METHOD FOR DETERMINATION OF FUSIBILITY OF COAL ASH

The method that the Bureau of Mines uses for making fusibility tests is the result of considerable experimental work[54] on the nature of the fusion of coal ash and the influence of various oxidizing, reducing, and neutral atmospheres on the softening temperature of ash molded in the form of Seger cones. On a nitrogen-free basis the total amount of reducing gases is maintained between the limits of 20 percent and 80 percent by volume of the sum of the reducing and the oxidizing gases. Hydrogen, hydrocarbons, and carbon monoxide are considered as reducing gases; and oxygen, carbon dioxide, and water vapor are considered as oxidizing gases. Nitrogen is inert. The atmosphere in which the ash is heated is controlled by burning an excess of gas; a reducing atmosphere is thus obtained by which the iron in the ash is reduced mainly to the ferrous state, giving the lowest temperature at which clinkering may result.

This change in the iron is especially important in testing coals that contain a relatively large proportion of iron in the form of pyrite. Higher softening temperatures may be expected in tests employing oxidizing atmospheres which oxidize the iron mainly to ferric oxide or in tests employing strongly reducing atmospheres which reduce the iron largely to the metallic state. Under both conditions a more refractory slag is formed than results if the atmosphere is such as to reduce the iron in the ash to ferrous oxide, which, with the silica present, forms readily fusible silicates. Ferric oxide combines with silica to form compounds that require high temperature for fusion; on the other hand, if the iron is reduced to the metallic state, one of the most active fluxing constituents is removed from the system, and high fusing points result.

Analyses of clinkers from boiler furnaces indicated that fuel-bed conditions favored the formation of clinkers in which the iron was chiefly in the ferrous state. The values obtained in the laboratory tests are in this respect comparable to such conditions, and the tests give the lowest temperatures at which the intimately mixed ash softens and forms clinker.

Furnace

Owing to the large number of samples tested by the Bureau, the coal-ash fusion furnaces of the Denver Fire Clay Company are used. The burners of these furnaces are arranged on a tangent near the base of the furnace and thus give a rotary flame that completely surrounds the crucible in which the ash cones are placed. This whirling flame heats the crucible uniformly, and when an excess of gas over air is used, a reducing atmosphere is maintained within the crucible, giving the lowest point at which the ash fuses. The furnace is supplied with natural gas; compressed air is furnished by a Maxon No. 1 Premix burner unit. The Premix burner unit is relatively small, so it can be mounted alongside the furnace. Temperatures up to 1,600° C are attained with the coal-ash fusion furnace. To conduct the hot gases from the room, counterbalanced sheet-iron canopies, connected with telescopic 8-inch flues to an exhaust system, are hung over the furnaces.

Figure 48 shows the interior of the coal-ash fusion furnace arranged for making a test. The corundite crucible is about 3 inches in inside diameter and about 4½ inches high

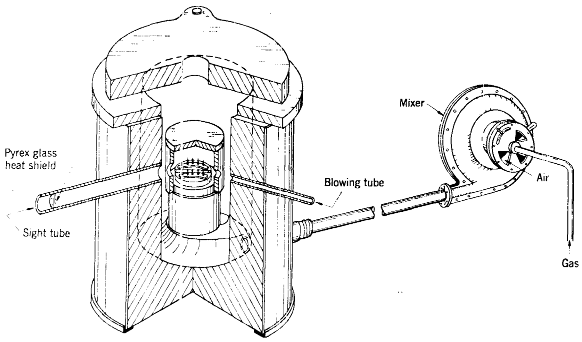

FIGURE 48.—Furnace for Determining Fusibility of Coal Ash.

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[54] Fieldner, A. C., A. E. Hall, and A. L. Feild. The Fusibility of Coal Ash and the Determination of the Softening Temperature. BuMines Bull. 129, 1918, 146 pp.

outside with a wall about ½ inch thick. The crucible has a cover and has two holes in the side, an observation hole 2 inches in diameter and a thermocouple hole 1 inch in diameter, 90° to the right of the observation hole. The bottoms of the two holes are in the same horizontal plane. The crucible is positioned on a corundite support so that the two holes in the crucible are in line with the corresponding holes in the furnace wall. The ash cones mounted on a refractory base are on a corundite disk so that they are visible through the observation hole of the crucible and the furnace wall.

A fused silica or alundum tube, 1⅞ inches in external diameter and 6 to 7 inches long, is placed in the 2-inch observation hole of the furnace; its inner end is flush with the inside furnace wall, and the other end projects from the furnace. A brass sleeve carrying a thin clear glass window is slipped over the outer end of the observation tube to prevent the escape of burning gas, which would hinder convenient observation of the cones. When observations at high temperature are made, the cones are viewed through a piece of colored glass, such as Corning No. 6 shade, Noviweld.

At furnace temperatures above 1,000° C, observation of the cones is very difficult. An open blowing tube of refractory porcelain about ¼ inch in inside diameter is inserted in the thermocouple hole, the inner end being flush with the inside of the furnace wall. This blowing tube is connected to a compressed-air line with rubber tubing. By means of a gas valve, air is let into the tube at the time of observation, momentarily cooling the ash cones and rendering them visible.

Temperature Measurement

Temperature measurements are made with a thermocouple of platinum and platinum-rhodium, protected from the furnace gases by a glazed-porcelain tube, and a high-resistance millivoltmeter or with an optical pyrometer of the disappearing-filament type, which has been calibrated to be accurate within 10° C up to 1,400° C, and within 15° C from 1,400 to 1,600° C.[55] If a thermocouple is used, the hot junction is placed in the immediate vicinity of the cones. The optical pyrometer is now preferred, because it obviates mounting the protection tube of the thermocouple in the furnace and is usable for temperatures above 1,500° C. As the optical pyrometer is sighted through the glass window of the observation tube, the following corrections are added to the observed temperature to correct for the loss of light at the glass window: 800° C, add 5°; 1,000° C, add 8°; 1,200° C, add 10°; 1,400° C, add 13°; and 1,600° C, add 16°. The pyrometer equipment is checked frequently by mounting pieces of pure gold and nickel in the same manner as the cones. With a strongly reducing atmosphere, a melting point of 1,452° C is obtained for nickel and of 1,063° C for gold. From time to time, the pyrometer equipment is standardized through the temperature range for which it is used.

Preparation of Coal Ash

Spread out approximately 50 to 100 grams of coal, ground to pass a No. 60 sieve, on a 5-inch fire-clay roasting dish, and completely convert it to ash in a muffle furnace at 800° to 900° C. Transfer 5 to 10 grams of this ash to an agate mortar and grind to pass a No. 200 sieve. A mechanical agate-mortar grinder saves time where many determinations are made. Place the finely ground ash in a silica or porcelain capsule about ⅝ inch deep and 1¾ inches in diameter and ignite for 2 hours in a current of oxygen at 800° to 850° C. The purpose of this ignition is to insure complete and uniform oxidation of the ash.

Preparation of Cones

Moisten the ignited ash with a 10-percent dextrin solution containing 0.1 percent salicylic acid as a preservative and work the ash into a plastic mass with a spatula. Mold the plastic material into small triangular pyramids ¾ inch high and ¼ inch wide at each side of the base. Form the pyramids by firmly pressing the plastic material with a steel spatula into a stainless steel mold of the dimensions given above, the mold being similar to that shown in figure 49. Strike off the surface smooth and remove the cone from the mold by applying a small knife blade at the base. Mount the cones when dry in a refractory base composed of a mixture of equal parts of kaolin and calcined alumina. Moisten the base mixture to make it workable, and spread a part of it on a sheet-iron plate. Then mount the cone in a vertical position in a small hole made in the base and put a little of the base material into the hole around the bottom of the cone to fill the crevices and to make the cone stand firmly. Usually five cones are mounted on one base in the manner shown in figure 50, *A*. Dry

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[55] For detailed information concerning the use of pyrometers see Pyrometric Practice. NBS Technol. Paper 170, 1921, 326 pp.

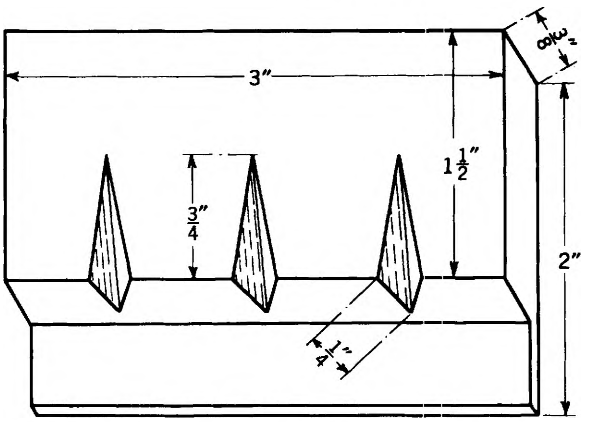

FIGURE 49.—Stainless Steel Cone Mold for Making Ash Cones.

the mounted cones in the laboratory by allowing them to stand overnight. Drying is hastened by placing the cones in a warm place.

