CHEMISTRY, USES, AND

LIMITATIONS OF COAL ANALYSES

O. W. Rees

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Topographic mapping in cooperation with the United States Geological Survey.

FOREWORD

This report is not a laboratory manual. Rather it supplements laboratory manuals by explaining some of the factors involved in making and using coal analyses. Although many details are not covered, I have attempted to discuss the factors I consider most important. No attempt has been made to provide a complete survey of the literature.

A number of the conclusions are those I have formulated during many years of coal analysis work. I owe much to my associates, past and present, at the Illinois State Geological Survey and to coal analysts and technologists in the United States and in several foreign countries with whom I have discussed numerous problems relative to this type of analysis. I hope that the report will be helpful to coal analysts and technologists.

O. W. Rees

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O. W. Rees

ABSTRACT

The mode of occurrence of various constituents of coal, the chemical and physical changes that take place during analysis, some of the difficulties that may be encountered during analysis and means of minimizing them are considered in this report. Uses of coal analyses and their limitations, both analytical and applied, also are discussed.

GENERAL COMMENTS

Coal is a heterogeneous material containing organic matter made up of carbon, hydrogen, nitrogen, oxygen, sulfur, and mineral matter. The mineral matter, in turn, is composed of clay minerals, pyrite and/or marcasite, calcite, and smaller amounts of other minerals. The coal classification system used in the United States also recognizes moisture, at least in part, as a constituent of coal in the bed or seam.

Various kinds of systems for classifying coal have been proposed, but the one most used in the United States is the American Society for Testing and Materials rank classification (ASTM, 1966), which is based on the degree of coalification of the parent plant material. In this system, fixed carbon and calorific value are the parameters.

The international classification of hard coals by type, developed by the classification working group of the United Nations Economic Commission for Europe (ECE, 1956), is basically a rank classification system for which volatile matter and calorific value are the principal parameters. However, certain other characteristics of coal, such as caking and coking properties, have been included so that, in effect, it is a rank classification on which has been superimposed a form of use classification.

Another kind of classification that receives considerable attention may be called a type classification because it is based on the kinds of plant material from which various components of coal were formed. Most bituminous coals are banded — that is, they are made up of layers variously called banded ingredients, petrographic constituents, or lithotypes. Stopes (1919) named these constituents vitrain, clarain, durain, and fusain on the basis of their macrovisual appearance. Thiessen proposed the names anthraxylon (1920), translucent and opaque attritus (1930), and fusain, all based on both macrovisual and microscopic appearance. The term

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fusain, used by both Stopes and Thiessen, was first introduced by Grand'Eury (1882).

In recent years a further subdivision of lithotypes into "macerals" has become possible through improved microscopic and reflectance techniques. Such names as vitrinite, inertinite, and fusinite have been assigned to these macerals. All of these components, whether macrovisual or microscopic, appear to have different chemical and physical properties, and their study is a definite help to a better understanding of the nature and uses of coal. Further petrographic information on coal may be found in the "International Handbook of Coal Petrography" (Internatl. Comm. Coal Petrog., 1963). The chemical analysis of coal as it is commonly practiced commercially, however, is made on whole coal and not on components thereof.

Reliable sampling of such a complex material is difficult, especially for moisture and size consist. A representative gross sample must be obtained, and much work has been done to establish reliable standard procedures for taking one. Ash content has been the characteristic most used in evaluating the reliability of sampling procedures, and, by experimentation and statistical treatment, procedures have been worked out that have a precision, in 95 cases out of 100, of plus or minus 10 percent of the ash present, or even greater precision when it is required.

Securing a reliable gross sample does not bring an end to the problems, for it is then necessary to prepare this sample, through reduction in both particle size and quantity, to what is known as the analysis sample, a procedure beset by many difficulties. First, the distribution of the mineral matter offers problems in both crushing and proper mixing at each step of the sampling procedure. Second, moisture may be lost or gained unless it is controlled. Moisture, of course, is a volatile material and can be readily lost during handling; it is also possible that moisture can be picked up by the coal on a highly humid day. Third, if the coal is exposed to air too long it may oxidize to some extent and certain properties will be changed. Fourth, if the sample contains too much extremely fine material it may later give considerable trouble when certain determinations are being made. Fifth, the sample can be contaminated — for example, by iron from the crushing

equipment. And, finally, the various densities of the materials in coal can easily cause their segregation.

Coal analysis may be divided into three categories — proximate analysis, ultimate analysis, and miscellaneous analysis. Included in the proximate analysis are moisture, ash, volatile matter, and fixed carbon. In ultimate analysis, determinations of hydrogen, carbon, nitrogen, oxygen, total sulfur, and chlorine are made. Ash also is commonly included in an ultimate analysis so that the oxygen value may be obtained by difference. Miscellaneous analysis deals with calorific value, ash softening temperature, forms of sulfur, mineral carbon dioxide, and special tests such as free-swelling index, plastic properties, grindability, screen analysis, and sieve analysis of crushed bituminous coal. Of these special tests only the free-swelling index test and the test for plastic properties of coal by the Gieseler plastometer are commonly made in the analytical laboratories of the Illinois State Geological Survey. Larger scale tests are often run on coal, such as those for coking, expansion, bulk density, and combustion, but these are beyond the scope of a strict coal analysis laboratory.

Many of the methods used for analyzing coal are directly applicable to the analysis of coke. In some cases, however, certain modifications are necessary. The miscellaneous analysis of coke also includes determinations of true and apparent specific gravity, porosity, sieve analysis, weight per cubic foot, and the running of the drop shatter, tumbler, and, in some instances, coke reactivity tests. Of these only the test for apparent specific gravity is commonly run in the Survey's analytical laboratories.

Many of the methods of coal analysis are empirical. That is, they involve strict adherence to certain specified conditions such as particle size, temperature, time and rate of heating, atmosphere, and size and shape of sample container. It is essential that the details of these specified conditions be adhered to closely to obtain repeatable and reproducible results. The establishment of specifications that are recognized as standards and backed by authoritative organizations is of the utmost importance. In the United States, standard methods for coal and coke analysis are developed and sponsored by the Amer-

ican Society for Testing and Materials (1966) through its Technical Committee D-5 on Coal and Coke. Some of these methods are adopted and sponsored by the American Standards Association. International standards for coal and coke are developed by Technical Committee 27, Solid Mineral Fuels, of the International Organization for Standardization (ISO/TC 27).

The various items commonly determined in coal analysis will be discussed separately. The methods will not be given in detail, as most have already been described elsewhere. Rather, such things as the mode of occurrence and chemical and physical properties of constituents as they occur naturally in coal, along with chemical changes that take place during analysis, will be emphasized. In addition, some of the difficulties that may arise, suggestions for minimizing them, and uses and limitations of the analytical data will be discussed.

PROXIMATE ANALYSIS

MOISTURE

Occurrence of Moisture in Coal

The moisture in coal may be fundamentally subdivided into four categories — inherent moisture, surface moisture, hydration water of mineral matter, and decomposition moisture. Less fundamentally, we deal with total moisture, as-received moisture, air-dry loss moisture, and air-dried moisture.

Inherent Moisture

Theoretically, inherent moisture is that which a coal can hold when in equilibrium with an atmosphere of 100 percent relative humidity. Actually, it is determined at 96 to 97 percent relative humidity, for reasons discussed later. Such terms as capacity moisture and equilibrium moisture are used frequently with the same meaning, and bed moisture may be synonymous with inherent moisture under the proper conditions. The theory is that the inherent moisture is held in the capillaries of the coal substance and the vapor pressure of the moisture is somewhat less than that of water on a plane surface. More energy is therefore required to expel this moisture than to evaporate water from the surface of the coal particles. Coal containing only true inherent moisture will have no moisture on the particle surfaces.

Surface Moisture

Surface moisture is that which occurs on the surface of the coal particles in excess of the inherent moisture. It is also called free water or extraneous water. Its vapor pressure is that of water for the existing temperature.

Hydration Water of Mineral Matter

Hydration water is part of the crystalline structure of the inorganic material of the mineral matter of coal. It occurs mainly in the clayey or shaly portions of the mineral matter and is actually part of the crystal lattice of the clay minerals. This water requires considerable energy for its expulsion. For example, in kaolinite the water of hydration is not released until a temperature of at least 500° C is reached.

Decomposition Moisture

Decomposition moisture is produced from the organic portion of the coal through thermal decomposition, which has been shown to be negligible up to a temperature of approximately 200° to 225° C. It is not commonly dealt with in ordinary coal analysis because the temperatures for expelling moisture are below these values.

The less fundamental kinds of moisture are defined largely on the basis of the methods used for their determination. *Total moisture* is the total amount of surface and inherent moisture in the coal at the time of analysis. If sampling is properly carried out, the total moisture should be representative of the lot from which the coal sample was taken. *As-received moisture* is usually synonymous with total moisture — that is, the as-received moisture is the total surface and inherent moisture present in the coal at the time of analysis. *Air-dry loss moisture* is that which is lost during "air-drying." This in itself is not a fundamental or significant type of moisture for interpretation of analyses. The *air-dried moisture* is that moisture present in the analysis sample after air-drying, and is not a significant value for interpretation but, rather, a step in analytical procedure.

Methods for Determining Moisture in Coal

So many methods for determining moisture in coal have been described that only the more commonly used methods are discussed here.

Probably the most common approach for moisture determination is through weight loss upon heating. There are many modifications of this procedure, including what is known as the indirect approach (weight loss) and a direct approach involving the release of the moisture and its subsequent absorption and weighing. Moisture loss is accomplished in air or in an inert atmosphere such as nitrogen. In the United States, one indirect method is used in which the loss in weight is taken as the measure of the moisture in the coal. At the Illinois Geological Survey, the loss is accomplished in a stream of air, but it may be done in an inert atmosphere, such as nitrogen, to prevent possible oxidation of the coal during drying. For most Illinois coals, not enough oxidation takes place in an air atmosphere to vitiate results beyond acceptable tolerances. However, we have encountered coal, particularly weathered and outcrop coal, for which it has been necessary to use an inert atmosphere during heat drying for moisture determination.

Probably the most accurate heat drying method involves the expulsion of moisture at 105° C to 110° C, its absorption in a weighing tube containing a desiccant, and measurement of the moisture released as gain in weight in the absorption bulb. Any adsorbed gas, such as methane, that may be present in the coal is thus excluded from the moisture value. Some coals are so gassy that error due to loss of gas during drying is appreciable, but in the United States this is not necessarily a serious problem.

Another means of determining moisture is the distillation method. The coal sample is suspended in an organic liquid, such as xylene or toluene, is distilled, and the distillate is collected in a graduated tube. The water and the organic liquid separate, and the volume of water may be measured. The weight percentage of moisture in the coal is obtained through calculation. This method lessens errors due to oxidation and gas loss. Its particular advantage lies in giving better moisture results for low-rank coals, such as subbituminous and lignitic coals. In general, values are somewhat higher than in the weight-loss method. Both methods probably give values for inherent moisture plus surface moisture.

Unfortunately, there is no reliable direct method for determining surface moisture because there is no sharp line of demarcation between inherent and surface moisture. Theoretically, it should be possible to estimate surface moisture by determining both total and inherent moisture and considering any positive difference (total minus inherent) as surface moisture. Conventional methods are available for determining total moisture, and various procedures have been proposed for determining inherent moisture. For example, Dulhunty (1947) proposed that surface moisture be expelled through controlled vaporization and the retained inherent moisture be determined by drying the sample at 105° C in a current of dry nitrogen. Dunningham (1944) removed surface moisture with blotting paper and determined the remaining inherent moisture. Schmidt and Seymour (1945) proposed that surface moisture be determined directly through the change of specific gravity of absolute alcohol when it was mixed with coal. Several other methods, dependent on dilution of various chemical reagents by the coal moisture, have been proposed but all are subject to error.

Inherent moisture is probably best determined by the equilibration method. A value for inherent moisture so obtained, together with a total moisture value, will permit estimation of surface moisture. While this approach is not perfect, it is believed the best available at present.

Equilibrium moisture (ASTM, 1966) is determined by bringing a sample of coal into equilibrium with an atmosphere of 96 to 97 percent relative humidity at 30° C. The amount of moisture retained in the coal at equilibrium is then determined by weight loss when the coal is heated.

The determination of hydration water of mineral matter is not simple, and therefore is not common in ordinary coal analysis. In the United States 8 percent of the determined ash is used to represent the hydration water of coal mineral matter. In Europe and in England 9 percent is more commonly used. Not long ago a French engineer proposed (Kreyenbuhl, 1957) a method for estimating water of hydration based on analytical data

such as calorific and hydrogen values, with extrapolation to arrive at a moisture value. His analyses are made on fractions of progressively increasing specific gravity in which the percentage of shaly portion is increased more and more in the heavier fractions.

Various other approaches to the determination of moisture in coal have been tried, among them electrical methods. An attempt also has been made to titrate the water directly with the Karl Fisher reagent. However, as far as I know, these methods have not been very successful.

Difficulties and Precautions

So many difficulties arise in the determination of coal moisture that it is impossible to discuss all of them. However, the following comments are offered.

Routine Moisture Value

Determining the usual routine moisture value (the so-called 105° to 110° C moisture) presents several problems. Some of these, together with suggested precautions for minimizing them, follow.

Loss or gain of moisture may occur during the actual taking and handling of the original sample. To counteract this, sample handling at the sampling site should be kept to a minimum.

Composite sampling is not very reliable if too long a time elapses between the taking of the component increments. Moisture may evaporate from the coal in the sample container and condense on the walls of the container. It is almost impossible to redistribute this moisture uniformly into the coal sample. In case such condensation is unavoidable, it may be minimized in the laboratory by drying both sample and container and determining the moisture loss of both. The total loss may be considered representative of the original moisture content of the coal in question. However, for reliable moisture determination, it is better to avoid long-time composite sampling.

Changes in the moisture content may occur during reduction of the gross sample to the analysis sample. Heat generated in the pulverizer used for sample grinding will cause moisture loss. In addition, if the relative humidity of the atmosphere in which analysis sample preparation is accomplished is appreciably different from that existing at the time of gross sampling, changes may occur in the moisture content of the sample. To overcome these difficulties, pulverizing equipment that generates the least possible heat should be used. The sample also should be air-dried prior to laboratory grinding and riffling. Air-drying will bring the coal sample to equilibrium with the laboratory atmosphere so that no change in moisture content will occur during analysis sample preparation. If this is done, however, the air-dry loss moisture and the analysis sample moisture must be determined and properly combined to give the total moisture value.

Oxidation — gain of weight by the sample as it takes up oxygen — may take place. This gain may offset part of the loss of moisture that occurs during weight loss and make results misleadingly low. To minimize oxidation, overheating the sample should be avoided or an inert atmosphere such as nitrogen should be used during drying. The distillation method probably keeps oxidation to a minimum.