Method of Heating

Put two test pieces in the muffle crucible in the position shown in figure 48, place the loosely fitting cover on the crucible, and ignite the gas. Let the gas burn about 10 minutes to heat the furnace parts before the large cover plate of the furnace is replaced; otherwise, the flame blows out. After the cover plate of the furnace has been put in position, increase the flow of gas and air enough to cause combustion just above the tuyeres and yet maintain a yellowish flame at least 6 inches above the opening in the cover plate of the furnace. While such a flame is maintained, gradually increase the temperature by a suitable adjustment of gas and air to 800° C; then reduce the rate of heat increase to approximately 10° C per minute. Maintain this rate until the end of the test.

It is important to maintain the 6-inch reducing flames at the furnace vent throughout the test, if possible, and at all events up to a temperature of 1,450° C. Temperatures above 1,450° C require larger proportions of air to gas; however, a strongly reducing atmosphere is not so essential at the higher temperatures, because refractory ashes, owing to their low iron oxide content, are only slightly affected by oxidizing or reducing atmospheres.

Observations

The initial deformation temperature is the temperature at which the apex of the cone rounds or melts, as shown in cone 1 of figure 50, *B*. Such bending must not be confused with a shrinking or warping of the cone.

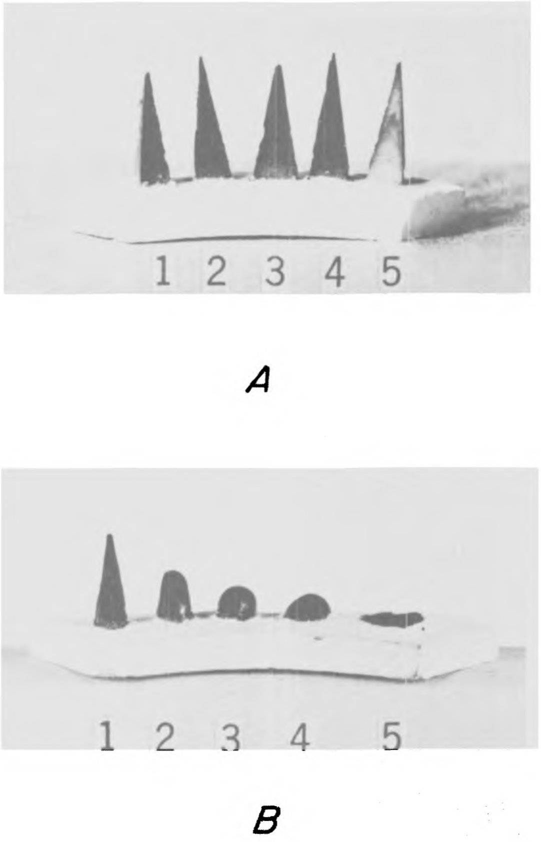

FIGURE 50.—Ash Cones. *A*, Cones mounted on base. *B*, Typical form of fused cones.

The softening temperature is defined as the temperature at which the cone has fused down to a spherical lump, as shown in cone 3 of figure 50, *B*. Cone 2 has almost reached the softening temperature; cone 4 has passed the softening temperature.

The fluid temperature is the temperature at which the cone has spread over the base in a flat layer, as represented by cone 5 of figure 50, *B*.

Report and Precision

For the convenience of fuel engineers the results of the test are reported in degrees Fahrenheit.

Permissible differences for the softening temperature of coal or coke ash are 30° C for duplicate determinations made in the same laboratory and 50° C for determinations made on duplicate samples in different laboratories.

METHODS FOR ANALYZING COAL AND COKE ASH

Introduction

Methods of analyzing coal and coke ash for major constituents include: The classical wet-chemical procedures based on recognized methods for analyzing silicate rocks,[56] and the more rapid physicochemical methods being applied in ash analysis.

The classical methods of ash analysis were described in the 1938 edition of Bureau of Mines Technical Paper 8, and later in Bureau of Mines Bulletin 492. Most of these methods have continued in use, and those now employed for occasional analyses and for checking results by other procedures are described in the following sections.

In 1957 the gravimetric methods of determing Na_2O and K_2O were replaced by a flame spectrophotometric method. Other developments in more rapid techniques of determining SiO_2, Al_2O_3, Fe_5O_3, TiO_2, P_2O_5, and the EDTA titration of CaO and MgO found increasing application. Finally, the newer methods were assembled in a coordinated procedure for further trial.[57] These methods were based mainly on the work of Shapiro and Brannock,[58] and Archer, Flint, and Jordan.[59] A recent modification shortened the colorimetric method for Fe_2O_3 by using sodium gluconate to minimize interference by phosphorus. Although future developments may change some of the methods, those now available have many applications and give results with almost the same accuracy as the classical procedures. The rapid methods currently used are described in a separate section.

Preparation of Ash Sample

Spread 100 to 200 grams of coal or coke passing a No. 60 sieve on 5-inch fire-clay roasting dishes and convert to ash in a muffle furnace at about 800° C. Transfer the ash to shallow opaque silica dishes (dishes 2⅜ inches in diameter are convenient) and continue heating until the weight is constant or the loss in weight is less than 0.1 percent per hour. Grind the ash in an agate mortar to pass a No. 100 sieve, and transfer it to a stoppered bottle.

This method is designed to prepare about 10 grams of ash sample. For analysis by rapid methods approximately half of this quantity of sample is prepared.

Ignition Loss at 800° C

To correct for any moisture or carbon dioxide that may be absorbed by the ash after its preparation, make an ignition-loss determination at the time of analysis by heating a 0.5 or 1-gram sample to constant weight in a muffle furnace maintained at a temperature of 800° C. Correct the final analysis of the sample to an ignition loss-free basis. Generally, ignition losses of coal ashes are low, ranging from 0.1 to 0.3 percent, but may be appreciably higher for ashes prepared from coals unusually high in calcite because of the possible absorption of water and carbon dioxide by the calcium oxide in the ash.

Classical Methods

Fusion with Sodium Carbonate

Mix a 1-gram sample of ash in a 30-ml platinum crucible with the larger part of 5 to 6 grams of sodium carbonate and cover the mixture with the remainder of the sodium carbonate. Place the lid on the crucible and heat at a low red heat over a Meker burner or blast lamp for 5 to 10 minutes. Gradually increase the heat until the mass sinters, so the carbon dioxide may pass off without spattering, and finally bring to complete fusion at a bright red heat.

The fusion is complete when the whole mass has been in a state of quiet fushion for about 15 minutes and gives off no more bubbles. The fusion will seldom be perfectly clear and transparent, since carbonates of iron, magnesium, and calcium form cloudy masses.

When fusion is complete, remove the crucible from the flame and swirl by a suitable circular motion as the melt cools so it solidifies in a thin sheet over the inside and bottom of the crucible. After the crucible is

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[56] Washington, Henry S. The Chemical Analysis of Rocks. John Wiley & Sons, Inc., New York, 4th ed., 1930, 296 pp.

Hillebrand, W. F. The Analysis of Silicate and Carbonate Rocks. U.S. Geol. Survey Bull. 700, 1919, 285 pp.

Hillebrand, W. F., G. E. F. Lundell, H. A. Bright, and J. I. Hoffmann. Applied Inorganic Analysis. John Wiley & Sons, Inc., New York, 2d ed., 1953, 1,034 pp.

[57] Gibson, F. H., and W. H. Ode. Application of Rapid Methods for Analyzing Coal Ash and Related Materials. BuMines Rept. of Inv. 6036, 1962, 23 pp.

[58] Shapiro, Leonard, and W. W. Brannock. Rapid Analysis of Silicate Rocks. U.S. Geol. Survey Bull. 1036–C, 1956, 56 pp.

Rapid Analysis of Silicate, Carbonate, and Phosphate Rocks. U.S. Geol. Survey Bull. 1144–A, 1962, 55 pp.

[59] Archer, K., D. Flint, and J. Jordan. The Rapid Analysis of Coal Ash, Slag, and Boiler Deposits. Fuel, v. 37, No. 4, 1958, pp. 421–443.

cool, place it and the lid in a 350-ml porcelain casserole, add 50 to 100 ml of water, cover with a watch glass, and slowly add 15 ml of concentrated hydrochloric acid.

A bluish-green color of the cooled cake indicates manganese; if present, chlorine will be evolved on the addition of hydrochloric acid, which will attack the platinum. A milliliter of alcohol added to the crucible will reduce the manganate and prevent attack of the platinum.

Heat on the hot plate until the melt is dissolved, wash the crucible and lid, and remove the last traces of silica from the crucible with a rubber-tipped stirring rod.

Silica

Evaporate on the steam bath until the residue begins to powder or crumble, and appears dry. Breaking up the lumps and crusts expedites the evaporation near the end of the process. Treat the residue with 15 ml of dilute hydrochloric acid (1:1) and cover; after warming on the steam bath a short time add 50 ml of water and heat gently to complete solution of the chlorides. Filter the silica and wash with a hot solution containing 5 ml of concentrated hydrochloric acid in 95 ml of water.

Return the filtrate to the casserole, evaporate to dryness, and dehydrate on the steam bath for 1 to 2 hours until free from hydrochloric acid. Moisten the residue with 8 ml of dilute hydrochloric acid (1:1), add water, and heat on the steam bath as before. Filter off the small amount of silica, collecting the filtrate in a 400-ml beaker, and wash with cold water containing 1 ml of concentrated hydrochloric acid to 99 ml of water. A little silica generally adheres to the side of the dish and is not removed by washing; this should be removed with a small piece of ashless filter paper which is later burned off during ignition of the silica.

Place the papers and silica from the first and second dehydration in a weighed 30-ml platinum crucible and heat over a Meker burner or blast lamp until the paper is burned off. Then ignite the silica for about 20 minutes, cool in a desiccator, and weigh quickly with the crucible covered. Repeat the ignition for 10-minute periods until the weight is constant. The silica thus obtained is never pure, and may contain small amounts of Fe_2O_3, TiO_2, P_2O_5, and Al_2O_3. Moisten the weighed residue with water and add 1 or 2 drops of dilute sulfuric acid (1:1) to retain the TiO_2, some of which would be vaporized as titanium fluoride in the absence of sulfuric acid. Add enough hydrofluoric acid, a few drops at a time, to dissolve the silica on warming; about 5 ml is usually sufficient. Evaporate the solution to dryness, preferably on an air bath,[60] and ignite at a bright red heat for at least 15 minutes. Cool in a desiccator and weigh; the loss in weight is SiO_2.

Fuse the nonvolatile residue with a little sodium carbonate, dissolve the fusion in dilute hydrochloric acid, and add to the filtrate from the silica for the succeeding determinations.

Aluminum Oxide

Aluminum, iron, titanium, and phosphorus oxides are precipitated by ammonium hydroxide and separated from the calcium, magnesium, and alkalies. Add 10 to 15 ml of concentrated hydrochloric acid to the filtrate from the silica to form, later, sufficient ammonium chloride to prevent the precipitation of magnesium along with the aluminum and iron hydroxides.

Heat the solution almost to the boiling point and add ammonium hydroxide gradually, stirring constantly until precipitation is complete and a very slight excess of ammonium hydroxide is present. The solution should be alkaline to methyl red. Heat to the boiling point, stirring occasionally to prevent bumping, and boil for not more than 1 minute. Allow the bulky gelatinous precipitate to settle for a few minutes, filter, and collect the filtrate in a 600-ml beaker. Decant the clear liquid as much as possible and then bring the precipitate on the filter paper, taking care that the filter is neither filled to within more than 2 or 3 mm of the edge nor that it runs dry; in the later case the gelatinous hydroxides will tend to consolidate, and filtration and washing will be long and tedious.

Wash the beaker and precipitate two or three times with a hot solution of ammonium nitrate made by neutralizing a solution of 2 ml of concentrated nitric acid in 100 ml of water with ammonium hydroxide. Thorough washing is not necessary at this point, but the precipitate should be collected in the bottom of the filter and the upper edge of the filter should be washed clean.

Since this first precipitate contains magnesium as well as calcium and alkalies, its solution and reprecipitation at least once are

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[60] A convenient form of air bath that may be used on a gas hot plate can be made from an asbestos board ¼ inch thick. Holes 1½ inches in diameter in the board will hold the crucibles so that about two-thirds of the crucible will extend through the hole. This top is set on a black iron frame having sides 1½ inches high so the bottoms of the crucibles are suspended about ½ inch above the hot plate.

necessary. Carefully remove the filter and its contents from the funnel and place in the 400-ml beaker. Add 10 ml of concentrated nitric acid, then 100 ml of water, and macerate the filter paper with a stirring rod while heating to dissolve the precipitate. Reprecipitate with ammonium hydroxide in a slight excess as before and boil for not more than 1 minute. Filter and wash the precipitate with the hot ammonium nitrate solution until free of chlorides. Small pieces of filter paper may be used to remove the last traces of precipitate from the beaker. Combine the filtrate with that from the first ammonium hydroxide precipitation and keep for determination of calcium and magnesium.

Transfer the filter and contents to a weighed 30-ml platinum crucible and dry cautiously on the hot plate or at a considerable distance over a small flame. Ignite at a low temperature until the paper is charred, then incline the crucible at an angle, and adjust the cover so the contents have free access to air. Heat at a bright red heat for about 30 minutes and then blast for 10 minutes to completely dehydrate the alumina. Cool in a desiccator, weigh, and repeat ignition to constant weight. The ignited precipitate consists of Al_2O_3, Fe_2O_3, TiO_2, and P_2O_5. The percentage of Al_2O_3 is obtained by difference after the Fe_2O_3, TiO_2, and P_2O_5 have been determined.

If no provision is made for manganese at this stage of the analysis, it will be distributed mainly between the calcium and magnesium, the largest part being precipitated and weighed as $Mn_2P_2O_7$ along with the magnesium. Very little will be precipitated with the alumina when two precipitations are made as described. For most coal ashes manganese may be disregarded, since the small amount usually present will cause only slight errors. When several tenths percent of manganese is present, it may be precipitated with the alumina and iron by adding about 1 gram of ammonium persulfate to the solution just before each precipitation with ammonium hydroxide. The manganese is then included with alumina, being weighed as Mn_3O_4, and a correction may be applied if the manganese is determined on a separate sample.

Ferric Oxide

Ferric oxide is determined in a separate sample of ash by the Zimmermann-Reinhardt method using stannous chloride reduction.[61]

SOLUTIONS.—Four solutions are used to determine ferric oxide.

0.1 N *potassium permanganate.*—Weigh 3.20 grams of potassium permanganate for each liter of solution required. Dissolve in distilled water and allow the solution to stand for several weeks before filtering through asbestos and standardizing with sodium oxalate.[62] Transfer 0.3 gram of sodium oxalate (dried at 105° C) to a 600-ml beaker. Add 250 ml of diluted sulfuric acid (5.95) previously boiled for 10 to 15 minutes and then cooled to 27° ± 3° C; stir until the oxalate has dissolved. Then add 39 to 40 ml of 0.1 *N* potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). To complete the titration heat to 55° to 60° C and add permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml drop by drop, taking care to allow each drop to become decolorized before the next is introduced. Deduct a blank (0.03 to 0.05 ml) determination made in another beaker having the same volume of acid and hot water. The standard is conveniently expressed as grams of Fe_2O_3 per milliliter of potassium permanganate.

Stannous chloride.—Add hydrochloric acid and water to stannous chloride and heat until solution is complete.

Stannous chloride	grams	62.5
Hydrochloric acid (specific gravity, 1.20)	ml	125
Water	ml	125

Titrating solution.—The titrating solution follows:

Manganous sulfate, crystallized	grams	90
Water	ml	650
Sulfuric acid (specific gravity, 1.84)	ml	175
Phosphoric acid (specific gravity, 1.71)	ml	175

Mercuric chloride, saturated solution.—Dissolve about 40 grams in 500 ml of hot water and cool to room temperature.

PROCEDURE.—Mix 0.5 gram of the sample in a platinum crucible with the larger part of 3 to 4 grams of sodium carbonate, and cover the mixture with the remainder of the sodium carbonate. Fuse the mixture for ½ to ¾ hour, heating gently at first until the mass sinters, then increasing the heat until fusion is complete. Place the cooled crucible and lid in a 250-ml beaker, add about 50 ml

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[61] Hillebrand, W. F., G. E. F. Lundell, H. A. Bright, and J. I. Hoffman. Applied Inorganic Analysis. John Wiley & Sons, Inc., New York, 2d ed., 1953, pp. 395–396.

[62] Fowler, R. M., and H. A. Bright. Standardization of Permanganate Solutions With Sodium Oxalate. Nat. Bureau of Standards Jour. Research, v. 15, November 1935, pp. 493–501.

of water, cover with a watch glass, and add 15 to 20 ml of concentrated hydrochloric acid. Heat on a hot plate until the melt is dissolved; then remove the crucible and lid and rinse with distilled water, using a rubber-tipped stirring rod if necessary.