Another precaution to be observed with reference to oxidation is alternate heating and cooling of the sample. Although it is necessary to attain constant weight in the weight-loss method, too many alternate heatings and coolings probably enhance oxidation and should be avoided.

When the distillation method is employed, a difference in the boiling points of the organic liquids used may affect the result obtained. The two most commonly used liquids are toluene and xylene whose boiling points differ appreciably (110° and 140° C). While there is some disagreement as to whether use of the two liquids gives values significantly different, I would recommend the use of toluene whose boiling point is close to the temperature specified in the method achieving weight loss by heat.

Equilibrium or Inherent Moisture

Difficulties also arise in determining the equilibrium or inherent moisture of the coal.

If complete equilibrium is not achieved, erratic results will be obtained. It is therefore important to allow enough time for equilibrium to be reached.

A sudden lowering of controlled temperature or evacuation of the desiccators may re-

sult in the condensation of moisture on the coal. To prevent error from this source, enough time must be allowed for equilibrium to be reestablished after evacuation of the container, or the determination must be made at atmospheric pressure in an inert atmosphere.

Over-drying of the coal before equilibration may result in low values for equilibrium moisture because the coal may be rendered incapable of attaining its original moisture-holding capacity. To prevent over-drying, the sample should be kept wet prior to equilibration.

Any oxidation of the sample will, as in the tests for routine moisture, result in low moisture values. A nitrogen atmosphere will prevent oxidation.

As any mechanical loss of the sample will completely vitiate results, precautions should be taken to prevent sudden pop-outs caused by a change of pressure such as may occur when atmospheric pressure is restored to the evacuated equilibration vessel.

Water of Hydration of Mineral Matter

Water of hydration of the mineral matter in coal is not commonly determined in regular coal analysis. Normally, the average value of 8 percent of the ash is used for this purpose.

Surface Moisture

All of the above-mentioned difficulties and means by which they can be minimized are applicable when surface moisture is estimated by subtracting equilibrium moisture from total moisture.

Uses and Limitations of Moisture Data

The moisture value is one of the most important determinations made in coal analysis. It has so many uses and limitations, as commonly determined, that only a brief series of comments can be made.

Air-Dry Loss Moisture

The chief purpose of air-drying coal is to bring it into equilibrium with the atmosphere of the room in which fine grinding is to take place, to prevent changes in moisture during grinding. Air-drying is also the first step in the determination of total moisture in coal by the aforementioned two-stage method.

Certain limitations should be placed on the use of air-dry loss moisture values. The air-dry loss moisture is probably not of fundamental significance in characterizing coal. It has been used as a value for excess or surface moisture, but this is an incorrect usage. The air-dry loss moisture as a percentage of the total coal moisture is variable. For different samples it may vary from 25 to 90 percent of the total moisture. Furthermore, the percentage is not characteristic of the particular rank of coal at hand, for it may vary widely for coals of the same rank.

Temperatures used for air-drying vary rather widely. In some places air-drying is accomplished at room temperature, while in the United States the ASTM specifications call for air-drying at temperatures 10° to 15° C above room temperature. Very warm climates may make it impossible to conduct air-drying below temperatures of 40° to 45° C. A temperature not exceeding 25° C probably would be best in order to prevent oxidation during air-drying, due to the fact that oxidation is a chemical reaction that depends on, among other things, duration of contact and temperature. However, at such a temperature air-drying might take more time, thus allowing more oxidation to take place instead of less. The practice in the United States of using a temperature of 10° to 15° C above room temperature might accelerate oxidation, but as the time needed for proper air-drying is shortened, this should compensate, at least in part, for any increase in oxidation due to the higher temperature. Temperatures much above 40° to 45° C, however, should not be used for air-drying.

Air-Dried Moisture

The air-dried moisture value is essential to the determination of total moisture by the two-stage method. It is also used to calculate other analytical items to the dry basis. However, the air-dried moisture value probably has no significant meaning and should not be used for any other purpose.

Total or As-Received Moisture

The total moisture is used for calculating other items to the as-received basis. In the

commercial buying and selling of coal, contracts are often based primarily on rigid specifications of as-received calorific values. To obtain these values, dry calorific values are converted to the as-received basis by means of total moisture values. Any error in the latter can be serious from the monetary standpoint. For example, for a coal with a calorific value of 12,000 Btu on a moisture-free basis, an error of 1 percent absolute in the total moisture will make a difference of 120 Btu in the as-received calorific value. When thousands of tons of coal are involved in a contract containing penalty and bonus clauses, a sizable amount of money could be involved.

Total moisture is also of definite importance in assessing and controlling commercial processing of coal. It is used to determine the amount of drying needed to meet a given moisture specification and to gauge what and how much dust-proofing and freeze-proofing agents should be added. Total moisture values, which include the inherent or equilibrium moisture plus any surface moisture that may be present, are essential in connection with handling and pulverizing coal. Surface moisture is particularly troublesome in these operations. For instance, the presence of only 0.5 percent surface moisture may cause coal to stick in a chute. A wet coal is difficult, and in extreme cases may actually be impossible, to pulverize.

The total moisture of coal as charged to coke ovens can be a guide for controlling bulk density and estimating yields of coke. The more moisture present in the coal, the less carbon can be charged, and the coke yield is correspondingly lowered. High moisture also requires more heat for vaporization and longer coking cycles, with the result that production is decreased.

In any scheme of preheating coal prior to coking, the total moisture of the coal affects both the technique and economics of the process.

Equilibrium Moisture

Equilibrium moisture is used for calculating moist mineral-matter-free calorific values for the rank classification of the high-volatile bituminous coals. It is also useful in estimating surface moisture as the difference between equilibrium moisture and total moisture.

Theoretically, the moisture-holding capacity of coal is the amount of moisture that the coal could hold at 100 percent relative humidity without any moisture present on the external surfaces of the coal particles. Furthermore, it should be the inherent moisture of the coal as it occurs in the unexposed seam, because the relative humidity in the immediate vicinity is probably at or near 100 percent. However, due to physical difficulties it is not feasible to try to make determinations at 100 percent relative humidity; equilibrium moisture determinations are therefore made at 96 to 97 percent relative humidity and used as moisture-holding capacity or inherent moisture values.

A high relative humidity must be used in the equilibration test to approach the theoretical holding capacity at 100 percent. It has been shown (Rees, Wagner, and Tilbury, 1948) that the banded ingredients, vitrain, clarain, durain, and fusain, vary considerably in the amount of moisture they will hold when in equilibrium at various relative humidities. Particularly pertinent in this respect is the fact that fusain holds relatively little moisture at humidities below about 90 percent, which is another reason for using a high relative humidity in the equilibrium moisture determination on whole coal. In work done at the Illinois Geological Survey many years ago, it was found that equilibrium moisture determined at 96.7 percent relative humidity and 30° C averaged about 95 percent of the extrapolated 100 percent value; when determined at 97.7 percent relative humidity it averaged about 96 percent of the 100 percent value (Rees, Reed, and Land, 1939). These values were based on data for the three ranks of coal occurring in Illinois, high-volatile A, B, and C bituminous coal.

Surface Moisture

Surface moisture data are used in connection with drying, handling, pulverizing, dust proofing, and freeze proofing of coal.

Surface moisture values can probably be no better than estimates. There are indications that the values obtained by the alcohol dilution method or the blotter paper absorption method include part of the inherent moisture. Even surface moisture values estimated by subtracting equilibrium moisture

from total moisture are not absolute. Unfortunately, no sharp line of demarcation exists between surface and inherent moisture. It is commonly thought that the inherent moisture is contained in the pores or capillaries of the coal. There is also evidence that the capillaries vary in diameter and that the vapor pressures of moisture in different sized capillaries vary. The water in these capillaries is believed to wet the capillary walls and form a concave meniscus. The vapor pressure of a liquid with a concave meniscus is less than that of a liquid with a plane surface or a convex meniscus. Hence, the vapor pressure of the inherent moisture is lower than that of surface moisture and more energy is necessary to remove it. The larger the capillary, the less concave the meniscus and the greater the vapor pressure, until in the largest capillaries the vapor pressure approaches that of the plane surface.

Another limitation applicable to the estimation of surface moisture by difference is the failure of equilibration at 96 to 97 percent relative humidity to attain the theoretical 100 percent value. Because of this a somewhat high surface moisture value may be obtained. As mentioned earlier, the equilibrium moisture determined in the range of 96.7 to 97.7 percent relative humidity has been found on an average to be about 95 to 96 percent of the 100 percent value. One might ask why the 96.7 percent value is not calculated to the 100 percent basis by using the 95 to 96 percent average. This average does not seem safe to use as it is derived from values ranging from 69 to 100 percent.

Water of Hydration

The prime use for water of hydration values is in the calculation of mineral matter from analytical items. Specifically, it is used to correct ash to the form of hydrated minerals in the mineral matter calculation.

In the absence of a simple and reliable method for determining water of hydration, the average value of 8 percent is commonly used in the United States. It is based on rather complicated investigations and is an average of values ranging from 2 to 3 percent to 15 to 20 percent. A further discussion of the derivation of this value will be found in the section on ash.

ASH

Occurrence of Ash in Coal

Ash, as determined in coal analysis, may be defined as the noncombustible residue that remains when coal is burned. It does not occur as such in the coal, but is formed as the result of chemical changes that take place in the mineral matter during the ashing process.

The ash-forming materials occurring in coal are of two kinds, extraneous mineral matter and "inherent ash." The extraneous mineral matter is composed of clayey or shaly constituents, calcite, pyrite or marcasite, and minor components such as inorganic sulfates, chlorides, and fluorides. "Inherent ash" includes inorganic elements combined with the organic part of the coal, the origin of which probably was the plant material from which the coal was formed. It is usually of insignificant quantity as far as the determined ash is concerned.

Determination of the Quantity of Ash

Methods

The regular combustion method for ash determination involves igniting a weighed sample of coal to constant weight. The determination has been carried out at temperatures varying from about 685° to 850° C. The ASTM standard procedure specifies that this determination be made at a temperature of 700° to 750° C. At the Illinois Survey the latter generally is used. Different rates of heating also have been used, and a slower rate is particularly important for coals containing large amounts of both calcite and pyrite. The slow heating rate used at the Illinois Survey involves heating the sample slowly to 750° C and continuing heating at that temperature until constant weight is attained. The purpose of slow heating is to effect elimination of as much sulfur as possible, probably as SO_2, before calcite decomposes.

The rapid combustion method of ashing involves burning a weighed sample of coal, usually in a combustion tube, in an oxygen atmosphere at a high temperature. Such a determination may be completed in from 7

to 10 minutes, whereas the ASTM regular combustion method requires 1½ hours as the minimum.

Changes in Mineral Matter During Ashing

The change that takes place in clayey and shaly materials during ashing is the loss of water of hydration. The most common clay mineral occurring in this portion of the mineral matter is kaolinite, which loses its water of hydration somewhere between 500° and 600° C.

Heating brings about a loss of carbon dioxide from calcium carbonate, leaving calcium oxide, which reacts to some extent with SO_3 to form calcium sulfate. It also may combine to some degree with silica to form calcium silicates.

Pyrite is converted to Fe_2O_3 and oxides of sulfur, probably predominantly sulfur dioxide. However, some of the SO_2 apparently is oxidized to SO_3 and reacts with calcium oxide to form calcium sulfate, which is harder to decompose by heat and remains in the ash.

The organically combined inorganic elements that may be retained in the ash probably are converted to oxides during the ashing process.

Difficulties and Precautions

The main difficulties encountered in the determination of ash are sulfur retention, incomplete oxidation of pyrite, and incomplete expulsion of carbon dioxide from calcite. All of these factors contribute to erratic results. Means of minimizing them are listed below.

1. Use a slow heating rate, particularly for coals containing relatively large amounts of both calcite and pyrite, to reduce the amount of sulfur retained as sulfate in the ash. However, complete elimination of sulfur does not appear to be possible by slow heating. For coals containing small amounts of calcite and pyrite, however, slow heating is probably quite adequate and, depending on the precision required, it may be satisfactory for those containing moderate amounts of these troublesome minerals.

2. Determine SO_3 in the ash and correct the ash to the SO_3-free basis. This is probably the most precise procedure that could be used. However, because it requires the SO_3 determination, it is not frequently used in routine analysis.

3. Maintain adequate circulation of air through the furnace to achieve complete oxidation of the iron and sulfur and sweep out the SO_2 formed.

4. Heat to constant weight to insure complete expulsion of CO_2 from calcite.

Ash Analysis—Composition

Preparation of Ash

In preparing coal ash for complete analysis, it has been considered necessary to try to prevent retention of sulfur in the ash. The difficulty is that indefinite amounts of sulfur are retained, which throws the complete analysis off unless all other items are corrected to the SO_3-free basis. In the past at the Illinois Geological Survey, the 60-mesh coal was first burned in air at about 750° C for 1½ to 2 hours. This was the procedure for a large sample of about 50 to 100 grams. After the burning in air, the ash was ground to minus 200-mesh and then burned in oxygen at 800° to 850° C for approximately 2 hours. This was done to make sure all of the iron was oxidized to the ferric state and all of the organic material was expelled. The burning in air was accomplished at a slow rate. In some instances only 1-gram samples of coal are ashed in duplicate, the two duplicates being combined for the ash analysis. When only 1 gram of coal is burned, experimental data indicate that a smaller amount of sulfur is retained, but it is not eliminated completely.

Analytical Methods and Difficulties Involved in Their Use

Conventional Wet Methods for Silicates

A rather large sample, possibly a minimum of 10 grams of ash, is needed for analysis by conventional wet methods. The methods are classical ones that have been described by

such analysts as Hillebrand (1919), Washington (1930), and Lundell (Hillebrand and Lundell, 1953). The difficulties that may be encountered in these methods are those of silicate analysis, primarily in analytical technique. Included are incomplete separations, incomplete dehydration of silica, and incomplete washing of precipitates.

Flamephotometer

Of late years the flamephotometer has been used for determining sodium and potassium. Earlier, the J. Lawrence Smith method, which is a well known procedure, was used. The determination of sodium and potassium by flamephotometry is not a trouble-free or fool-proof approach. Interference by other elements may take place, and the operator must be constantly aware of this possibility, know what elements may interfere, and take precautions to minimize or eliminate such interference.

Rapid Methods

Rapid methods include colorimetric and volumetric procedures and have the very definite advantage of requiring a considerably smaller sample of ash than does the procedure involving wet methods. Schemes of analysis of this type have been fully described by investigators both in the United States (Gibson and Ode, 1962) and in England (Archer, Flint, and Jordan, 1958). When colorimetric determinations are used, the difficulties of colorimetry enter in. Small samples are used and large factors are often necessary for calculation of results. In general, colorimetric methods normally are used for small amounts of material and their use for determining major constituents may be questionable unless great care is used.

X-ray Fluorescence

X-ray fluorescence is comparatively new and offers real promise for ash analysis. It requires extensive calibration. Preparation of test specimens may be difficult and must be very precise. Furthermore, interferences are possible and must be sensed and taken care of.