Add ammonium hydroxide to the hot solution until the iron is precipitated, add 2 or 3 drops in excess, and boil for one minute. If the solution contains ferrous iron, as shown by a greenish color of the precipitate, bromine water should be added to oxidize the iron before the precipitation is completed. Filter and wash the precipitate five or six times with hot water, then transfer it to the beaker in which the precipitation was made by spreading the filter paper out on the side of the beaker and washing the precipitate off with a small quantity of water. Dissolve any precipitate adhering to the paper by washing alternately with hot, dilute hydrochloric acid (1:1) and hot water, using 10 to 15 ml of the acid.

Heat on a hot plate to dissolve the iron, and evaporate it without boiling to 10 to 20 ml. Add stannous chloride drop by drop to the hot solution, shaking gently, until colorless, and then add 1 drop in excess. Wash down the sides of the beaker with cold water and dilute to about 75 ml. Cool rapidly to room temperature, add 10 ml of saturated mercuric chloride solution, and transfer to a 600-ml beaker containing 300 ml of cold water and 10 ml of titrating solution. Titrate with standard potassium permanganate until a faint pink color persists. Subtract a blank titration made on the reagents. This determination gives total iron which is calculated as Fe_2O_3.

Note the following:

(1) Silica is not removed as it does not interfere with the titration. Breaking up the flakes of silica with a glass rod will facilitate reduction of the last traces of iron with stannous chloride.

(2) The precipitation with ammonia removes the excess chloride salts. Chlorides are then kept down to a safe limit by using only 10 to 15 ml of dilute hydrochloric acid (1:1) to dissolve the iron precipitate.

(3) Total iron in coal-ash slags and clinkers may be determined by this procedure.

Titanium Dioxide

Fuse the ignited iron and aluminum oxides from the aluminum determinations with 5 to 10 grams of potassium bisulfate (fused lump), heating gently until the salt is melted and the moisture driven off without boiling or spattering. Then gradually increase the heat until the bottom of the crucible is faint red. The liquid mass becomes dark brown as the oxides are dissolved, but when the flame is removed and the crucible is allowed to cool somewhat, the fusion becomes lighter in color, and any undissolved substance is visible. Continue fusion until solution is complete.

Place the cooled crucible in a 250 ml beaker with 100 ml of water, add 25 ml of dilute sulfuric acid (1:1), and heat to dissolve the melt. Remove the crucible and transfer the solution to a 250 ml volumetric flask. When cooled to room temperature, the solution is diluted with water to the mark, and mixed.

Pipet a 10 ml portion into a 50 ml volumetric flask (1) and for a reference solution add a second 10 ml portion to another 50 ml flask (2). Add 4 ml 1:1 H_2SO_4 to each flask, mix, and cool to room temperature. Add 5 ml of 3 percent hydrogen peroxide to flask 1. Fill both flasks 1 and 2 with water to the mark and mix. Measure absorbance at 410 $m\mu$ of solution in flask 1 using solution from flask 2 as reference.

As this test solution contains 40 mg of sample in 5 percent H_2SO_4, make a calibration test and calculate results according to the photometric method for TiO_2 described later.

Phosphorus Pentoxide

Volumetric, colorimetric, and gravimetric methods are available for determining phosphorus in ash.[63] A volumetric method that complies with ASTM standards follows.

SOLUTIONS.—The following solutions are used to determine phosphorus content.

Ammonium molybdate.—Dissolve 65 g molybdic acid (85 percent) in a mixture of 143 ml ammonium hydroxide and 142 ml water. Add solution slowly, stirring constantly, to 715 ml nitric acid (sp gr 1.20). If solution is cloudy, add 2 drops of a solution of ammonium phosphate (20 percent) and allow precipitate to settle, then filter the solution.

0.1 N *sodium hydroxide.*—Prepare concentrated solution of sodium hydroxide (100 g NaOH to 100 ml water) in a stoppered flask and allow to settle. Draw out required amount (about 11 ml) of clear liquid with pipet and dilute to 2 liters with recently boiled and cooled distilled water. Store solu-

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[63] Gibson, F. H., and W. H. Ode. Determining Phosphorus in Coal and Coke. Evaluation of Volumetric, Colorimetric, and Gravimetric Methods. BuMines Rept. of Inv. 5743, 1961, 21 pp.

tion in a plastic bottle fitted with rubber stopper carrying a siphon tube connected with a 15-ml buret or pipet and a soda-lime guard tube.

Standardize 0.1 *N* sodium hydroxide solution as follows: Weigh to nearest 0.1 mg about 0.2 g potassium hydrogen phthalate and dissolve in 100 ml water. Add 15 ml sodium hydroxide solution and titrate excess alkali with 0.1 *N* nitric acid, using phenolphthalein indicator. Calculate grams phosphorus equivalent to 1 ml of sodium hydroxide solution, taking 1 ml of a normal solution as being equivalent to 0.20422 g potassium hydrogen phthalate and 0.00135 g phosphorus.

0.1 N *nitric acid.*—Prepare a solution containing 6.3 ml nitric acid (sp gr 1.42) per liter.

Standardize nitric acid against sodium hydroxide solution under conditions similar to regular phosphorus determination. Macerate a filter paper with a glass rod in 50 ml water and remove rod. Add 15 ml standard sodium hydroxide, close flask with a rubber stopper, and swirl for 1 minute. Allow solution to stand about 5 minutes, then remove stopper, add 50 ml water and 4 drops 0.5 percent phenolphthalein, and titrate with nitric acid.

Nitric Acid (Sp Gr 1.20).—Solution containing 400 ml nitric acid (sp gr 1.42) and 600 ml water is approximately correct. Check specific gravity of mixture with a hydrometer and adjust to correct value if necessary.

PROCEDURE.—Add 10 ml concentrated nitric acid and 5 ml hydrofluoric acid to 0.5 g ash in a platinum crucible and evaporate to dryness. Repeat evaporation to dryness with same quantities of nitric and hydrofluoric acids. Add 15 ml nitric acid (sp gr 1.20) to residue and evaporate to a volume of approximately 7 ml, then transfer to a 150-ml beaker, dilute to 50 ml, cover with a watch glass, and boil for 15 minutes. Filter solution through 9-cm paper into 300-ml Erlenmeyer flask and wash the paper and the small residue six to eight times with hot water. Add 5 ml ammonium hydroxide (sp gr 0.90) to solution in flask; if a permanent precipitate is not produced add more ammonium hydroxide dropwise until iron is precipitated. Next add concentrated nitric acid slowly until precipitate just dissolves, then add 4 ml nitric acid in excess and dilute solution to 100 ml. Heat solution to 80° C, add 50 ml ammonium molybdate solution, and shake for 10 minutes. Allow solution to stand for one hour and filter through 9-cm paper. Transfer precipitate to paper while washing flask five times with 1-percent potassium nitrate solution. Continue washing paper and precipitate with approximately 10-ml portions of wash solution, directing stream first around rim of paper and circling down to precipitate until 10 ml of last washings show alkaline to phenolphthalein with one drop 0.1 *N* sodium hydroxide solution. Ten to fifteen washings are usually sufficient.

Return filter paper and precipitate to original flask, add 50 ml recently boiled distilled water that has cooled to room temperature, and macerate paper with a glass rod. Add 15 ml 0.1 *N* sodium hydroxide, close flask immediately with rubber stopper, and swirl contents for one minute to dissolve precipitate. Allow flask to stand about 5 minutes before titrating. Remove stopper, add 50 ml water and 4 drops 0.5 percent phenolphthalein, and titrate excess sodium hydroxide at once with 0.1 *N* nitric acid.

Calculate phosphorus content of sample from number of milliliters of standard 0.1 *N* sodium hydroxide neutralized by phosphomolybdate precipitate. Report as percent P_2O_5 in ash.

Note the following:

(1) Weight of sample may be varied according to phosphorus content; 0.0005 to 0.002 g P (0.0011 to 0.0046 g P_2O_5) gives suitable amount of ammonium phosphomolybdate precipitate for convenient filtering and washing.

(2) Relatively large amounts of titanium retard precipitation of phosphorus. In this method titanium in ash sample goes into solution. If ash is abnormally high in titanium so that approximately 0.01 g or more TiO_2 is present in sample, trouble may be experienced owing to retarding effect of titanium. This retarding effect may be overcome by digesting ammonium phosphomolybdate precipitate at 50° C for 30 minutes and allowing it to cool to room temperature and to stand for 3 hours before filtering.

Manganese Oxide [64]

Treat a 1-gram sample of ash in a platinum crucible with 4 ml of concentrated sulfuric acid, 10 ml of water, and 10 to 20 ml of hydrofluoric acid and evaporate until the sulfuric acid fumes freely. Allow the mixture to cool and dissolve in 25 ml of dilute nitric acid (1:3). Filter into a 300-ml Erlenmeyer flask and if an appreciable residue remains ignite and fuse the residue with a

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[64] Low, A. H. Technical Methods of Ore Analysis. John Wiley & Sons, Inc., New York, 10th ed., 1927, p. 150.

small amount of potassium bisulfate (fused lump). Dissolve in dilute nitric acid (1:3), add to the main solution, and dilute to 50 ml with the nitric acid. Add about 0.5 gram of sodium bismuthate and heat to boiling to destroy any reducing substances present; then add a few drops of a 5-percent solution of ferrous sulfate or sodium thiosulfate to remove any manganese dioxide and permanganate that may have formed, and boil for a few minutes until all nitrous oxide has been driven off. Cool to 10° to 20° C, add an excess of sodium bismuthate to the cold solution, and shake for 1 minute. Add 50 ml of dilute nitric acid (3:100) through which air has been bubbled to remove nitrous oxide, filter through asbestos on a Gooch crucible, and wash with 50 to 100 ml of the same acid. Add exactly 0.5 g of ferrous ammonium sulfate to the filtrate, shake to dissolve the salt, add another 0.5 g if the permanganate is not decolorized, and titrate the excess ferrous salt with 0.1 *N* potassium permanganate. Determine the number of milliliters of standard permanganate equivalent to 0.5 g of the ferrous ammonium sulfate under similar conditions. The iron value of the standard permanganate times 0.1967 equals its manganese value. Manganese is reported as Mn_3O_4; this is subtracted from the alumina value when the manganese is collected in the ammonium hydroxide precipitate.

Calcium Oxide

Evaporate the combined filtrates from the precipitation of iron and aluminum by ammonium hydroxide to about 400 ml. Add enough ammonium hydroxide to make the solution decidedly ammoniacal and heat to boiling. Slowly add 1 gram of ammonium oxalate dissolved in 25 to 50 ml of hot water to the boiling ammoniacal solution, stirring constantly to precipitate the calcium. Continue the boiling for a few minutes and allow the solution to stand for an hour or more before filtering. Filter and wash the precipitate two or three times with hot water.

Dissolve the precipitate with 25 to 50 ml of warm dilute hydrochloric acid (1:5), washing through the filter into the beaker in which the precipitation was made, and dilute to 100 ml. Add about 1 ml of saturated ammonium oxalate solution, heat to boiling, and reprecipitate the calcium by slowly adding ammonium hydroxide until the solution is alkaline to methyl red and an excess of 1 to 2 ml of ammonium hydroxide is present. Continue boiling for a few minutes and allow to stand for 1 hour before filtering. Wash the paper and precipitate two or three times with hot water. Avoid more washing because of the appreciable solubility of calcium oxalate. Ignite the paper and precipitate in a platinum crucible over a Meker burner for about 20 minutes, cool in a desiccator, and weigh as calcium oxide. Repeat the ignition for 5-minute periods until the weight is constant.

Magnesium Oxide [65]

Evaporate the filtrates from the calcium to 300 to 400 ml and add methyl red indicator, about 5 ml of concentrated hydrochloric acid, and 10 ml of a saturated solution of $(NH_4)_2HPO_4$. Then add ammonium hydroxide (sp gr 0.90) slowly, while stirring, to neutralization; when the precipitate is well-formed add an excess of 10 to 15 ml. Let stand at least 4 hours, preferably overnight, filter, and wash with water containing 3 percent by volume of ammonium hydroxide. Dissolve the precipitate on the filter by washing with warm dilute hydrochloric acid (1:5) and dilute the solution to 100 to 150 ml. Add methyl red indicator and about 1 ml of $(NH_4)_2HPO_4$ solution. Cool and finish the precipitation as before, using an excess of 5 to 10 ml of ammonium hydroxide, and allow to stand at least 4 hours. Filter the solution and wash the precipitate free of chlorides with 3 percent ammonium hydroxide. Place the paper and precipitate in a weighed platinum crucible, char without flaming, and ignite at a low temperature, with the crucible lid adjusted to permit circulation of air. Finally ignite to constant weight at the highest temperature of a Meker burner. Multiply the weight of ignited $Mg_2P_2O_7$ by 0.3623 to obtain the weight of MgO.

Sulfur Trioxide

Weigh 0.5 to 1.0 gram of ash sample, mix in a 30-ml platinum crucible with 4 to 5 grams of anhydrous sodium carbonate and about 0.2 gram of potassium nitrate. Carefully fuse the mixture, cool the crucible, and place it in a 250-ml beaker. Add 10 ml of hot water, 1 ml of alcohol to reduce any sodium manganate that may be present, and digest on a hot plate till the mass disintegrates. Remove and wash the crucible and break up any lumps of residue with a glass rod. Filter into a 400-ml beaker, first by decantation, then transfer the residue to the paper, and wash with a 0.1 percent solution of sodium

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[65] Epperson, A. W. The Pyrophosphate Method for the Determination of Magnesium and Phosphoric Anhydride. J. Am. Chem. Soc., v. 50, 1928, pp. 321–333.

carbonate until the volume of the filtrate is about 200 ml. Add 2 or 3 drops of methyl orange indicator, carefully neutralize with hydrochloric acid, then add a slight excess. Heat to boiling and add 10 ml of 10-percent barium chloride solution. Boil the mixture for a few minutes and allow it to stand for at least 2 hours at a temperature just below boiling. Filter on a close-textured paper and wash with hot water until free of chloride. Ignite in a weighed porcelain crucible, cool in a desiccator, and weight the barium sulfate. From this weight calculate the percentage of SO_3 in the sample.

Rapid Methods

Two solutions of the ash sample are prepared in the following methods, solution A for determination of SiO_2 and Al_2O_3, and solution B for the other determinations. Solution B containing 0.4 gram of sample in 250 ml is designed to provide enough portions of test solution for the various determinations described. In the spectrophotometric methods described the absorbance readings are made in 1 cm cells.

Preparation of Analysis Solutions

SOLUTION A.—Weigh accurately 0.0500 g of sample and transfer to a 50-ml nickel crucible. Add 1.5 g sodium hydroxide, cover crucible, and heat to melt the sodium hydroxide. Swirl gently to ensure that no particles of sample float on the surface of melt. Continue fusion for about 5 minutes at a dull red heat, then remove crucible from flame, swirl melt around sides, and allow to cool.

Add about 25 ml water and let stand for an hour or overnight if convenient. Pour contents of crucible into a 600-ml beaker containing 400 ml water and 20 ml 1:1 HCL. With a rubber policeman remove any residue from crucible and wash into beaker. Do not allow nickel crucible to come in contact with the acid.

Transfer solution to a 1,000-ml volumetric flask, dilute with water to mark, and mix. Clean the flask with 1:1 HCL and rinse with water before use.

Prepare duplicate standard solutions in the same manner using 0.0500 g portions of National Bureau of Standards sample No. 99, soda feldspar. Also prepare a blank solution. Store the standard and blank solutions in plastic bottles. The standard soda feldspar contains 68.66 percent SiO_2 and 19.06 percent Al_2O_3.

SOLUTION B.—Treat 0.400 ± 0.0005 g of sample in a 30-ml platinum crucible with 3 ml 1:1 H_2SO_4 and 10 ml HF. Evaporate on an air bath until most of the HF is removed, then add 1 ml HNO_3, and continue heating until strong fumes of SO_3 evolve.

Cool the crucible and contents, add water to dissolve the residue, and digest on air bath for one-half hour. Transfer contents of crucible to a 250-ml volumetric flask. When cooled to room temperature dilute to the mark and mix. Also prepare a blank solution.

Although some calcium sulfate from samples high in calcium may not dissolve during digestion in the crucible, it normally will dissolve on further dilution. A small quantity of insoluble barium sulfate may still remain with some samples. This will settle to the bottom of flask and not interfere in determining the main constitutents. If appreciable insoluble residue is present, the solution can be filtered into another 250-ml flask before finally diluting to the mark.

Because of the possibility of alkali contamination from the flask, determine sodium and potassium the same day that solution B is prepared, or withdraw 25 ml with a pipet and store in a plastic bottle.

Description of Methods

SILICA.—The following method is used for the determination of silica.

Reagents.—Ammonium molybdate solution: Dissolve 7.5 g ammonium molybdate in 75 l of water, add 10 ml 1:1 H_2SO_4, and dilute to 100 ml. Store in plastic bottle.

Tartaric acid solution, 10 percent; store in plastic bottle.