Emission Spectrography

Emission spectrography is used to some extent, but it is usually considered more useful for determining minor constituents than major ones. When the precision requirements are not too rigid it can be used to good advantage. The same types of difficulties mentioned for flamephotometry and X-ray fluorescence analysis are applicable.

Mineral Matter Evaluation

Evaluation by Calculation

Several formulas have been proposed for calculating mineral matter in coal, but probably the two most used are the Parr formula (1932) and the King, Maries, Crossley formula (1936). The Parr formula is the one most used in the United States, whereas the other is commonly used in Great Britain and Europe. In the Parr formula the percentage of mineral matter (% M M) is derived from the formula:

$$\% \ M\,M = 1.08\,A + 0.55\,S$$

where

A = percentage of ash in coal

S = percentage of total sulfur in coal.

The King, Maries, Crossley formula is:

$$\% \ M\,M = 1.09\,A + 0.5\,S_{Pyr} + 0.8\,CO_2 -$$
$$1.1\,SO_3 \text{ in ash } +$$
$$SO_3 \text{ in coal} + 0.5\,Cl$$

where

A = percentage of ash in coal

S_{Pyr} = percentage of pyritic sulfur in coal

CO_2 = percentage of mineral carbon dioxide in coal

SO_3 in ash = percentage of SO_3 in ash

SO_3 in coal = percentage of SO_3 in coal

Cl = percentage of chlorine in coal.

In making mineral matter calculations by means of these formulas, the percentage values for the various analytical items are expressed as decimal fractions. For example, if the ash value were 8.0 percent it would

be expressed in the calculation as 0.08. The Parr formula is considerably simpler and requires less analytical data than the other formula. Possibly the latter will provide slightly more precise mineral matter values, but it is questionable whether this small improvement in precision will justify the additional analytical work necessary.

In view of the fact that the Parr formula is the one used in the United States, its derivation will be discussed here. First, the fact that ash, as commonly determined in coal analysis, is not a direct measure of mineral matter must be kept in mind. Coal mineral matter is composed primarily of shaly material (including aluminum silicates and silica), pyrite, and calcite. Changes take place in these constituents during the ashing process. The shaly material loses water of hydration, pyrite (FeS_2) is converted to Fe_2O_3 and oxides of sulfur, and calcite loses carbon dioxide. It is therefore necessary to correct these analytically determined items to restore them to the forms in which they occurred originally in the coal. In this connection attention is called to the work of Gilbert Thiessen (1934). The following derivations are similar to those of Parr and Thiessen. As the amount of calcite in coal mineral matter is generally relatively small, a correction for the loss of carbon dioxide is usually negligible and is ignored in these derivations.

In the ash portion of the formula, the amount of ash is multiplied by 1.08 to restore the water of hydration lost during ashing. The lost water of hydration is considered as 8 percent of the mineral matter and, while this is an average and somewhat arbitrary value, it is possible to substantiate its reasonableness by using ash analysis data. Such substantiation is offered in table 1 for 19 Illinois coals and 11 high-volatile coals from the eastern United States (Selvig and Gibson, 1956). To derive the data in this table the following assumptions and factors were used:

1. Coal mineral matter is composed of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), silica ($SiO_2$), and pyrite ($FeS_2$).

2. The water of hydration of the coal mineral matter is solely that of the kaolinite.

3. When more SiO_2 is present than is required for the kaolinite, the Al_2O_3 is considered to be the factor determining the amount of kaolinite present, assuming that all of the Al_2O_3 is present as kaolinite. Therefore, kaolinite (k) may be calculated (coal basis) as follows:

$$k = Al_2O_3 \times \frac{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}{Al_2O_3} =$$

$$Al_2O_3 \times \frac{258.14}{101.96} = Al_2O_3 \times 2.5321.$$

4. The excess SiO_2 equals the total SiO_2 in the coal minus the SiO_2 of the kaolinite as calculated in point 3 above. The SiO_2 of kaolinite (k) is calculated as follows:

$$SiO_2 \text{ of } k = k \times \frac{2SiO_2}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} =$$

$$k \times \frac{120.18}{258.14} = k \times 0.4655.$$

5. Pyrite (FeS_2) may be calculated from Fe_2O_3 (coal basis) as follows:

$$FeS_2 = Fe_2O_3 \times \frac{2FeS_2}{Fe_2O_3} = Fe_2O_3 \times \frac{240.0}{159.7} =$$

$$Fe_2O_3 \times 1.5026.$$

6. The amount of water of hydration (see assumptions 2 and 3) may be calculated from the Al_2O_3 (coal basis) as follows:

$$H_2O \text{ of hydration} = Al_2O_3 \times \frac{2H_2O}{Al_2O_3} =$$

$$Al_2O_3 \times \frac{36}{101.96} = Al_2O_3 \times 0.3535.$$

7. After the above calculations have been made, the percentage of water of hydration equals

$$\frac{H_2O \text{ of hydration}}{\text{mineral matter}} =$$

$$\frac{H_2O \text{ of hydration}}{k + \text{excess } SiO_2 + FeS_2} \times 100.$$

TABLE 1—DERIVATION OF VALUES FOR WATER OF HYDRATION OF COAL MINERAL MATTER

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
		Al_2O_3 (%)		SiO_2 (%)		Fe_2O_3 (%)		Kaolinite (%) (Al_2O_3 in coal x 2.5321)	Water of hydration (%) (Al_2O_3 in coal x 0.3535)	SiO_2 in kaolinite (%) (col. 9 x 0.4655)	Excess of SiO_2	FeS_2 in coal (%) (Fe_2O_3 in coal x 1.5026)	Mineral matter in coal (Sum of cols. 9, 12, 13)	Water of hydration (%) $\frac{Col. 10}{Col. 14}$ x 100
I.S.G.S. Lab. No.	Ash in coal (%) (dry)	In ash	In coal	In ash	In coal	In ash	In coal							
					ILLINOIS COALS									
C-10142	10.9	18.12	1.98	34.76	3.79	23.38	2.55	5.01	0.70	2.33	1.46	3.83	10.30	6.8
10143	12.1	18.44	2.23	32.10	3.88	22.68	2.74	5.65	0.79	2.63	1.25	4.12	11.02	7.2
10144	10.9	18.25	1.99	31.58	3.44	23.44	2.55	5.04	0.70	2.35	1.09	3.83	9.96	7.0
10291	12.1	16.71	2.02	39.73	4.81	21.86	2.65	5.11	0.71	2.38	2.43	3.98	11.52	6.2
10292	12.0	18.20	2.18	44.58	5.35	22.17	2.66	5.52	0.77	2.57	2.78	4.00	12.30	6.3
10293	11.2	16.96	1.90	42.70	4.78	27.33	3.06	4.81	0.67	2.24	2.54	4.60	11.95	5.6
C-10603	9.9	17.54	1.74	42.18	4.18	14.86	1.47	4.41	0.62	2.05	2.13	2.21	8.75	7.1
10604	9.0	17.36	1.56	41.31	3.72	11.23	1.01	3.95	0.55	1.84	1.88	1.52	7.35	7.5
10605	9.9	15.44	1.53	34.18	3.38	17.88	1.77	3.87	0.54	1.80	1.58	2.66	8.11	6.7
11621	11.4	18.67	2.13	32.29	3.68	27.74	3.16	5.39	0.75	2.51	1.17	4.75	11.31	6.6
11622	11.5	17.61	2.03	30.53	3.51	27.00	3.11	5.14	0.72	2.39	1.12	4.67	10.93	6.6
C-14	18.2	13.83	2.52	25.26	4.60	38.71	7.05	6.38	0.89	2.97	1.63	10.59	18.60	4.8
C-10288	10.1	25.79	2.60	51.54	5.21	25.31	2.56	6.58	0.92	3.06	2.15	3.85	12.58	7.3
10289	7.5	27.89	2.09	55.24	4.14	7.14	0.54	5.29	0.74	2.46	1.68	0.81	7.78	9.5
10290	9.7	22.30	2.16	47.97	4.65	6.04	0.59	5.47	0.76	2.55	2.10	0.87	8.44	8.7
C-15	16.7	17.04	2.85	33.94	5.67	32.75	5.47	7.22	1.01	3.36	2.31	8.22	17.75	5.7
C-10617	8.4	23.76	2.00	39.14	3.29	15.40	1.29	5.06	0.71	2.36	0.93	1.94	7.93	9.0
11203	8.6	20.81	1.79	41.34	3.56	33.09	2.85	4.53	0.63	2.11	1.45	4.28	10.26	6.1
18	9.7	20.81	2.02	36.91	3.58	35.07	3.40	5.11	0.71	2.38	1.20	5.11	11.42	6.2
												Average for Illinois coals		6.89
U.S. Bur. Mines No.						EASTERN COALS*								
39985	11.5	28.2	3.24	47.2	5.43	10.3	1.18	8.20	1.15	3.82	1.61	1.77	11.58	9.9
39986	12.2	29.6	3.61	49.5	6.04	10.3	1.26	9.14	1.28	4.25	1.79	1.89	12.82	10.0
39993	13.0	29.9	3.89	49.7	6.46	10.2	1.33	9.85	1.38	4.59	1.87	2.00	13.72	10.1
39994	12.7	30.2	3.84	50.4	6.40	9.9	1.26	9.72	1.36	4.52	1.88	1.89	13.49	10.1
39995	12.6	29.7	3.74	49.6	6.25	10.3	1.30	9.47	1.32	4.41	1.84	1.95	13.26	10.0
40002	12.1	29.3	3.55	47.3	5.72	12.0	1.45	8.99	1.25	4.18	1.54	2.18	12.71	9.8
16018	7.9	24.2	1.91	38.4	3.03	22.4	1.77	4.84	0.68	2.25	0.78	2.66	8.28	8.2
40542	10.8	28.8	3.11	54.6	5.90	10.8	1.17	7.87	1.10	3.66	2.24	1.76	11.87	9.3
36656	9.7	38.4	3.72	46.8	4.54	7.9	0.77	9.42	1.32	4.39	0.15	1.16	10.73	12.3
37636	8.8	18.0	1.58	36.4	3.20	18.9	1.66	4.00	0.56	1.86	1.34	2.49	7.83	7.2
39957	6.1	32.9	2.01	58.7	3.58	3.8	0.23	5.09	0.71	2.37	1.21	0.35	6.65	10.7
												Average for Eastern high-volatile coals		9.78
												Average for all coals		7.95

* From Selvig and Gibson, 1956.

Values for Al_2O_3, SiO_2, and Fe_2O_3 used in the calculations were determined and reported as percentages of ash. They were converted to the coal basis by use of ash values for the coals involved.

Some of the assumptions involved in these calculations are not entirely true. For example, the presence of sodium, potassium, magnesium, and calcium compounds, as well as compounds of iron other than FeS_2, has been ignored. However, the purpose of the calculations has been to demonstrate the derivation and to offer some support for the 8 percent water of hydration value used in the Parr formula. As the additional constituents are usually present in relatively small amounts and the 8 percent value is an average and somewhat arbitrary value, the calculations probably are adequate.

In column 15 of table 1, in which calculated values for the percentage of water of hydration are listed, it is evident that these values differ considerably for different coals. The average for the 19 Illinois coals is 6.89 percent and for the Eastern high-volatile coals 9.78 percent. The average for all coals listed is 7.95 percent, which is very close to the value of 8.0 percent used in the Parr formula. It might appear more logical to use a value of 7 percent for Illinois coals and 10 percent for the Eastern coals, but the Parr formula was designed to apply to a wide range of coals and the 8 percent value seems reasonable.

The differences involved when the 7, 10, and 8 percent values are used in the Parr formula for calculating calorific value on the "unit coal" (dry, mineral-matter-free) basis are shown below for a coal of 13,000 Btu, 8.0 percent ash, and 2.0 percent sulfur, all values on the moisture-free basis. The formulas and results for the three calculations are:

$$\frac{13000 - 5000\,S}{(1.07\,A + 0.55\,S)} = \frac{12900}{0.9034} = 14279 \text{ Btu}$$

$$\frac{13000 - 5000\,S}{1 - (1.10\,A + 0.55\,S)} = \frac{12900}{0.9010} = 14317 \text{ Btu}$$

$$\frac{13000 - 5000\,S}{1 - (1.08\,A + 0.55\,S)} = \frac{12900}{0.9026} = 14292 \text{ Btu.}$$

The widest difference shown (between the first and second equations) is 38 Btu, which is well within the permissible difference (50 Btu) between duplicate determinations for calorific value made on the same sample, in the same laboratory, by the same analyst.

In the 0.55 sulfur portion of the Parr formula, the sulfur correction is a combination of two corrections which Parr based on the assumption that all of the coal sulfur was present as FeS_2. The first correction is to restore the Fe_2O_3, as weighed in the ash, to FeS_2 as it occurred in coal. In the ashing process, three oxygen atoms replace four sulfur atoms, or, on a weight basis, 48 parts of oxygen replace 128 parts of sulfur. This means that only three-eighths of the weight of the sulfur (48/128) as it originally occurred in the coal has been accounted for by oxygen in the ash. It is then necessary to add to the ash five-eighths sulfur (eight-eighths minus three-eighths) to restore the Fe_2O_3 to FeS_2.

The second correction for sulfur is made to exclude Fe_2O_3 from the ash. The reason for this is that only the shaly portion of the coal mineral matter is hydrated—FeS_2 is not—and therefore only that portion of the ash derived from the shaly material should have the hydration factor applied to it. The Fe_2O_3 molecule in the ash is equivalent to four sulfur atoms in the coal—160/128, or 10/8. Therefore, by subtracting 10/8 of the coal sulfur from the ash it is converted to the Fe_2O_3-free condition.

The Parr formula can be completed by combining the factors previously discussed to arrive at the mineral matter ($M\,M$) value:

$$M\,M = A + 5/8\,S + 0.08\,(A - 10/8\,S) =$$
$$A + 0.08\,A + 25/40\,S - 4/40\,S =$$
$$1.08\,A + 21/40\,S = 1.08\,A + 0.525\,S.$$

Although Parr assumed that all the coal sulfur was present as FeS_2, he knew that this was not true. To correct for this assumption, however, it would be necessary to determine the amount of pyritic sulfur in the coal. His formula is designed for use with a minimum of analytical data, particularly the data most commonly determined in coal analysis. To partially compensate for the sulfur not in the pyritic form and to simplify the calculation,

he changed the fraction 21/40 to 22/40, or 0.55, and the final equation became

$$M M = 1.08 A + 0.55 S.$$

Evaluation by Direct Determination

Radmacher and Mohrhauer (1955) published a method for the direct determination of mineral matter in coal. With a few modifications this method now has advanced to the status of a Draft ISO Recommendation in the International Organization for Standardization. The principle of the method, as stated, is as follows:

> The coal sample is partially demineralized by treatment with hydrochloric and hydrofluoric acids under such conditions that the coal substance remains unaffected. The loss in mass of the coal due to the acid treatment is recorded and the insoluble part of the mineral matter is determined by ashing the partially demineralized coal. In addition, the iron content of the ash is determined so that the pyrite present in the extracted coal can be calculated. The amount of hydrochloric acid absorbed by the coal substance is also determined.

The method has not been widely used in the United States, but data obtained and submitted by investigators in other countries seem to support its reliability. A few years ago samples of two Illinois coals were sent to Dr. Mohrhauer in Germany for such determinations. The samples were also analyzed in the Survey laboratory and mineral matter was calculated by the Parr formula. The two values were then compared. For one of the coals the values checked fairly well, but for the other coal the agreement was not as good as might be desired.

Uses of Ash Data

Coal is cleaned by various processes to reduce its sulfur and ash content. The ash content of raw coal must be known for determining the best cleaning method, and the ash content of the cleaned product must be found to gauge the adequacy of the cleaning process. The ash value is also the analytical item most commonly used for assessing the adequacy of sampling procedures. It is one of the values normally specified in coal contracts. The supplier must know the ash content of the coal he proposes to supply, and the purchaser must determine whether the coal received meets contract specifications. Both steam coal and coking coal are analyzed for ash value.

In the commercial pulverization of coal, the amount and nature of ash plays a part in the selection of pulverizing equipment, in the amount of power necessary for desired pulverization, and indirectly in the actual cost of pulverization.

The amount of ash in coking coal is an indication of the amount of ash that will be present in coke made from the coal. In commercial coking this is important in two ways; first, the more ash in the coal, as charged to the coke oven, the lower the production of usable carbon; second, the more ash in the coke the more fluxing limestone must be added in the blast furnace to take care of the ash, and the production of hot metal is lowered.

In combustion, the higher the ash content, the lower the heat obtainable from the coal. Furthermore, the problems of efficient combustion are increased as are those of handling and disposing of the larger amount of ash produced during combustion.

In the American system of classifying coals by rank, certain of the parameters involved are calculated to the mineral-matter-free basis. The ash value is used in these calculations.

The composition of coal ash is involved in such practical problems as clinkering, boiler-tube slagging, and removal of "dry" ash, as well as "wet" ash, from a slag tap furnace.

Limitations of Ash Data

The indefinite amount of sulfur that may be retained in the ash may reduce the reliability of ash values and values for other ash components.

The ash value does not give an exact picture of the noncombustible material occurring in coal. It is a somewhat empirical quantity, yet useful for practical applications.

The relation of ash composition to clinkering, boiler-tube slagging, and other high-temperature behaviors of ash is very complex and thus not subject to exact interpretation. Coal ash is a mixture of various components that change when heated and probably interact chemically to form new compounds. Ash is

TABLE 2—CONSTITUENTS OF VOLATILE MATTER

Constituents of volatile matter	Origin
Water	Organic material Water of hydration of mineral matter
Hydrogen	Organic material
Carbon dioxide	Organic material Mineral carbonates
Carbon monoxide	Organic material
Hydrogen sulfide	Organic sulfur Pyrite
Organic sulfur compounds, such as thiophene, organic sulfides	Organic sulfur compounds
Organic compounds composed of carbon and hydrogen, such as CH_4, C_2H_6, C_3H_8; olefins, such as C_2H_4; aromatic compounds, such as benzene, toluene, or naphthalene	Organic material
Oxygen-containing organic compounds	Organic material
Tar (complex mixture of higher molecular weight organic compounds)	Organic material
Chlorine (probably as HCl or NH_4Cl)	Probably inorganic chlorides
Ammonia (NH_3)	Organic nitrogen compounds

considered a multicomponent system difficult to study and for which behavior is hard to predict.

VOLATILE MATTER

Occurrence of Volatile Matter in Coal

Volatile matter, as commonly determined in coal analysis, does not occur as such in coal. Rather, it is composed of thermal decomposition products formed during heating under rigidly specified conditions. Some of the constituents of coal volatile matter and the materials from which they originated are shown in table 2.

The volatile matter of coke, as analytically determined, has been reported as being composed of water, oxides of carbon, hydrogen, and methane. The water and oxides of carbon are the result of chemisorbed oxygen or of products of decomposition of a complex of carbon, hydrogen, and oxygen, and are formed after carbonization, chiefly during quenching and storage. Gas analyses of volatiles distilled under vacuum at 965° C from dried cokes indicate that water and carbon dioxide are the chief products evolved up to 700° C. Above that temperature increasing amounts of carbon monoxide, hydrogen, and methane are given off. Inasmuch as water and carbon dioxide compose the major portion of the volatile matter lost up to 700° C, and inasmuch as these are formed chiefly after carbonization has been completed, the coke volatile matter that is ordinarily determined is probably not the true volatile matter of coke.

Methods for Determination

Volatile matter is determined by an empirical weight-loss method that involves heat and requires close adherence to detailed specifications. The two chief factors that influence results are temperature and rate of heating. Such details as the type of heating equipment, size, shape, and material of sample holders (crucibles), and the type of sample holder support used may influence both temperature and rate of heating. These details are thus of real importance in method specification. Methods commonly in use are classified as rapid heating or slow heating.

ASTM Regular Method

The regular ASTM method involves rapid heating of a 1-gram sample at 950° ± 20° C for exactly 7 minutes. Platinum crucibles with closely fitting covers and a vertical electric furnace (Fieldner furnace) are specified,

although Meker burner heating is permitted for certain applications.

ASTM Modified Method

The same equipment is specified for the ASTM modified method as for the ASTM regular method. However, a considerably slower heating rate is specified. The specified top temperature is $950° \pm 20°$ C. Use of the modified method is particularly recommended for noncaking coals and chars.

British Single Crucible Method

The British single crucible method specifies a cylindrical quartz sample crucible with a closely fitting cover. The crucible is placed in a refractory ceramic mantle with three short legs which permit it to be slightly raised from the furnace floor, thus slowing the heating rate. The heating rate may be reduced still further by inserting two discs of asbestos paper in the heating mantle on which the crucible is placed. A muffle furnace is specified for heating. A heating time of 7 minutes at $925°$ C is specified. By means of this assembly a heating rate between the ASTM regular and modified methods is achieved. It is recommended for all coals, chars, and cokes. The method is not often used in the United States but is favorably viewed by the International Organization for Standardization.

Franco-Belgian Double Crucible Method

The Franco-Belgian double crucible method specifies a small, inner crucible of porcelain for the sample with a cover of the same material, and a larger outer quartz crucible and cover. The two crucibles are separated by a layer of crushed wood charcoal. The sample is heated in this assembly at $960° \pm 10°$ C for 20 minutes in a muffle furnace. Judging from comparative results, the heating rate obtained is approximately the same as that obtained in the ASTM modified method. The Franco-Belgian method is applicable to all coals, chars, and cokes. It is not used in the United States but has been considered by the International Organization for Standardization.

A comparison of results obtained by these four methods was reported by Rees, Coolican, and Pierron (1957). They found that high-est values were obtained with the ASTM regular method, the next highest with the British single crucible method, and the lowest with the ASTM modified and Franco-Belgian methods, which two showed good agreement.

Difficulties and Precautions

Sparking is caused by the escape of incandescent particles from the test crucible during the determination. The particles are probably carbon, and their loss will result in volatile matter values that are too high. Excessively fine grinding of the sample to be tested for volatile matter may increase the tendency towards sparking. A large proportion of minus 100- to 200-mesh material in the test sample should be avoided. Air-dried coal (coal containing some moisture) should be used for the determination, not "bone dry" coal. Use of a method that specifies slower heating also will help to reduce sparking.

Popping is a sudden explosive type of behavior that may be vigorous enough to blow off the crucible cover. It is caused by a sudden release of gases formed during the decomposition of the coal. If a sample contains appreciable moisture, popping may result because of the sudden expulsion of the moisture and of other volatile decomposition products. A method of determination with a slower heating rate will help to reduce popping. Determinations should be repeated until two are obtained in which no popping occurs.

In an empirical determination such as evaluation of volatile matter, any deviation from the rigid specifications of temperature, duration of heating, or rate of heating, may produce a distorted result. Equipment specifications, such as size, shape, weight and material of crucibles, crucible supports, and heating equipment are very important in attaining the specified temperature and especially the proper rate of heating. Therefore, the analyst should first be thoroughly familiar with the specifications of equipment and procedure and then follow them exactly.

Because thermocouples may break or change without visual evidence, and calibration of pyrometers may change, equipment must be checked frequently because any drift from proper standardization will produce erratic results. Probably no two furnaces have

exactly the same heating characteristics. It is necessary, therefore, to check them occasionally, especially when a new furnace is put into operation or when any change is made in an older furnace.

As heating rate influences volatile matter values it is necessary to calibrate equipment to achieve a satisfactory and reproducible heating rate, particularly when the ASTM modified method is used. In the Survey laboratories this has been accomplished by using the Fieldner furnace into which the crucible with the sample is lowered by a manually operated mechanical device. This device is so calibrated that the position of the crucible and, thus, the heating rate are reproducible. The procedure, which meets ASTM specifications but is more detailed, was developed to obtain satisfactory volatile matter results on a series of chars under study. It also has been found satisfactory for noncaking coals, weathered coals, and low-temperature cokes when the regular method for determining volatile matter was not satisfactory. The heating rate attained by this procedure is shown in figure 1.

Any oxidation of the sample results in a loss of carbon and makes the volatile matter values too high. Oxidation is increased when the crucible covers do not fit tightly, permitting an influx of air and loss of additional carbon as volatile oxides. Crucibles and covers must be kept properly shaped to insure a proper fit. Oxidation is probably not very serious in determination of volatile matter in coal because the rapid release of rather large amounts of gases will prevent, to a large extent, the entry of air into the crucible. For cokes of low-volatile matter content it could be more serious. Addition of a few drops of a volatile substance like benzene may, in some cases, help to prevent appreciable oxidation.

Moisture (105° to 110° C) is included in the volatile matter as determined and it must be separately determined and deducted. The analyst must make this moisture determination as accurate as possible.

Loss of carbon dioxide may render volatile matter values too high, particularly for coals containing large amounts of mineral carbonates. For some coals it may be advisable to determine the mineral carbon dioxide and correct the volatile matter for it. However, for most coals in the United States the carbonate content is so low that no significant error results if that step is eliminated.

Water of hydration is not properly a part of volatile matter but it is normally included as such because of the impossibility of accurately differentiating it from other volatile matter constituents. Not much can be done about this until a satisfactory method for its determination is developed.

Some years ago, in determining volatile matter in high-temperature coke, analysts at the Illinois Survey obtained values that appeared to be too high. Normally the volatile matter of high-temperature coke is approximately 1.0 percent; the values obtained at the Survey were about 2.0 to 2.5 percent. It had been the practice to burn out the crucibles between determinations by heating them to redness in air in an open flame. About that time we heard that another laboratory had obtained similar high values, and that they had achieved more normal results simply by wiping out the crucibles with a cloth between determinations. We tried this, and obtained lower results more in line with normal values. We found we were able to vary results at will depending on whether crucibles were burned out or wiped out. We did clean crucibles periodically by boiling them in hydrochloric acid and by fusing bisulfate in them. However, after thorough cleaning, we made two or three runs with coke in the crucibles before accepting results.

Our explanation of this behavior follows. Coke ash contains iron, and iron alloys with platinum. When the platinum crucibles are burned out between determinations, this iron may be oxidized to Fe_2O_3, which may react with carbon with loss of CO or CO_2. Results for the volatile matter in a sample of coke will then be high. When crucibles are simply wiped out between determinations, there is no opportunity for the iron to be oxidized and no extra loss of carbon occurs.

Uses of Volatile Matter Data

In certain coal classification schemes—for example, in the international classification system of the Economic Commission for Europe—the volatile matter value is used as a parameter. In the ASTM classification system used in the United States, indirect use of volatile matter values is made.

Volatile matter values also are used for selecting coals and for determining in what
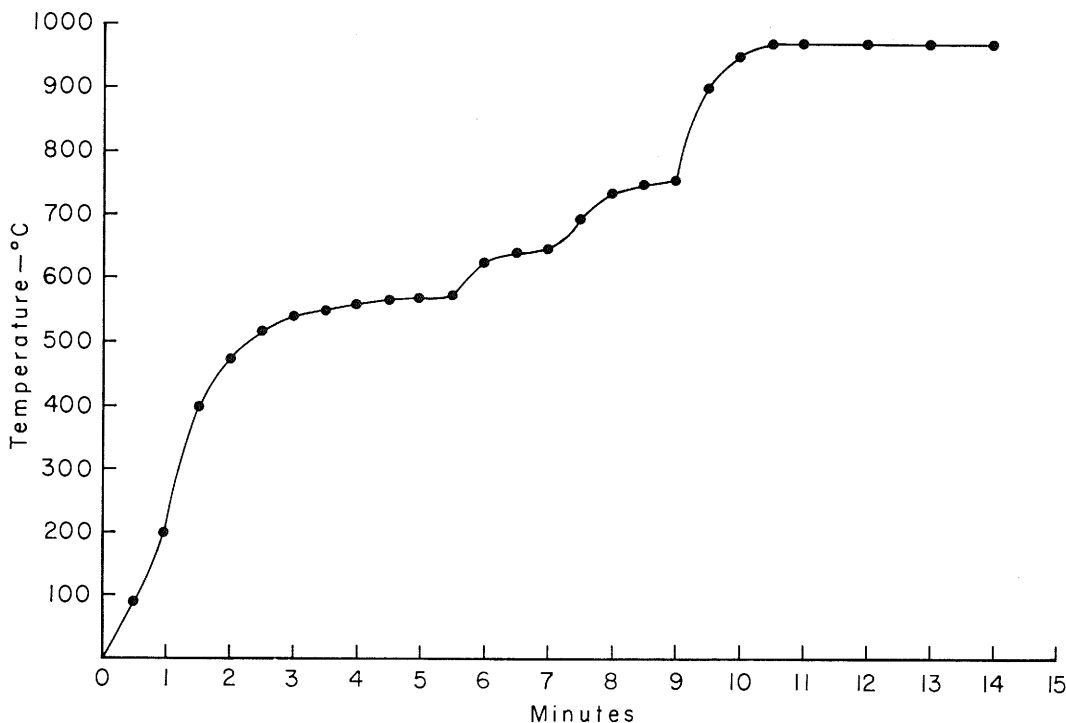
FIG. 1—Rate of heat rise in Illinois Geological Survey equipment for volatile matter determination by the ASTM modified method.

proportions they are to be blended for satisfactory coking. They are useful, too, in estimating yields of coke and by-products to be obtained in carbonizing coal. In addition, the volatile matter value is used to evaluate extent of coking. For metallurgical coke, a volatile matter content of 1 to 1.5 percent is desirable. For high-temperature domestic coke, a somewhat higher volatile matter content, approximately 2.5 to 4.0 percent, is advantageous. For low-temperature coke the more common volatile matter content ranges from 9 to 13 percent; for char, the volatile matter content may range from approximately 11 to 25 percent, depending on what use is contemplated for the char.