Reducing solution: Dissolve 0.7 g sodium sulfite in 10 ml water. Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid and stir until dissolved. Dissolve 9.0 g of sodium bisulfite in 90 ml water, add this solution to the solution above, and mix. Store in plastic bottle.

Procedure.—Pipet 10 ml aliquot of sample solution A, 10 ml of each standard solution, and blank solution in to separate 100-ml volumetric flasks. Dilute to 50 to 60 ml with water and mix.

Add 1.5 ml ammonium molybdate solution with a measuring pipet, mix, and let stand 10 minutes.

Pipet 4 ml tartaric acid solution, followed immediately by 1 ml reducing solution, into the first flask, mixing during the additions. Dilute contents of this flask immediately to the mark and mix before proceeding to the next flask.

Let each solution stand 1 hour then determine its absorbance at 650 mμ using the blank solution as reference.

Calculation.—Compute factor for each standard test =

$$\frac{\text{Percent } SiO_2 \text{ in standard}}{\text{absorbance of standard}}$$

Compute average factor.

Percent SiO_2 in sample = (average factor X absorbance of sample).

ALUMINUM OXIDE.—The following procedure is used for determination of aluminum oxide.

Reagents. — Calcium chloride solution: Transfer 7 g $CaCO_3$ to a 250-ml beaker. Add about 50 ml water and 1:1 HCL in drops until the $CaCO_3$ is dissolved. Boil the solution for 1 to 2 minutes, cool, and dilute to 500 ml.

Hydroxylamine hydrochloride solution, 10 percent.

Thioglycollic acid: Dilute 5 ml of reagent with water to 100 ml.

Buffer solution: Dissolve 70 g sodium acetate in water, add 30 ml glacial acetic acid, and dilute to 500 ml.

Alizarin red S solution, 0.1 percent: Dissolve 0.2 g alizarin red S in 200 ml water and filter to obtain a clear solution.

Procedure.—Pipet a 10-ml aliquot of sample solution A, 20 ml of each standard solution A, and 20 ml of blank solution into separate 100-ml volumetric flasks. Then pipet 10 ml of blank solution to the flask containing 10 ml of sample solution to maintain correct pH. For ash samples that contain less than 20 percent Al_2O_3 take a 20-ml aliquot directly from solution A.

Add 1 ml $CaCl_2$ solution to each flask and mix.

Add 1 ml hydroxylamine hydrochloride solution to each flask and mix.

Add 1 ml thioglycollic acid solution to each flask and mix.

Add 10 ml buffer solution, measured with a graduate, to each flask, mix, and allow to stand 10 minutes.

Add 5 ml alizarin red S solution with a pipet, dilute to 100 ml, and mix.

Allow to stand for 1 hour, then measure absorbance at 475 $m\mu$ using blank solution as reference.

Calculation.—Compute factor for each standard test =

$$\frac{\text{Percent } Al_2O_3 \text{ in standard}}{\text{absorbance of standard}}$$

Calculate average factor.

Percentage of Al_2O_3 in sample for 10 ml-aliquot = 2 X average factor X absorbance of sample solution; or for 20-ml aliquot = average factor X absorbance of sample solution.

FERRIC OXIDE.—The procedure for determination of ferric oxide follows:

REAGENTS. — Hyldroxylamine hydrochloride, 10 percent.

Soduim gluconate solution, 10 percent.

Orthophenanthroline solution, 0.1 percent.

Sodium citrate, 10 percent.

Standard iron solution: Dissolve 0.2455 ± 0.0005 g $FeSO_4 \cdot (NH_4)_2\ SO_4 6 \cdot H_2O$ in water, add 3 ml 1:1 H_2SO_4, and dilute to 500 ml; 1 ml contains equivalent of 0.1 mg Fe_2O_3.

Procedure.—Dilute 10 ml of sample solution B to 50 ml in a volumetric flask.

Pipet 10 ml of diluted sample solution into a 100-ml volumetric flask, pipet 5 ml of standard iron solution into another 100-ml flask, and add nothing to a third flask for reagent blank.

Add 5 ml hydroxylamine hydrochloride solution to each flask and mix.

Add 10 ml sodium gluconate solution to each flask and mix.

Add 10 ml orthophenanthroline solution to each flask and mix.

Add 10 ml sodium citrate solution to each flask, dilute to 100 ml with water, and mix.

Measure absorbance at 510 $m\mu$ using reagent blank as reference.

Calculation.—The standard test solution contains 0.5 mg of Fe_2O_3, and a 10-ml aliquot of the diluted sample solution contains 3.2 mg of sample. For these conditions, percentage of

$$Fe_2O_3 = \frac{0.5 \text{ X absorbance of sample}}{\text{absorbance of standard X } 3.2} \times 100$$

Note: For samples containing more than 15 percent Fe_2O_3, take a 5-ml aliquot of the diluted sample solution which contains 1.6 mg of sample.

TITANIUM DIOXIDE.—The following method is used for determination of titanium dioxide.

Reagents.—Hydrogen peroxide, 3 percent solution.

Standard titanium solution: Transfer 0.2008 ± 0.0005 g of Bureau of Standards sample No. 154a (99.6 percent TiO_2) or the appropriate amount of reagent TiO_2 of known composition to a platinum crucible. Fuse with potassium pyrosulfate. Dissolve the melt in 50 ml 1:1 H_2SO_4, cool, and dilute to 1,000 ml in a volumetric flask. The concentration of TiO_2 is 0.20 mg/ml.

Procedure.—Pipet a 25-ml portion of sample solution B into a 50-ml volumetric flask (1), and for the reference solution add a second 25-ml portion of solution B to another 50-ml flask (2).

Add 5 ml 1:1 H_2SO_4 to each flask, mix, and cool to room temperature.

Add 5 ml hydrogen peroxide solution to flask 1. Fill both flasks 1 and 2 to the mark with water and mix.

Measure absorbance at 410 mμ of solution in flask 1 using solution from flask 2 as reference.

Calibration.—Transfer 5.0 ml standard TiO_2 solution to 50-ml volumetric flask 1 and add about 25 ml water. Add 25 ml water to flask 2.

Add 5 ml 1:1 H_2SO_4 to each flask, mix, and cool to room temperature.

Add 5 ml hydrogen peroxide to flask 1. Fill both flasks to the mark with water and mix.

Measure absorbance at 410 mμ of solution in flask 1 using reagent blank in flask 2 as reference.

Calculation.—For an example, assume 5 ml of standard = 1.00 mg TiO_2. This is equivalent to 2.5 percent for a 25-ml aliquot of sample solution B that contains 40 mg of sample.

Percentage of TiO_2 =

$$\frac{2.5 \text{ X absorbance of sample}}{\text{absorbance of standard}}$$

PHOSPHORUS PENTOXIDE. — Phosphorus pentoxide is determined as follows.

Reagents. — Molybdivanadate solution: Dissolve 0.625 g of ammonium metavanadate in 200 ml 1:1 HNO_3 Dissolve 25 g ammonium molybdate in 200 ml water. Pour the ammonium molybdate solution into the metavanadate solution while stirring and dilute with water to 500 ml.

Standard P_2O_5 stock solution: Dissolve 0.3835 ± 0.0005 g potassium dihydrogen phosphate (dried at 110° C) in water and dilute to 1,000 ml.

Standard working P_2O_5 solution: Dilute 50 ml of stock solution to 500 ml. Then 25 ml contains 0.50 mg of P_2O_5, which is equivalent to that in the solution prepared from a sample containing 1.25 percent P_2O_5 as directed in preparation of sample solution B.

Procedure.—Pipet a 25-ml aliquot from sample solution B, 25 ml of standard working solution, and 25 ml of the blank solution into separate 50-ml volumetric flasks.

With a pipet add 10 ml molybdivanadate solution to each flask, dilute with water to the mark, mix, and allow to stand for at least 5 minutes.

Measure absorbance at 430 mμ using the reagent blank as reference.

Calculation.—Percentage P_2O_5 =

$$\frac{1.25 \text{ X absorbance of sample}}{\text{absorbance of standard}}$$

CALCIUM AND MAGNESIUM OXIDES.—*Reagents.*—EDTA solution: Dissolve 3.720 g of the disodium salt of ethylene diamine tetraacetic acid in water and dilute to 1,000 ml. Standardize against the standard calcium solution using calcein or phthalein purple indicator.

Standard calcium solution: Dissolve 1.000 g calcium carbonate in water with 4 ml 1:1 HCl. Heat to boiling to expel carbon dioxide, cool, and dilute to 1,000 ml. 1 ml is equivalent to 0.00056 g CaO.

Triethanolamine solution: Dilute 500 ml of triethanolamine with water to 1,000 ml and mix.