Volatile matter values are important in choosing proper burning equipment for specific coals or in the selection of the best coal for burning in a specific type of equipment. They are also useful in selecting proper conditions for efficient combustion. Volatile matter values also have been the basis of smoke ordinances that set top limits of permissible volatile matter for the purpose of reducing smoke nuisance.

The volatile matter content also is important in the selection of processes and conditions for gasification and liquefaction of coals.

Limitations of Volatile Matter Data

The empirical nature of methods for determining volatile matter, and the complexity of the constituents of coal that undergo thermal decomposition during the determination, make somewhat wide tolerances necessary for repeatability and reproducibility. This limits the closeness of interpretation of results.

Values obtained by the ASTM modified method may be lower by 1 to 3 percent absolute than those obtained by the ASTM regular method. This is unfortunate, as results obtained by the two methods are thus not directly comparable. The methods employing slower heating rates appear to be applicable to a wider range of coals and chars than is the regular ASTM method, but results so obtained would not be comparable with many of the published values. Hence, there is reluctance in the United States to adopt one method of slower heating rate as the standard.

FIXED CARBON

Fixed carbon is the carbon residue that remains after determination of the volatile matter. It does not occur as such in coal, but is the result of thermal decomposition. The fixed carbon value is arrived at by difference —that is, it is obtained by subtracting from 100 the sum of moisture, ash, and volatile matter values.

Difficulties and Precautions

Because the fixed carbon value is arrived at by difference, the difficulties involved and ways of minimizing them are the same as those involved in the determination of moisture, ash, and volatile matter.

Uses and Limitations of Fixed Carbon Data

Fixed carbon data are used in classification, combustion, and carbonization of coals. The fixed carbon, however, probably carries with it small percentages of nitrogen, sulfur, hydrogen, and possibly oxygen as adsorbed or chemically combined material.

Dry, mineral-matter-free fixed carbon values are used as parameters in the ASTM coal classification system.

Fixed carbon is a measure of the solid combustible material that remains in the burning equipment after the volatile materials of the coal have been expelled. It is one of the values used in calculating the efficiency of burning equipment. For the best efficiency calculations, ultimate carbon values probably are more reliable.

Fixed carbon is used as an indication of the yield of coke to be expected when coal is coked. The fixed carbon plus ash represents, approximately, the yield of coke produced.

ULTIMATE ANALYSIS

CARBON AND HYDROGEN

Occurrence of Carbon and Hydrogen in Coal

Inasmuch as carbon and hydrogen are usually determined in one operation, they are considered together in this discussion. Neither carbon nor hydrogen occur to any extent in their elemental form in coal. Both are present in the organic material of the coal, which is made up of complex organic compounds with both aromatic and aliphatic portions. The aliphatic portions are probably side chains or alkylene bridges attached to the ring structures of the more aromatic portions. Carbon also occurs as inorganic carbonate, primarily calcite. In addition to its occurrence in the organic material, hydrogen is also present in water, both chemically combined as water of hydration of the shaly portion of the coal mineral matter and non-chemically combined as the ordinarily determined moisture of coal.

Methods for Determination

Fortunately, methods for determining carbon and hydrogen involve quantitative chemical reactions. Carbon is converted by combustion to carbon dioxide and hydrogen to water under carefully controlled conditions, and these products are absorbed in appropriate reagents. Carbon and hydrogen are then calculated from the weight gained by the reagents.

The methods used for determining carbon and hydrogen differ from those used for determination of many other values in the size of sample analyzed, the equipment and reagents used, and in the conditions of combustion. Available methods are discussed briefly below.

In the ASTM standard method, a 0.2-gram sample is normally used. Regular macro-scale equipment is specified. A combustion tube contains a section of heated copper oxide in wire form to complete the combustion. Lead chromate or silver are specified for removing oxides of sulfur, and silver for removing chlorine. Various reagents are used in the purification and absorption trains, two particularly good ones being anhydrone for absorbing water and ascarite for absorbing carbon dioxide. A temperature of 850° to 900° C is specified for burning the sample. In some instances when more exact results are desired, oxides of nitrogen formed during combustion may be removed from the combustion products prior to absorption of the carbon dioxide. For this purpose manganese dioxide, or in some cases lead dioxide, may be used.

For the high-temperature combustion method, a coal sample of approximately 0.5 gram (accurately weighed) is used, and combustion is accomplished, without copper oxide, with a rapid flow of oxygen at a temperature of from 1250° to 1350° C. Macro-scale equipment is used. Sulfur oxides and chlorine are removed by silver. The reagents specified in the ASTM method are used in the purification and absorption trains. Manganese dioxide may be used for removal of oxides of nitrogen.

Semimicro- and micro-methods are not used as often for coal analysis as are the macro-methods. Basically, they are the same as the macro-methods except that smaller samples and smaller equipment are used.

Difficulties and Precautions

Incomplete combustion, with resulting incomplete conversion of carbon to carbon dioxide and of hydrogen to water, will cause inaccurate results. A proper flow of oxygen must be maintained through the system, the temperature of the combustion must be at the proper level, and enough time must be permitted to allow complete combustion.

During analytical combustion, sulfur burns to oxides that must be removed before they are absorbed in the reagent used for carbon dioxide absorption. As stated previously, lead chromate is used to remove the sulfur oxides, and silver is used for removing both sulfur oxides and chlorine. The temperature of the furnace section covering the lead chromate and/or the silver must be maintained carefully and must not be too high. When lead chromate is used, a very high temperature may make it fuse with the quartz combustion tube and cause it to crack. When silver is used, an excessively high temperature will cause decomposition of silver sulfate or silver chloride and release the sulfur or chlorine, which will then be absorbed in the carbon dioxide absorption bulb.

Chlorine in coal is released during the combustion analysis and must be removed before it can be absorbed in the carbon dioxide bulb.

Nitrogen of the coal is converted, to some extent, to oxides of nitrogen during combustion. As the oxides are acidic in nature, they will be absorbed in the carbon dioxide absorption bulb, and a small amount may be absorbed in the water absorption bulb, possibly through solution in the water held in this particular bulb. Considerable work was done in the United States several years ago to determine whether errors due to oxides of nitrogen would be large enough to make their removal necessary. Data were obtained in five different laboratories that indicated the hydrogen value would not be greatly influenced but that the carbon value could be influenced by as much as 0.35 percent. However, it was the opinion of those working on the project that this error would not be significant in the ultimate analysis for commercial purposes. Hence, removal of nitrogen oxides was not made mandatory in the national standard.

Organic carbon is burned to carbon dioxide in the combustion analysis. At the temperature of combustion, carbon dioxide is also released from inorganic carbonates. In coals in which the carbonates are high, it may be necessary to determine the carbonate carbon and correct the combustion carbon for it.

Whenever a combustion tube is put into use after being provided with new packing or standing idle for some time, it is necessary to condition it before making an actual determination. Conditioning usually consists of passing oxygen through the system until the absorption bulbs on successive weighings do not vary appreciably. In some instances it may be advisable to burn a sample in the system, during which the combustion products are passed through the absorption train, but the absorption bulbs need not be weighed. The whole system must be in good equilibrium before an actual determination is attempted, or nonconcordant results will be obtained.

In the determination of carbon and hydrogen, volatile matter is released from the sample. If the unit used for the actual burning of the sample is heated too rapidly, volatile matter may be released suddenly and some of it may pass unburned through the entire system and be lost. It is therefore necessary to conduct the analysis at a rate slow enough to allow all combustible products to be burned and converted to carbon dioxide and water.

At the exit end of the combustion tube and the entry to the water absorption bulb, water may condense and not be completely swept into the absorption bulb. Some means of

heating this particular portion of the system to a point where the water will be vaporized should be provided.

All connections in the apparatus used must be made gas tight before analysis is begun.

Uses of Carbon and Hydrogen Data

Carbon and hydrogen values are used as parameters in certain proposed classification systems. They are also used in the calculation of heat values for checking determined calorific values and for calculating heat balances in boiler efficiency tests. They are probably most often used, however, in research investigations.

Limitations of Carbon and Hydrogen Data

Two factors that limit the reliability of carbon values, as normally determined, are high-carbonate carbon and oxides of nitrogen, both of which make carbon values too high. Hydrogen values, too, are usually high because of the inclusion of the hydrogen of moisture and water of hydration.

In the combustion analysis, because the hydrogen of the organic matter, of the moisture, and of the water of hydration are included, the hydrogen value is too high for the most precise use. For example, if it is to be used for calculating calorific value, it is obvious that the hydrogen of moisture and of water of hydration can contribute no heat value because it is already oxidized to water. It is possible to make a reasonably reliable correction for the hydrogen of moisture by subtracting one-ninth of the determined moisture from the determined hydrogen. But a correction for the hydrogen of the water of hydration found in the shaly portion of the coal mineral matter is more difficult. As a direct determination of water of hydration is not simple and not commonly made, the correction is made by calculation. For this purpose the average value of 8.0 percent for water of hydration may be used. Thus ash, as determined, multiplied by 0.08 will give an estimate of the water of hydration, and one-ninth of that figure will give the correction to be subtracted from the determined hydrogen. A correction so derived will not necessarily be precise because the average

value of 8.0 percent for water of hydration may not be exact for a particular coal.

The inclusion of the hydrogen of moisture and water of hydration in the hydrogen value is common practice for the "as-analyzed" and "as-received" bases. However, hydrogen values on the "dry coal" basis are commonly corrected for the hydrogen of moisture. Normally, no corrections for the hydrogen of the water of hydration are made.

NITROGEN

Occurrence of Nitrogen in Coal

Nitrogen is unique in that it is the only element in coal that occurs entirely in the organic matter. The nitrogen organic compounds appear to be stable and are thought to be heterocyclic, or possibly complex noncyclic, compounds. The original material may have been, at least in part, both plant and animal protein. Plant alkaloids, chlorophyll, and other porphyrins have their nitrogen in cyclic structures stable enough to have withstood changes during coalification, and they may have contributed to the nitrogen content of coal. If proteins, which are made up of amino acids, were precursors of coal nitrogen, it would seem logical to suspect the presence of amino nitrogen in coal. However, there is little evidence of this in bituminous coals. While proteins are known to decompose with loss of nitrogen as nitrogen gas and ammonia, it is possible they may have reacted with carbohydrates to form very stable nitrogen compounds and thus have contributed to the nitrogen content. Further information regarding the occurrence of nitrogen in coal can be found in the extensive summary by Kirner (1945).

Methods for Determination

Methods for determining nitrogen in coal are based on quantitative chemical reactions. The nitrogen must first be liberated, in measurable form, from the organic material in which it occurs. For this purpose it may be converted to ammonia (NH_3) or to elemental nitrogen (N_2). Various methods designed to accomplish one or the other of these conversions are available.

Probably the most commonly used method for determining nitrogen in coal and coke is the Kjeldahl macro-method by which nitrogen is converted to ammonium sulfate through digestion with hot concentrated sulfuric acid. Various modifications of this procedure are used, depending primarily on the catalyst employed. The current ASTM standard method specifies mercury as the catalyst and is known as the Kjeldahl-Gunning method. The use of other catalysts, such as mercuric sulfate with selenium, mercuric selenite, and cupric selenite, is permitted. Varying amounts of potassium sulfate, depending on the catalyst used, are added to raise the boiling point of the sulfuric acid. After the digestion mixture has been made alkaline with sodium or potassium hydroxide, ammonia (NH_3) is expelled by distillation, caught in acid, and the determination completed by titration. Both the acid-alkali and boric acid finishes are permitted.

The Kjeldahl semimicro-method differs primarily from the macro-methods in that smaller sized equipment is used, smaller samples are analyzed (0.1 gram compared with a 1.0-gram sample for the macro-methods), and ammonia is separated from the alkalinized digestion mixture by steam distillation. The same catalysts may be used, although it is more common to use a mixed catalyst in this method. The acid-base finish may be used, but the boric acid finish is more common.

The Dumas method, or a modification thereof, has been used to some extent for determining nitrogen in coal but not as widely as the Kjeldahl methods. In the Dumas method the coal nitrogen is converted to elemental nitrogen by combustion in the presence of copper oxide in an atmosphere of carbon dioxide. After removal of interfering gases, the volume of elemental nitrogen is measured and its value, on a weight percentage basis, is obtained by calculation.

Difficulties and Precautions

In the Kjeldahl methods, incomplete conversion of the nitrogen to ammonium sulfate will lead to low results. Pyridine carboxylic acids may be formed that are resistant to decomposition. Thus in the digestion step of these procedures, the mixture may become clear but have a light straw color. If digestion is stopped at this point not all of the nitrogen will be recovered. To secure complete conversion, digestion of the sample must be continued well beyond the straw-colored stage. An additional 1½ to 2 hours of digestion may be required. For bituminous coals and coals of lower rank from 4 to 6 hours may be required to accomplish complete digestion, and for anthracite and coke 12 to 16 hours may be required. Finer grinding of these more resistant materials will shorten the digestion time. The addition of chromic acid (Cr_2O_3) to the digestion mixture will help speed the digestion of coke.

In the distillation step, a too-rapid distillation rate may result in carry-over of the alkaline digestion mixture, which will ruin the determination. Addition of a few boiling stones, such as mossy zinc, will help to prevent carry-over.

When mercury or a mercury compound is used as the catalyst in the Kjeldahl digestion, it may form a stable complex with ammonia and make it impossible to recover all of the coal nitrogen. To prevent this, a solution of sodium or potassium sulfide and sodium or potassium hydroxide is added for the distillation. The mercury is precipitated as mercuric sulfide so that its interference is prevented. It is not necessary to remove this precipitate prior to distillation. When cupric selenite is used as the catalyst, addition of sulfide is not necessary.

In the Dumas method, incomplete conversion of the coal nitrogen to nitrogen gas may cause results to be low. In the combustion of some coals in an atmosphere of carbon dioxide, a small amount of coke may be formed. This coke may retain enough nitrogen to make results erroneous.

Some investigators have indicated that modification of the Dumas method may be necessary to account for all the nitrogen in coal and more particularly for the nitrogen in coke. Any coke, whether it be formed during the combustion of coal in carbon dioxide or whether it is the original sample being analyzed, may retain a little nitrogen. The suggested modification provides for further burning of the sample in an oxygen atmosphere following its combustion in carbon dioxide. If this is done, provision must be made for removing excess oxygen before it enters the nitrometer in which the nitrogen

is measured. One way to remove the oxygen is to place a section of reduced copper in the combustion tube.

It has been reported that gases other than nitrogen, such as methane and carbon monoxide, may be formed and measured as nitrogen. Substances containing a large number of methyl groups may contribute these gases. While some investigators have reported that serious error may arise, others have found that the Kjeldahl and unmodified Dumas methods give results in close agreement when applied to solid fuels. If gases such as methane and carbon monoxide are formed in large enough amounts to affect the nitrogen value seriously, it might be necessary to analyze the evolved gases completely and thus arrive at the actual nitrogen content.