Potassium hydroxide: Dissolve 224.4 g potassium hydroxide in water and dilute to 1,000 ml. Store in plastic bottle.

Calcein indicator: Mix 0.2 g calcein, 0.12 g thymolphthalein, and 20 g finely ground potassium chloride.

Phthalein purple indicator: Mix 0.1 g phthalein purple, 0.005 g methyl red, and 0.05 g naphthol green B with 10 g finely ground potassium chloride.

Procedure for CaO.—Pipet 25 ml of sample solution B and 25 ml of the blank solution into separate 500-ml Erlenmeyer flasks. Dilute with water to approximately 100 ml.

Add 1 ml of concentrated HCl, 5 ml of the triethanolamine solution, 5 ml ammonium hydroxide, and 10 ml potassium hydroxide solution in that order, mixing after addition of each reagent. Dilute with water to about 200 ml.

Add approximately 40 mg calcein indicator and titrate with standard EDTA solution until the color changes from a green fluorescence to purple. Observe the color change in diffused light looking down through the flask to a black surface.

Procedure for MgO.—Pipet 25 ml of sample solution B and 25 ml of blank solution into separate 500-ml Erlenmeyer flasks. Dilute with water to about 100 ml.

Add 1 ml concentrated HCl, 20 ml triethanolamine solution, and 25 ml ammonium hydroxide, mixing after addition to each reagent. Dilute with water to approximately 200 ml.

Add a volume of standard EDTA solution slightly less than the calcium titer, then add about 40 mg phthalein purple indicator. Continue the titration until the color changes from pale purple to colorless or pale grey. A slight excess of EDTA produces a green coloration. Observe the color change in diffused light looking down through the flask to a white surface.

Calculation.—Let V_1 = milliliters of EDTA required for calcium titration, corrected for blank.

V_2 = milliliters of EDTA required for Ca ± Mg titration, corrected for blank.

F = grams $CaO \equiv 1$ ml EDTA; ($0.719\ F$ = grams $MgO \equiv 1$ ml EDTA).

W = weight of sample, grams.

A = volume of aliquot, milliliters.

$$\text{Percentage of CaO} = \frac{V_1\ X\ F\ X\ \frac{250}{A}}{W} \times 100.$$

Thus, if $W = 0.4$ g, $F — .00056$, and $A = 25$ ml, percentage of $CaO = V_1 \times 1.4$.

Percentage of MgO =

$$\frac{(V_2 — V_1 \times 0.719\ X\ F\ X\ \frac{250}{A}}{W} \times 100.$$

SODIUM AND POTASSIUM OXIDES.—*Reagents.*—Synthetic ash solution: Dissolve 2.0 g iron in 5 ml 1:1 H_2SO_4 and 100 ml water.

Dissolve 1.0 g aluminum in 5 ml 1:1 H_2SO_4 and 100 ml water.

Dissolve 1.25 g $CaCO_3$ in 3 ml 1:1 H_2SO_4 and about 600 ml water.

Dissolve 1.0 g $MgSO_4 \cdot 7H_2O$ in water.

Combine the solutions, filter, and dilute with water to 1,000 ml.

Stock Na solution, 100 parts per million (ppm): Dissolve 0.3088 ± 0.0005 g Na_2SO_4 in water and dilute to 1,000 ml.

Stock K solution, 100 ppm: Dissolve 0.2228 ± 0.0005 g K_2SO_4 in water and dilute to 1,000 ml.

Standard Na solution: Pipet 10 and 50 ml of stock Na solution into separate 100-ml volumetric flasks. Add 10 ml synthetic ash solution and 10 ml stock K solution to each flask, dilute with water to the mark, and mix. The solutions contain 10 and 50 ppm Na.

Standard K solution: Pipet 50 ml stock K solution into a 100-ml volumetric flask. Add 10 ml synthetic ash solution and 10 ml stock Na solution, dilute with water to the mark, and mix. The solution contains 50 ppm K. As the standard 10-ppm Na solution contains 10 ppm K, use it also for the standard 10-ppm K solution. Store in plastic bottles.

Calibration.—Prepare additional standard Na solutions containing 1, 4, 20, 30, and 40 ppm Na, and standard K solutions containing 1, 4, 20, 30, and 40 ppm K. Also prepare blank solutions, the Na blank containing 10 ml synthetic ash solution and 10 ml stock K solution per 100 ml, and the K blank containing 10 ml synthetic ash solution and 10 ml stock Na solution per 100 ml. Rinse each sample cup two times with the solution it is to contain before filling with the test solution.

After adjusting flame spectrophotometer according to manufacturer's directions, set the wavelength to 589 mμ and aspirate the 50 ppm Na solution. Move the wavelength control slightly back and forth at the sodium wavelength to find setting for maximum response. Finally, while aspirating the 50 ppm Na solution adjust the slit width and sensitivity to achieve a transmittance reading of 80. Rinse aspirator with water, and determine transmittance reading for the 40-ppm Na solution. Repeat this operation, checking that the transmittance reads 80 for the 50-ppm Na solution, and determine readings for the 30-, 20-, and 10-ppm Na solutions. Test the blank solution, and subtract blank readings from each determination. Prepare a working curve for the range 10 to 50 ppm Na. Make another working curve for the range 1 to 10 ppm Na. To do this aspirate the 10-ppm Na solution and increase slit width sufficiently to obtain a transmittance reading of 80, and then determine readings for the 4- and 1-ppm Na solutions.

Make similar measurements for the standard K solutions at a wavelength of 768 mμ.

PROCEDURE. — Operate flame spectrophotometer in the manner used for calibration. Rinse sample cup with solution it is to contain, and fill separate cups with standard 50- and 10-ppm Na solution, sample solution B, blank solution B, and water. Adjust instrument for the 10–50-ppm range at the sodium wavelength using the standard 50-ppm Na solution, and determine readings for sample solution and blank. When sample solution contains less than 10 ppm Na, make determination in the 1–10-ppm range after setting instrument with the 10-ppm Na solution. For samples rich in sodium, dilute an aliquot of solution B for the test.

Make similar determinations for potassium using the standard 50- and 10-ppm K solutions to adjust the spectrophotometer. Subtract the blank reading from the sample reading, and determine the concentration of Na and K in the test solution from the appropriate working curve.

Calculation.—When using 0.4 g of sample in 250 ml for solution B, calculate percentage of Na_2O and K_2O as follows:

$$\text{Percentage of } Na_2O = \frac{\text{ppm Na} \times 1.348}{16}$$

$$\text{Percentage of } K_2O = \frac{\text{ppm K} \times 1.2046}{16}$$

Method of Reporting Analysis

An example of the method used in reporting an analysis of a coal ash follows. Manganese oxide (Mn_3O_4) is not listed among the constituents, as it seldom is determined.

Constitutent:	*Percent*
Silica (SiO_2)	45.4
Aluminum oxide (Al_2O_3)	24.1
Ferric oxide (Fe_2O_3)	19.9
Titanium dioxide (TiO_2)	1.0
Phosphorus pentoxide (P_2O_5)	.20
Calcium oxide (CaO)	3.6
Magnesium oxide (MgO)	.6
Sodium oxide (Na_2O)	.6
Potassium oxide (K_2O)	.9
Sulfur trioxide (SO_3)	3.5

METHODS FOR DETERMINATION OF FERRIC OXIDE, FERROUS OXIDE, AND METALLIC IRON IN COAL-ASH SLAGS AND CLINKERS

The forms of iron in coal-ash slags and clinkers are sometimes determined in connection with studies concerning ash composition as related to ash fusibility and ash viscosity. The degree of oxidation of the iron is one of the variables that affect the temperature at which various stages of fusion occur. The method is empirical in nature, and it is difficult to determine its accuracy. It is given here because of occasional requests for such information.

Preparation of Sample

A hard steel mortar should be used in crushing the sample. The pestle should not be twisted or turned as such motion will contaminate the sample with metallic iron from the mortar and pestle. The sample should be crushed to pass a No. 60 sieve.

Total Iron

Determine total iron in 0.5 g of sample according to the method described for ferric oxide in coal ash. When more than 0.1 percent of metallic iron or much carbon is present it is advisable to treat the sample first with hydrochloric acid and filter the solution. Ignite the residue, and fuse with sodium carbonate. Dissolve the melt in hydrochloric acid, add to the first solution, and proceed with the iron determination.

The total iron calculated to Fe_2O_3 minus Fe_2O_3 equivalents of the ferrous oxide and metallic iron equals the ferric oxide in the sample.