Uses of Nitrogen Data

Of all the items determined in an ultimate analysis, the nitrogen value probably is the least used in practical application. Certainly there is a relation between the nitrogen content of coal and the ammonia formed during coking of the coal. However, as far as I am aware, the nitrogen value of coal cannot be used for reliable estimation of the amount of ammonia that will be produced during carbonization. This is due to the many variables involved, such as other nitrogen compounds formed and varying conditions. In combustion, the coal nitrogen probably is converted primarily to elemental nitrogen, ammonia, and possibly small amounts of nitrogen oxides. It is possible that these may play some part in atmospheric pollution.

Nitrogen data are used in comparing coals and in research. When the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination. Nitrogen data probably have no other important uses.

Limitations of Nitrogen Data

Certain combinations of nitrogen do not respond to the Kjeldahl methods. For example, nitro-nitrogen is not included unless provision is made to reduce the nitro group to ammonia. This has been accomplished by adding a metal such as zinc or an organic compound to the digestion mixture. The Dumas method does include nitro-nitrogen. The nitro group does not occur naturally in coal, but in certain research samples of oxidized coals or in humic acids that have been prepared by nitric acid oxidation of coal, nitro-nitrogen may exist.

Semimicro-methods appear to be satisfactory for determining nitrogen in coals of bituminous and higher rank, even though they may be banded. However, there is evidence that the nitrogen of the lower-rank subbituminous and lignitic coals is not so uniformly distributed, which makes it difficult to obtain the reliable small samples used in such methods. For this reason it is advisable to limit the use of semimicro-methods to the analysis of the higher rank coals.

TOTAL SULFUR

Occurrence of Sulfur in Coal

Sulfur occurs in coal as part of the organic matter and in inorganic combination in pyrite, marcasite, and sulfates.

In the organic matter, sulfur probably occurs in very stable compounds. There is evidence that these compounds are cyclic in nature. This sulfur is commonly referred to as organic sulfur, and it probably is uniformly distributed throughout the pure coal material.

The inorganically combined sulfur in pyrite or marcasite (FeS_2) is commonly known as pyritic sulfur and generally is not uniformly distributed in the coal. Rather, it may be disseminated as very fine crystals throughout the organic material, or it may occur as layers or slabs in the coal.

A small amount of sulfur may occur in coal as sulfate, such as calcium sulfate or iron sulfate. In fresh coals the amount is normally small, but it may be more plentiful in oxidized or weathered coals.

While a few reports claim that free sulfur occurs in coal, no firm evidence of such occurrence has come to my attention. In one instance, a sample of coal containing some light yellow material thought to be free sulfur was brought to the Survey laboratory, but analysis of the material showed it to be primarily iron sulfate.

Methods for Determination

Because of the variety of forms of sulfur present in coal and their relative stability, methods for determining total sulfur must involve drastic conditions. The sulfur is generally converted to sulfate for final determination, and this may be done by several methods, four of which are explained following.

In the Eschka fusion method, the coal sample is combined with Eschka mixture, which is composed of sodium carbonate and magnesium oxide, and the combination is then heated at approximately 800° to 850° C in an oxidizing atmosphere to convert the coal sulfur to sulfate. The sulfate is then leached from the mixture and determined either gravimetrically or volumetrically. The gravimetric determination is used at the Illinois Geological Survey.

In the bomb washing method, washings from a calorific value determination are oxidized with an oxidant such as bromine water in order to convert all sulfur to sulfate, and the sulfur determination is completed as in the Eschka method.

In the sodium peroxide bomb method, the coal sample is mixed with sodium peroxide and fused in a special bomb. With this procedure a closed system is obtained and there is no chance for oxides of sulfur to escape. Following successful fusion, the sample is taken into solution and the sulfur determined as in the other two methods.

In the high-temperature combustion method, the coal sample is burned at a temperature of 1250° C or higher, and the products of combustion are absorbed in a proper reagent. Frequently these products are absorbed in hydrogen peroxide, which effects further oxidation of sulfur to sulfate in case this may be necessary. The sulfate is then determined either gravimetrically or volumetrically.

Difficulties and Precautions

Due to the nonuniform distribution of the pyritic portion of total sulfur in coal, adequate sampling is complicated. It is often necessary to take many increments to make the gross sample representative of the lot in question. The number and size of increments will depend on how much total sulfur is present in the coal and on how uniformly it is distributed. Pyrite is both hard and heavy, and the pulverization and reduction of the gross sample from which the analysis sample is derived may be somewhat difficult. All of the pyrite must be ground to pass the particular sieve in use, and mixing must be thorough to avoid obtaining a nonrepresentative sample.

Failure to completely convert all the sulfur to sulfate will result in erratic values. It is necessary therefore to provide sufficient quantities of reagents, the temperature must be high enough, and enough time must be allowed to complete the conversion.

Inasmuch as sulfur normally is first oxidized to sulfur dioxide during analysis, some of it may be lost if precautions are not taken. When the Eschka method is used, the sample should be thoroughly mixed with Eschka mixture and a generous covering layer of the mixture should be placed over the fusion mix. This will help prevent loss of sulfur as sulfur dioxide. When the bomb washing method is used, the pressure of the bomb should be released slowly after the sample is burned in oxygen so that the sulfur dioxide will not be carried out of the bomb before it can be fixed for determination. In the high-temperature combustion method, the combustion products should be passed into an oxidant to secure complete conversion to sulfate.

Certain difficulties may arise in connection with the barium sulfate precipitate. It may be extremely fine and very difficult to filter off. To secure a barium sulfate precipitate that is easily filtered and readily washed, proper precipitation can be accomplished by adding barium chloride precipitant to the hot solution and stirring it vigorously. The mixture may then be placed on a hot plate or a steam bath and digested for some time to improve the filterability of the precipitate. The precipitate is then filtered off and washed several times with hot water to remove other materials that would cause values to be high. Barium sulfate is a rather strong adsorbing agent and will adsorb iron during the precipitation. When the iron content of the sample is high, it should be removed before the sulfate is precipitated.

The rate of combustion also affects the complete conversion of sulfur to sulfate. If burning and sweeping in the high-temperature combustion method are too rapid, difficulties may arise. It is possible that combustion products in a rapid efflux may pass through the system so quickly that they can-

not be completely absorbed. Consequently, some of the sulfur can be lost.

Uses of Total Sulfur Data

One of the chief purposes of cleaning coal is to reduce the total sulfur content. Sulfur values, therefore, must be available for use as a guide to successful commercial processing of coal.

During the burning of coal, sulfur is converted to oxides that may contribute to corrosion in the equipment, to slagging of the combustion or boiler equipment, and to atmospheric pollution. Sulfur data are therefore necessary for evaluation of coals to be used for combustion purposes.

Coke for metallurgical purposes should be low in sulfur content. Analysis to determine the sulfur value of the coal being coked and of the final coke is therefore required.

The sulfur of coal will appear in the gas produced by various gasification processes. Sulfur must be removed from this gas before it is used. Therefore, the sulfur content of the coal to be gasified must be known.

The total sulfur value is one of the items often specified in coal contracts. It also is determined for mineral matter calculations.

Limitations

Some limitations are involved in three of the analytical methods discussed—the Eschka fusion, bomb washing, and sodium peroxide bomb methods. In the laboratories at the Illinois Geological Survey, the bomb washing method has generally been found to give somewhat lower results than do the other two methods. However, it appears to give fairly reliable results for coals containing up to 3 or 4 percent sulfur. In our experience, the Eschka method gives good results up to 10 or 12 percent sulfur. The sodium peroxide method gives good results for all levels of sulfur, including values as high as 30 to 40 percent, which might occur in waste materials from coal washing plants. However, the sodium peroxide method requires a special bomb that must be handled very carefully to prevent an explosion.

Total sulfur data alone are not an adequate guide for reducing the sulfur content of coal by cleaning because only pyritic sulfur can be removed by specific gravity sep-

aration. Even the removal of pyritic sulfur depends on how it is distributed in the coal. If it occurs in very small crystals widely dispersed throughout the coal, it is difficult or even impossible to remove by specific gravity methods. When it is present in larger pieces it can be successfully removed by gravity separation. If the sulfur in coal is largely organic sulfur, the chances are that it cannot be reduced appreciably. Further discussion of the forms of sulfur in coal appears in a later section of this report.

The methods for determining total sulfur generally have good precision if properly used. Low repeatability and reproducibility tolerances are therefore specified by ASTM.

CHLORINE

Occurrence of Chlorine in Coal

Apparently there are two theories regarding the mode of occurrence of chlorine in coal. The first of these holds that chlorine occurs in coal almost entirely as inorganic chlorides. The most common ones thought to be present are sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals. The other theory is that chlorine is combined, at least partially, with the coal organic matter. Recently, Gluskoter and Rees (1964) attempted to learn more about the mode of occurrence of chlorine in Illinois coal. They concluded that most, if not all, of the chlorine in Illinois coal occurs as inorganic chlorides.

Methods for Chlorine Determination

The three best known analytical methods for determining chlorine in coal are the Eschka method, the bomb combustion method, and the high-temperature combustion method. The first two of these have received the most attention in the United States, and they have been used almost exclusively at the Illinois Geological Survey. All three methods have been considered as possible international standards. All of them accomplish complete destruction of the coal material, converting the chlorine to a determinable (ionic) form. In the Eschka method, decomposition of the coal is accomplished by fusion with Eschka mixture. In the bomb combustion method, the coal is decomposed in a bomb, usually

the one used in the bomb combustion method for determining calorific value. Decomposition takes place in an atmosphere of oxygen under pressure. In the high-temperature combustion method, the coal is burned in an oxygen atmosphere at about 1250° C, and the liberated chlorine is absorbed and determined volumetrically.

Comparison of results obtained by the three methods, particularly by workers in countries other than the United States, has indicated that they check closely. In some laboratories bomb equipment may not be available for use of the bomb combustion method. The Eschka method offers a reliable substitute procedure for determining chlorine and does not require so much expensive special equipment. Only one decomposition can be made at a time by the bomb method. The Eschka method, however, lends itself more readily to multiple determinations.

Difficulties and Precautions

In both the Eschka fusion method and the bomb combustion method it is possible to lose chlorine unless proper precautions are taken. In the Eschka method, loss of chlorine may be minimized by thoroughly combining the reagent with the coal sample and then placing a layer of reagent on top. Such precautions should ensure that all the chlorine is trapped during fusion. In the bomb combustion method, a little Echka mixture is normally mixed with the sample as fired in the bomb, and a little alkaline solution is placed in the bottom of the bomb to absorb the chlorine as it is released. The pressure in the bomb must be released slowly after decomposition in order to prevent the escape of chlorine.

The final titration of chlorine is frequently made by the Volhard method, in which a colorimetric end point is used. The end point is described as salmon pink and may be difficult for some operators to observe accurately. Use of a potentiometric titration may eliminate this difficulty because the end point is an electrical one.

An impure reagent can cause difficulties in the Eschka method. The reagent should be prepared by mixing chemically pure magnesium oxide and sodium carbonate of American Chemical Society specifications in the proper proportions. The specifications for magnesium oxide state that a loss on ignition of not more than 2 percent is permissible. I believe this to be important.

In some instances simple water extraction of the chlorine from coal has been attempted. Theoretically, if the chlorine occurs as inorganic chlorides, particularly those that are water soluble, the determination of total chlorine in coal could be made in this way. In the laboratories of the Illinois Geological Survey we have attempted to recover the chlorine by extracting it with warm water from a sample of coal ground to pass a 60-mesh sieve. A relatively low percentage of the total chlorine present was obtained. Finer grinding of the coal increased the amount of total chlorine extracted by water, but from a sample ground to 89 percent minus 5-micron size only about 69 percent of the total chlorine could be extracted with water. Water extraction is obviously an inadequate method for determining total chlorine in coal.

Uses and Limitations of Chlorine Data

While the chlorine in coal has been thought to contribute to slagging problems in high-temperature boilers, it seems possible that it may only indicate the presence of other elements that contribute more directly to these problems than the chlorine itself. For example, the chlorine may be present in coal as chlorides of such elements as sodium and potassium, which may play a larger part in slagging than the chlorine.

The chlorine in coal, or in products derived from coal, is known to cause corrosion to equipment in which the coal or its derivatives are used or processed, yet, to my knowledge, no precise quantitative relation of the amount of coal chlorine to corrosion has been established. For example, part of the chlorine in coal appears in the tar produced during carbonization of coal and it may cause serious corrosion to the tar refining equipment. However, there is apparently no definite information available on how much of the coal chlorine appears in the tar or how it relates quantitatively to the corrosion.

The chlorine value is useful in ultimate analysis when oxygen is estimated by difference. It may be included in the sum of the nonoxygen items determined, which sum is subtracted from 100 to give the oxygen value.

OXYGEN

Occurrence of Oxygen in Coal

Oxygen occurs in combination in the organic portion of coal and in inorganic combination in water, silicates, carbonates, oxides, and sulfates. The water involved includes the inherent moisture and the water of hydration of the mineral matter. The silicates are aluminum silicates found in the shaly portion of the coal, most of the carbonate is calcium carbonate, the oxides are mainly iron oxides, and the sulfates are mostly calcium and iron sulfates. Normally the amount of oxides and sulfates is low in fresh coal.

Methods for Oxygen Determination

For many years the oxygen of coal has been estimated by difference, i.e., the oxygen value has been obtained by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, chlorine, total sulfur, and ash from 100 percent. This method is still widely used, and in fact is the present ASTM standard method. In the coal analysis laboratory of the Illinois Geological Survey it is the currently used procedure.

More recently, considerable attention has been given to the direct determination of oxygen in coal, and progress has been made by ISO/TC 27 toward establishing an international standard method. While the direct determination of oxygen in pure organic compounds has been possible for several years, the application of such a method to a heterogeneous material like coal has involved many difficulties. Workers in Britain, Germany, the Netherlands, Poland, and Russia have developed methods that are being used. All of these methods are basically the same, being modifications of the Unterzaucher (1940) method published earlier. While there is some activity in this direction in the United States, we have as yet no recognized standard method.

Basically the methods in use today may be summarized as follows: the coal sample is pyrolyzed and the products of pyrolysis are passed over hot carbon which converts the coal oxygen to carbon monoxide (CO). The carbon monoxide is then oxidized to carbon dioxide (CO_2), which may be absorbed and determined volumetrically or gravimetrically.

Iodine pentoxide probably has been used most often to oxidize CO to CO_2, although mercuric oxide is used for this purpose in one method. When iodine pentoxide is used, the iodine released may be titrated with sodium thiosulfate. In another method provision is made for titrating the released iodine and for absorbing the carbon dioxide at the end of the train and determining it gravimetrically. By this means the analyst can check the volumetric and gravimetric results with each other.

Although the main principles of these methods are essentially the same, details vary considerably. The variations include details of equipment, temperatures of heated sections, reagents, procedures, and final determination steps. For example, most of the methods employ pure carbon at a temperature of 1100° to 1150° C for converting the coal oxygen to carbon monoxide, but one method specifies platinized carbon at approximately 900° C for this purpose.

The brief discussion of the basic principles involved in this determination may make it seem a relatively simple method, but there are several complicating factors involved.

Difficulties and Precautions

Estimation by Difference

In estimating oxygen by difference, errors in determined values for all other constituents included in the sum to be subtracted from 100 percent will be reflected in the oxygen value. These errors may be additive or partially compensating. It is therefore important that all determinations be as precise as possible.

In the combustion determination of hydrogen, the value obtained will include not only the organic hydrogen but also the hydrogen of any moisture, including the water of hydration of mineral matter. If only the oxygen determination of the coal organic material is needed, its estimated value will be somewhat low unless the hydrogen value is corrected for the hydrogen of moisture and water of hydration. Corrections for the hydrogen of the coal moisture may be made by calculation from the determined moisture value. Correction for the hydrogen of the water of hydration of the coal mineral matter also may be made by calculation, but it can be only an estimate because the water of hy-

dration is usually calculated rather than directly determined.

In the combustion determination of carbon, carbonate carbon is included and, unless appropriately corrected for, will contribute to a low oxygen value. Correction for the carbonate carbon can be calculated if a determined CO_2 value is available.

Direct Determination

In the direct determination of oxygen in coal organic material, the oxygen of moisture, of water of hydration, and of inorganic compounds all offer difficulties. The method itself is a complicated one requiring a special equipment assembly, dependable reagents, and careful technique. Provisions are made for eliminating, or at least minimizing, the interference of moisture, water of hydration, and oxygen-containing inorganic compounds. These provisions include preliminary thorough drying of the test sample to remove moisture and reduction of troublesome inorganic compounds (mineral matter) by specific gravity separation and by chemical treatment. The reduction of mineral matter largely eliminates difficulties due to the water of hydration, carbonates, and the complicating factor of the oxygen of inorganic compounds such as silicates, oxides, or sulfates. Theoretically, therefore, use of these provisions in the determination should permit the analyst to obtain directly a reasonably good value for the oxygen of the coal organic substance. Just what an oxygen value for coal should include, whether organic oxygen only or organic oxygen plus all or part of the inorganic oxygen, is somewhat complicated and will be discussed later.

Uses of Oxygen Data

In calculating heat balances for boiler efficiency studies, a correction is sometimes calculated for the oxygen content of the coal. In carbonization, a coal of high oxygen content is judged to be less suitable for making good metallurgical coke than one with a lower oxygen content. In gasification and liquefaction of coal, however, higher oxygen (lower rank) coals may be more reactive and thus easier to gasify or liquefy, but greater amounts of useless products may be obtained. In research, oxygen data, as a part of the ultimate analysis, help to characterize coal reserves and are useful in various technical investigations.

Limitations of Oxygen Data

Oxygen Estimated by Difference

The question of what should be included in the oxygen value is important, and some of the factors involved when oxygen is estimated by difference must be reconsidered. Hydrogen, as commonly determined in the analysis sample, includes the organic hydrogen plus the hydrogen of moisture and of water of hydration of the mineral matter. Thus a value is obtained that is too high for organic hydrogen, and it is responsible for a low organic oxygen value. Carbon determinations, too, include any carbonate carbon present, and use of this high value lowers the estimated organic oxygen value. The inclusion of both total sulfur and ash in the sum subtracted from 100 percent in estimating oxygen by difference also lowers the oxygen value because part of the sulfur may be retained in the ash and thus be included twice in the sum for subtraction.

With analytical data available for moisture, mineral CO_2, sulfur in ash, and calculated water of hydration (8 percent of ash) corrections can be made to the hydrogen, carbon, and ash values that will provide a somewhat better oxygen value by difference. In such circumstances oxygen might be estimated by a formula (in which all values are expressed as percent):

$$O = 100 - [(H - \frac{1}{9} H_2O - \frac{1}{9} H_2O \text{ of hydration}) + (C - \frac{12}{44} CO_2) + N + Cl + S_t + (ash - SO_3 \text{ in ash}) + H_2O]$$

where

H = determined hydrogen

H_2O = determined moisture (105° to 110° C)

H_2O of hydration = 8.0% of ash

C = determined carbon

CO_2 = determined mineral carbon dioxide

N = determined nitrogen

Cl = determined chlorine

S_t = determined total sulfur

ash = determined ash

SO_3 in ash = determined SO_3 in ash.

Application of the above corrections should provide an estimate of a somewhat more accurate oxygen value, which, if divided by 100 percent minus ash, will result in an ash-free oxygen value. Such a value may be useful, but it will not represent the actual percentage of oxygen in the coal as mined because ash as determined is not truly representative of the mineral matter as it occurs in coal. Changes to the mineral matter occur during the determination of ash and further corrections are necessary to obtain an oxygen value for the organic or combustible portion of the coal as mined. The following formula is offered for calculating such an oxygen value:

$$O = 100 - [(C - \frac{12}{44} CO_2) + (H - \frac{1}{9} H_2O -$$

$$\frac{1}{9} H_2O \text{ of hydration}) + N + S_t +$$

$$(ash - \frac{3}{8} S_p - SO_3 \text{ in ash} + CO_2 +$$

$$H_2O \text{ of hydration}) + Cl + H_2O]$$

where

C = determined carbon

CO_2 = determined mineral carbon dioxide

H = determined hydrogen

H_2O = determined moisture (105° to 110° C)

H_2O of hydration = 8.0% of ash

N = determined nitrogen

S_t = determined total sulfur

ash = determined ash

S_p = determined pyritic sulfur

SO_3 in ash = determined SO_3 in ash

Cl = determined chlorine.

Oxygen Determined Directly

In the direct determination of oxygen, assuming that the analysis sample has first had all moisture and mineral matter removed and that no change in the organic matter has occurred during removal of these interfering constituents, the oxygen value obtained should be that of the organic material of the original coal. This, then, should eliminate the necessity for making complicated analyses and calculations, such as those discussed for obtaining oxygen by difference.

Just what the hydrogen and oxygen values in coal should include should be considered briefly. In the United States system for classifying coals by rank, moist mineral-matter-free calorific values are used. The moisture is considered an integral part of the coal and, as such, it would seem logical to include the hydrogen and oxygen of moisture in the determined ultimate items. On the other hand, when ultimate analyses are used for heat balance calculations it would seem illogical to include the hydrogen and oxygen of moisture in reported values. The magnitude of differences involved in uncorrected hydrogen values is shown in the following example. Let us assume that we are dealing with a coal containing 7.0 percent moisture and 8.0 percent ash. The hydrogen of the moisture is equal to 7.0 percent multiplied by 0.1119, or 0.78 percent. The water of hydration may be calculated by multiplying the ash by 0.08, which gives 0.64 percent, and this multiplied by 0.1119 gives 0.07 percent hydrogen in the water of hydration. Summing up these two products shows that a hydrogen value, so determined as to include the hydrogen of moisture and of the water of hydration, will be 0.85 percent absolute higher than it would be if appropriate corrections were made.

MISCELLANEOUS ANALYSIS

CALORIFIC VALUE

The constituents of coal whose combustion accounts for the calorific value of coal are the carbon and hydrogen of the organic material and both organic and pyritic sulfur.

Methods for Determining Calorific Value

The procedures commonly used for determining calorific value involve complete combustion in oxygen of a sample of coal in a bomb under pressure. There are two methods. In the isothermal method, a jacket surrounds the calorimeter proper and is maintained at constant temperature. A correction must be made for the heat lost from the calorimeter to the jacket. In the adiabatic method, the jacket temperature is adjusted during the determination so that it is essentially the same at all times as the calorimeter temperature. No heat loss correction is needed.

Calorific Value by Calculation

Various ways of calculating calorific value have been suggested, three of which are mentioned here. It may be derived from ultimate analysis, and several formulas have been suggested for this purpose. The Dulong formula, which makes use of carbon, hydrogen, and sulfur values, is the one most used at the Illinois Geological Survey. It is employed primarily for the purpose of evaluating the reasonableness of determined values. Several formulas also have been suggested for calculating heating value from proximate analysis, using the volatile matter and the fixed carbon values. Another method used to some extent utilizes values of moisture, ash, sulfur, and the average unit coal calorific value for the particular coal in question.

Difficulties and Precautions

Many difficulties may be encountered in determining calorific value, several of which are mentioned below.

Temperature measurement is probably the major source of error in determining calorific value. Equipment used for this purpose must therefore be reliable. The platinum resistance thermometer, together with accurate reading equipment, is probably best for the purpose, but satisfactory mercury-in-glass calorimeter thermometers are available. The calorimeter thermometers are of two kinds — the solid stem, fixed range thermometer and the enclosed scale, adjustable range thermometer such as the Beckman thermometer. All of these must be carefully standardized, preferably against a reference electrical standard by a recognized standardizing authority. In the United States the National Bureau of Standards is the authority. Both centigrade and Fahrenheit thermometers are permissible for this purpose, and the centigrade thermometers are available with ranges of 6, 10, and 16 degrees in the solid stem, fixed range type. The 6- and 10-degree thermometers are preferable as they permit shorter interval markings with spacings wide enough apart to permit more accurate readability. At the Illinois Geological Survey a solid stem calorimeter thermometer of 10° C fixed range is used. Calibration by the National Bureau of Standards and proved reliable readability permit the determination of calorific values with good precision. This thermometer has an advantage over the 6° C range thermometer in that it is more adaptable in laboratories in which ambient temperatures may vary considerably.

There is some question in regard to permissible intervals of calibration for calorimeter thermometers. For the best precision, calibrations probably should be made at least every 0.1 degree. However, the uniformity of composition, physical characteristics, and bore of capillary glass tubing now available for making such thermometers makes calibrations every 0.5 degree permissible for calorific value determinations of acceptable precision.

Firing or igniting the sample can be difficult. The sample may actually blow out of the holder during introduction of oxygen or at the time of firing. Samples such as anthracite, coke, and coals quite high in mineral matter may be hard to ignite. The blow-out difficulty may be overcome by introducing oxygen to the bomb at a very slow rate and directing it away from the coal. The sample may also be pelleted to prevent blow-out. For firing anthracite and coke, the ASTM standard method suggests that the sample holder be closely lined with asbestos paper on which the sample to be tested is sprinkled. The sample is then fired in the bomb, and the heat is concentrated at the sample instead of being conducted away from it by the sample holder. For other hard to fire materials, such as coal that is quite high in mineral matter, mixing the sample with standard benzoic acid and pelleting it may be helpful. Proper correction can be made for the amount and heat value of the standard benzoic acid.

A tarnished or badly corroded adiabatic calorimeter bucket will lead to unstable conditions in the system and make determination of the calorific value difficult. When the bucket's highly reflective surface is corroded to the point where its heat capacity is changed, errors will be introduced into the determination. The bucket should be replaced immediately.

The combustion-bomb should be tested occasionally under pressure to make sure it is absolutely tight. If it is found to be defective it should either be repaired or replaced by a new one. At the Illinois Survey a bomb that had been in service for many years was submitted for test and found to be full of pinholes and had to be replaced.

A too rapid restoration of bomb pressure to atmospheric pressure after the sample has been burned may result in the loss of sulfur and nitrogen oxides for which a correction must be made. At the end of sample burning, pressure in the bomb should be released slowly to prevent loss of these gases.

Change of heat capacity (water equivalent) for any reason will cause erratic results. The water equivalent of a calorimeter may change for several reasons and it should be checked regularly.

The use of oxygen containing combustible material such as hydrogen or oil will cause calorific values to run high. Oxygen obtained by the fractional distillation of liquid air is preferred for these determinations as it is free from combustible materials.

Introduction of heat to the calorimeter system by friction of stirrers or by a short circuit in the electrical system will cause erratic values to be obtained. The operator should be sure that the stirrer in the unit runs smoothly without production of troublesome heat. Furthermore, the instrument should be checked for any possible short circuits.

In the adiabatic calorimeter the temperature of the jacket should be very carefully adjusted to follow that of the calorimeter proper. In this way heat loss will be prevented and a reliable result obtained.

Oxidation of the sample before the determination is made may result in a low calorific value. To prevent this the sample should be carefully protected and it should not be subjected to heat prior to analysis. The determination should be made without delay after sampling.

Uses of Calorific Values

The calorific value is the most important determination made on coal that is to be used for heating purposes. It is normally the basic item of specification in contracts for steam coals.

Calorific value is also used in estimating energy resources and reserves. In the ASTM system for classifying coals by rank, the calorific value is used as one of the main parameters for the classification of the bituminous, subbituminous, and lignitic coals.

Limitations of Calorific Value Data

In coal contracts the calorific value is generally specified on the "as-received" basis. Any error in the moisture value will be reflected in "as-received" Btu values.

Calorific values as determined and reported are gross calorific values. The gross calorific value may be defined as the heat produced by combustion of unit quantity, at constant volume, in an oxygen bomb calorimeter under specified conditions such that the products of combustion at the end of the determination are in the form of ash, *liquid water,* gaseous carbon dioxide, sulfur dioxide, and nitrogen.

A correction is sometimes made for differences between the laboratory condition and conditions occurring in burning the coal as fuel; such corrected values are designated as net calorific values. Net calorific value is lower than gross calorific value. It is calculated from the gross calorific value and is defined as the heat produced by combustion of unit quantity, at constant atmospheric pressure, under conditions such that all water in the products remains in the form of *vapor.*

FUSIBILITY OF COAL ASH

Source of Ash and Nature of Test

As described in the discussion of ash, the ash of coal and coke is the noncombustible residue that remains after all the combustible material has been removed by burning. It is a complex mixture of products resulting from chemical changes that take place in

the components of the mineral matter during combustion. Ash for the fusibility test is prepared by burning the coal or coke under controlled conditions, as in the preparation of ash for ash analysis.

The fusibility test is intended to provide information on the fusion characteristics of ash. The older ASTM Standard (D271-58) recognized three points, all determined in a mildly reducing atmosphere: (1) the initial deformation temperature, which is the temperature at which the first rounding or bending of the apex of the cone (triangular pyramid) takes place; (2) the softening temperature, which is the temperature at which the cone has fused down to a spherical lump; and (3) the fluid temperature, the temperature at which the cone spreads out over the base in a flat layer.

A revision of D271-58 has been published as Tentative Standard (D1857-64T), which recognizes four points and makes provision for determining them in both a mildly reducing atmosphere and an oxidizing atmosphere. The four points are A, the initial deformation temperature, which is the temperature at which the first rounding of the apex of the cone occurs; B, the softening temperature, spherical, which is the temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base; C, the softening temperature, hemispherical, which is the temperature at which the cone has fused down to a hemispherical lump at which point the height is one-half the width of the base; and D, the fluid temperature, the temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of one-sixteenth of an inch. Further revisions of D1857-64T are being considered.