Ferrous Iron

Weigh 0.2 to 0.5 g of sample, depending on the amount of ferrous iron present, and transfer to a 50-ml platinum crucible. A small spiral of platinum wire placed in the crucible will prevent bumping during boiling. The crucible should be placed in a hole cut in a piece of asbestos board so its lower two-thirds is exposed to the flame of a Meker burner. Add 15 ml of dilute sulfuric acid (1:3), cover the crucible and heat almost to boiling; then add 5 to 10 ml of hydrofluoric acid and boil gently for 5 to 10 minutes. Place the crucible and contents in a 600-ml beaker containing 350 ml of recently boiled and cooled boric acid solution (15 g H_3BO_3 to 350 ml of water) and titrate with standard potassium permanganate. Subtract a blank titration made on the reagents. This determination gives the ferrous iron plus any metallic iron that may be present. The determined iron, calculated to FeO, minus the FeO equivalent of the metallic iron equals the ferrous oxide in the sample.

Metallic Iron

Transfer 0.5 to 1.0 g of the sample to a 250-ml beaker and add 60 ml of a 5-percent mercuric chloride solution. Cover the beaker with a watch glass and digest on the hot plate for one hour but do not allow to boil. Filter into a 400-ml beaker and wash with a cold 2-percent solution of mercuric chloride. Dilute the filtrate to 300 ml with cold water, add 10 ml of titrating solution, and titrate with the standard potassium permanganate. Deduct a blank determination made on the reagents. If more than 2 percent of metallic iron is present, reduce the amount of sample to give not more than 0.01 g of metallic iron. This titration gives the metallic iron in the sample.

APPENDIX

TABLE A-1.—*Nominal dimensions, permissible variations, and limits for wire cloth of standard sieves (U.S. Standard Series (4th root of 2 ratio))*

Sieve designation		Sieve opening		Permissible variations in average opening, percent	Permissible variation for not more than 5 percent of openings, percent	Permissible maximum variation in individual openings, percent	Nominal wire diameter[1]	
Standard	Alternate	Millimeters	Inches (approximate equivalents)				Millimeters	Inches approximate equivalents)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
107.6 mm	4.24 in	107.6	4.24	±3	+4	+5	6.40	0.2520
101.6 mm	4 in[2]	101.6	4.00	±3	+4	+5	6.30	.2480
90.5 mm	3 ½ in	90.5	3.50	±3	+4	+5	6.08	.2394
76.1 mm	3 in	76.1	3.00	±3	+4	+5	5.80	.2283
64.0 mm	2 ½ in	64.0	2.50	±3	+4	+5	5.50	.2165
53.8 mm	2.12 in	53.8	2.12	±3	+4	+5	5.15	.2028
50.8 mm	2 in[2]	50.8	2.00	±3	+4	+5	5.05	.1988
45.3 mm	1 ¾ in	45.3	1.75	±3	+4	+5	4.85	.1909
38.1 mm	1 ½ in	38.1	1.50	±3	+4	+5	4.59	.1807
32.0 mm	1 ¼ in	32.0	1.25	±3	+4	+5	4.23	.1665
26.9 mm	1.06 in	26.9	1.06	±3	+5	+6	3.90	.1535
25.4 mm	1 in[2]	25.4	1.00	±3	+5	+6	3.80	.1496
[3] 22.6 mm	⅞ in	22.6	.875	±3	+5	+6	3.50	.1378
[3] 19.0 mm	¾ in	19.0	.750	±3	+5	+6	3.30	.1299
[3] 16.0 mm	⅝ in	16.0	.625	±3	+5	+6	3.00	.1181
13.5 mm	0.530 in	13.5	.530	±3	+5	+6	2.75	.1083
12.7 mm	½ in[2]	12.7	.500	±3	+5	+6	2.67	.1051
[3] 11.2 mm	7/16 in	11.2	.438	±3	+5	+6	2.45	.0965
9.51 mm	⅜ in	9.51	.375	±3	+5	+6	2.27	.0894
[3] 8.00 mm	5/16 in	8.00	.312	±3	+5	+6	2.07	.0815
6.73 mm	0.265 in	6.73	.265	±3	+5	+6	1.87	.0736
6.35 mm	¼ in[2]	6.35	.250	±3	+5	+6	1.82	.0717
[3] 5.66 mm	No. 3-½	5.66	.223	±3	+5	+10	1.68	.0661
[3] 4.76 mm	No. 4	4.76	.187	±3	+5	+10	1.54	.0606
[3] 4.00 mm	No. 5	4.00	.157	±3	+5	+10	1.37	.0539
[3] 3.36 mm	No. 6	3.36	.132	±3	+5	+10	1.23	.0484
[3] 2.83 mm	No. 7	2.83	.111	±3	+5	+10	1.10	.0430
2.38 mm	No. 8	2.38	.0937	±3	+5	+10	1.00	.0394
[3] 2.00 mm	No. 10	2.00	.0787	±3	+5	+10	.900	.0354
[3] 1.68 mm	No. 12	1.68	.0661	±3	+5	+10	.810	.0319
[3] 1.41 mm	No. 14	1.41	.0555	±3	+5	+10	.725	.0285
1.19 mm	No. 16	1.19	.0469	±3	+5	+10	.650	.0256
[3] 1.00 mm	No. 18	1.00	.0394	±5	+7-½	+15	.580	.0228
841 μ	No. 20	.841	.0331	±5	+7-½	+15	.510	.0201
[3] 707 μ	No. 25	.707	.0278	±5	+7-½	+15	.450	.0177
595 μ	No. 30	.595	.0234	±5	+7-½	+15	.390	.0154
[3] 500 μ	No. 35	.500	.0197	±5	+7-½	+15	.340	.0134
420 μ	No. 40	.420	.0165	±5	+12-½	+25	.290	.0114
[3] 354 μ	No. 45	.354	.0139	±5	+12-½	+25	.247	.0097
297 μ	No. 50	.297	.0117	±5	+12-½	+25	.215	.0085
[3] 250 μ	No. 60	.250	.0098	±5	+12-½	+25	.180	.0071
210 μ	No. 70	.210	.0083	±5	+12-½	+25	.152	.0060
[3] 177 μ	No. 80	.177	.0070	±6	+20	+40	.131	.0052
149 μ	No. 100	.149	.0059	±6	+20	+40	.110	.0043
[3] 125 μ	No. 120	.125	.0049	±6	+20	+40	.091	.0036
105 μ	No. 140	.105	.0041	±6	+20	+40	.076	.0030
[3] 88 μ	No. 170	.088	.0035	±6	+20	+40	.064	.0025
74 μ	No. 200	.074	.0029	±7	+30	+60	.053	.0021
[3] 63 μ	No. 230	.063	.0025	±7	+30	+60	.044	.0017
53 μ	No. 270	.053	.0021	±7	+30	+60	.037	.0015
[3] 44 μ	No. 325	.044	.0017	±7	+30	+60	.030	.0012
37 μ	No. 400	.037	.0015	±7	+30	+60	.025	.0010

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[1] The average diameter of the warp and of the shoot wires, taken separately, of the cloth of any sieve shall not deviate from the nominal values by more than the following:

Sieves coarser than 595 μ .... 5 percent
Sieves 595 μ to 125 μ .... 10 percent
Sieves finer than 125 μ .... 15 percent

[2] These sieves are not in the 4th root of 2 series, but they have been included because they are in common usage.

[3] These sieves correspond to those proposed as an International (ISO) Standard. It is recommended that wherever possible these sieves be included in all sieve analysis data or reports intended for international publication.

Note.—All measurements of openings and wire diameters shall be made on the completed sieve.

Courtesy American Society for Testing and Materials, 1965 Book of ASTM Standards, Part 9.

TABLE A–2.—*Comparison of selected square-mesh-wire - test sieves of different countries: Equivalent values*

United States			Great Britain		Germany DIN 4188, inside mesh width in mm (6)	Japan JIS, nominal measure in μ (7)
ASTM		Tyler openings per linear inch (3)	Standard openings per linear inch (4)	I.M.M. sieve number (5)		
Sieve designation in μ (1)	Openings per linear inch (2)					
5,660	3-½	3-½	......	......	6.3	5,660
4,000	5	5	......	......	4.0	4,000
3,360	6	6	5	......	3.15	3,360
2,380	8	8	7	5	2.5	2,380
2,000	10	9	8	6.4	2.0	2,000
......	......	......	10	8	1.6	1,680
1,190	16	14	14	10	1.25	1,190
1,000	18	16	16	12	1.0	1,000
841	20	20	18	16	.8	840
500	35	32	30	25	.5	500
250	60	60	60	50	.25	250
210	70	65	72	60	.2	210
105	140	150	150	120	.1	105
88	170	170	170	150	.08	88
74	200	200	250	200	.063	74
44	325	325	......	289	.04	44

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