Methods for Determining Ash Fusibility

The methods now in use for determining fusibility of ash are basically the same, involving heating a formed test specimen under controlled conditions. The most important condition to be controlled is the atmosphere in the test furnace. In addition, rate of heating, temperature measurement, and observation of test specimens during the heating program are important. Various kinds of furnaces have been and are used for the test, including both electrical and gas-heated furnaces. Examples of the electrically heated furnace are the carbon-resistance furnace and one using platinum heating elements. The carbon-resistance furnace had the advantage of providing a reducing atmosphere through conversion of carbon to carbon monoxide, but it was large enough for only one test specimen. Not many of these furnaces were used. The platinum-wound furnace is used today. In this unit a reducing atmosphere is provided by introducing into the furnace a mixture of gases, and an oxidizing atmosphere is provided by introducing air.

In the gas-heated furnaces, the atmosphere is controlled by regulating the ratio of air to combustible gas. For reducing conditions an excess of gas over air is maintained, and for oxidizing conditions an excess of air over gas is maintained. Temperature measurements are made either by an optical pyrometer or by a platinum, platinum-rhodium thermocouple with a calibrated, high-resistance millivoltmeter or potentiometer. Various shapes of test specimens, such as cones, cubes, or cylinders, are used. All test specimens should have sharp edges to facilitate observation of changes, and the mass of the specimen should be low to insure equalization of temperature within it. In the ASTM standard method, provision is made for observing changes with the naked eye in the test specimen during heating. An optical device with provision for measuring the dimensions of test specimens throughout the test is used in some laboratories.

Difficulties Encountered in Fusibility Tests

Proper control of the atmosphere surrounding the test specimen is probably the greatest difficulty encountered in determining ash fusibility. This is particularly true when the determination is made in a reducing atmosphere. In such case only a mildly reducing atmosphere is specified, as it is believed this more closely approximates conditions existing in fire beds when coal is burned in some types of combustion equipment. Lower softening temperature values are obtained than in either strongly reducing or strongly oxidizing atmospheres. The chemistry responsible for this

behavior involves the iron present in the ash. With a mildly reducing atmosphere the iron is present predominantly in the ferrous state; with a strongly reducing atmosphere iron is reduced, at least partially, to the metallic state; and in an oxidizing atmosphere the iron is in the ferric state. Both metallic and ferric iron increase the refractory quality of the ash. Determined softening temperature values may vary as much as 300° to 400° F, depending on the atmosphere in which the test is made.

Ash that is not completely oxidized may contain iron in both the ferrous and ferric state, as well as some unburned organic material. Both of these may be troublesome in fusibility tests. As the form taken by the iron has an influence on fusibility characteristics, all of it should be in the ferric condition in the test sample. The presence of organic material may result in the formation of bubbles or blisters in the specimen and thus ruin the test.

Difficulty has been experienced with supports for the test specimens. If materials that are not refractory enough are used in making these supports, they may soften and cause the test cones to tilt or bend out of shape. Furthermore, some ashes appear to act as a flux on the support, or vice versa, with the result that the test specimen may tilt, bend, sink into the support, or show early and false indication of fusion.

Errors in temperature measurement in this test, of course, will render values undependable. Equipment such as optical pyrometers, thermocouples, millivoltmeters, and potentiometers can become inaccurate. Furthermore, when an optical pyrometer is used, a background that is too bright (too hot) may lead the analyst to misjudge the temperature of the test specimen.

Proper identification of the significant temperature points may offer some difficulty, particularly to an inexperienced operator.

Precautions to Minimize Difficulties

In the gas-fired furnace the atmosphere around the test specimens is controlled by adjusting the ratio of gas to air. The ASTM methods for determining fusibility in a mildly reducing atmosphere specify that the ratio by volume of reducing gases to oxidizing gases shall be between the limits of 20 to 80 and 80 to 20 on a nitrogen-free basis. Hydrogen, hydrocarbons, and carbon monoxide are considered as reducing gases, and oxygen, carbon dioxide, and water vapor as oxidizing gases. Nitrogen is inert. Means for assuring that the desired atmosphere is being attained are not very precise, but it has been determined that a flame above the furnace 6 to 8 inches high with a faint yellowish tinge will usually assure the proper reducing conditions. It is not always possible to maintain a flame with these characteristics, particularly for the higher temperatures, but, fortunately, the atmosphere does not seem to influence the higher fluid point as much as it does the other points.

A more reliable way to assure the proper reducing atmosphere in the gas-fired furnace is to take samples of gas from the furnace during heating and analyze them. Flow meters may be installed in both the gas and air feed lines to the furnace, and the settings of these meters may be regulated until the atmosphere is shown to be correct by the analysis of the gas samples. Once the proper settings of the flow meters have been established they may be duplicated and the proper atmosphere assured as long as the primary pressures of gas and air remain reasonably constant. This approach is complicated and presents some problems, particularly the removal of good samples of hot gases from the furnace. It is therefore not often used.

For an oxidizing atmosphere in the gas furnace, the ratio of air to gas is increased. An indication of proper conditions is a distinctly blue flame about 2 inches high above the furnace. Further confirmation of proper conditions may be established by analysis of furnace gases.

In the electric furnace with platinum heating elements, a mildly reducing atmosphere is obtained by introducing a reducing mixture of gases of known composition. This is successful if the furnace muffle and gas introduction system are gas tight and if the gases are thoroughly mixed. An oxidizing atmosphere is obtained by introducing air into the furnace.

In preparing ash for the fusibility test it is important that the coal or coke be spread out in a thin layer. Adequate circulation of air must be maintained during burning. Occasional stirring helps. A slow initial heating

rate tends to minimize the retention of sulfur in the ash. Following burning in air, pulverizing the ash to minus 200-mesh and burning it in oxygen will ensure that all of the iron in the ash is converted to the ferric state and that all of the combustible (organic) matter is removed.

The support for the test specimen must be highly refractory so that warping, cracking, or softening does not occur. A mixture of equal parts by weight of kaolin and ignited alumina has been found satisfactory in most cases. If the test specimen should tend to react with the support material, other support materials, such as a mixture of kaolin and alundum cement, refractory brick, or possibly a metal plate, may be tried.

Temperature measuring equipment must be properly calibrated by reliable means. Small pieces of gold or nickel wire of high purity and known melting points should be mounted with the cones in each run to provide a check on temperature readings. Both gold and nickel are satisfactory for the test in a reducing atmosphere, but only gold should be used in an oxidizing atmosphere. If the various temperature points are identified visually, the inexperienced operator should check his results with those obtained by an experienced operator. Use of optical observation equipment with its provision for measuring the height and width of test specimens may be of help.

Uses of Ash Fusibility Data

Ash fusibility values are frequently specified in coal contracts because they are thought to furnish information regarding the clinkering tendencies of the ash of the coal. Softening temperatures probably are used most for this purpose, although the initial deformation and fluid temperatures may have some significance, depending on the type of combustion equipment to be used for burning the coal. The way in which ash is to be removed from the combustion equipment will control the specified ash softening characteristics. For example, in the domestic stoker from which ash is removed by hand, the softening temperature should be low enough to allow the ash to fuse and form a clinker that can be removed as a coherent mass. The ash, however, should not soften at a temperature too

far below the fire bed temperature, as it may become fluid enough to run through the fire bed, solidify in the cooler air ports, and thus cut down air flow.

When combustion equipment is used in which provision is made for removing ash in relatively small particle size rather than in fused masses, the ideal ash probably would have a higher softening temperature. This would apply to such equipment as domestic stokers with provision for automatic ash removal, and to chain grate stokers.

Attempts have been made, particularly with powdered fuel installations, to associate initial deformation temperatures with deposition of ash particles on various parts of boiler systems, such as boiler tubes, but have not been very successful.

Fluid temperature data are more applicable to equipment from which the ash is removed by slag tapping.

Limitations of Ash Fusibility Data

Ash fusibility data are too often over-interpreted. In practice, types of burning equipment, rate of burning, temperature of fire bed, thickness of fire bed, distribution of ash-forming mineral matter in the coal, and viscosity of the molten ash may influence ash behavior more than the ash fusibility characteristics determined in the laboratory test. Furthermore, conditions existing during applied combustion of coal are so complex that they are impossible to duplicate completely in a small-scale laboratory test. Therefore, the test should be considered an empirical one and the data, at best, only qualitative.

FORMS OF SULFUR IN COAL

Occurrence of Forms of Sulfur

The three commonly recognized forms of sulfur in coal are sulfate, pyritic, and organic sulfur, the last two accounting for almost all the sulfur. The amount of sulfate sulfur is usually very low in fresh coals, but it may be appreciably higher in weathered coals. The relative amounts of pyritic and organic sulfur vary widely. In some coals the total sulfur is almost entirely organic and in others the reverse is true. In Illinois coals organic and pyritic sulfurs occur, on an average, in

TABLE 3—AVERAGE PYRITIC AND ORGANIC SULFUR VALUES FOR ILLINOIS COALS

Coal No.	County	Average total S (%)	Range (%)	Average pyritic S as % of total S	Range (%)	Average organic S as % of total S	Range (%)
2	Hancock	4.9	4.1–5.7	76.6	70.7–82.5	23.4	29.3–17.5
	LaSalle	4.5	5.2–4.7	61.8	54.5–69.6	38.2	45.5–30.4
	Will	1.7	1.3–2.2	60.4	53.8–77.3	39.6	46.2–22.7
	Woodford	1.2	0.7–1.6	44.8	25.0–60.0	55.2	75.0–40.0
5	Fulton	3.3	2.7–3.6	52.8	50.0–55.6	47.2	50.0–44.4
	Gallatin	4.5	4.3–4.6	60.6	58.1–63.0	39.4	41.9–37.0
	Gallatin	4.1	4.0–4.1	57.4	56.1–58.5	42.6	43.9–41.5
	Saline	2.3	1.9–2.7	65.9	63.2–68.2	34.1	36.8–31.8
	Sangamon	4.5	3.6–5.8	49.4	41.7–56.3	50.6	58.3–43.7
6	Franklin	1.2	0.6–2.4	48.6	16.7–70.8	51.4	83.3–29.2
	Jefferson	1.2	1.2–1.3	52.7	52.0–53.3	47.3	48.0–46.7
	Macoupin	5.0	4.6–5.2	49.4	47.8–51.9	50.6	52.2–48.1
	Madison	3.5	0.7–5.7	46.5	28.6–59.3	53.5	71.4–40.7
	Perry (west)	4.0	3.7–4.2	53.9	50.0–60.0	46.1	50.0–40.0
	Randolph	4.3	3.7–4.7	53.4	43.2–57.4	46.6	56.8–42.6
	Saline	3.9	3.2–4.6	59.0	*	41.0	—
	St. Clair	4.4	3.7–5.6	50.0	44.2–55.4	50.0	55.8–44.6
	Washington	4.8	4.5–5.1	53.9	51.1–57.8	46.1	48.9–42.2
	Williamson	1.4	1.0–1.7	65.1	58.3–70.6	34.9	41.7–29.4
7	Vermilion	3.4	2.8–5.2	49.3	43.3–59.6	50.7	56.7–40.4

* Only one sample was available.

approximately equal amounts. However, relative amounts vary greatly in individual coals, with both pyritic and organic sulfur ranging from 20 to 80 percent of the total. Some available data showed a statewide average of 54 percent pyritic sulfur and 46 percent organic sulfur. The range was from 83 percent pyritic sulfur and 17 percent organic to 17 percent pyritic sulfur and 83 percent organic. Table 3 shows average values for pyritic and organic sulfur in Illinois No. 2, No. 5, No. 6, and No. 7 Coals from 18 counties.

Methods for Determination of Sulfur Forms

Sulfate sulfur is commonly determined by extracting it from the coal with dilute hydrochloric acid, precipitating it with barium chloride solution, and weighing the barium sulfate ($BaSO_4$) precipitate after it has been filtered off, washed, and ignited.

Two basic approaches have been used for determining pyritic sulfur, the reduction method and the oxidation method. In the first, the sulfur is reduced to hydrogen sulfide, which is evolved, absorbed in an appropriate reagent (acid cadmium acetate has been found satisfactory), and finally determined by iodometric titration. In the oxidation method, the sulfur of the pyrite is extracted and oxidized to sulfate, and the iron is oxidized to the ferric state by digestion with dilute nitric acid. Final determination of the sulfur has been accomplished by precipitating and weighing it as barium sulfate or by determining the iron as representative of the pyritic sulfur. The latter procedure seems to be preferred today.

Details of the methods for determining sulfate and pyritic sulfur by the oxidation method published by Powell and Parr (1919) have been modified considerably. For example, these investigators proposed that sulfate sulfur be extracted with dilute hydrochloric acid for 40 hours at 60° C and that pyritic sulfur be extracted with dilute nitric acid for 3 to 4 days at room temperature. Today it is more common to make these extractions by boiling samples for 30 minutes with the

dilute acids. This speeds up the determinations, and abundant evidence has been presented showing that results are not adversely affected.

Organic sulfur is estimated by difference— the sum of the sulfate and pyritic sulfur is subtracted from the total sulfur. The direct determination of organic sulfur through extraction with an organic solvent has been attempted, but it is not used.

Difficulties and Precautions

Sulfate Sulfur

The extraction of sulfate sulfur in dilute hydrochloric acid is a simple matter of solubility, and its success is based on the fact that sulfates found in coal are soluble and the sulfur in pyritic and organic combination is not. Oxidation of pyritic sulfur to sulfate sulfur is promoted by weathering, generation of heat during pulverization in contact with air, and storage. Fortunately, this oxidation is a relatively slow process, but any such reaction will lead to high values for sulfate sulfur. Rees and Kalinowski (1940) found very definite increases of sulfate sulfur in column samples of coal stored for 4½ years in sealed boxes at 30° to 32° F. The increase was 900 percent in one sample, and the average increase for 13 samples was 330 percent. Obviously, samples should be analyzed as soon as possible. Another difficulty that may be encountered stems from the fact that precipitated barium sulfate adsorbs other materials, such as iron, and makes the sulfate sulfur values high. This may be particularly objectionable for coals containing large amounts of nonpyritic iron, in which case iron should be removed prior to precipitation with barium chloride.

Pyritic Sulfur

The extraction of pyritic sulfur from coal with dilute nitric acid involves an oxidative chemical reaction in which the ferrous iron of pyrite is converted to soluble ferric iron and the sulfur to soluble sulfate. Its success depends on the fact that organically combined sulfur is not greatly affected by dilute nitric acid. If sulfate sulfur and nonpyritic iron have not previously been removed, they must be determined and corrections made.

Some investigators have reported their inability to extract all of the pyritic sulfur from coal with dilute nitric acid, although others have reported success. Reliable results are obtained if samples are adequately pulverized and mixed and if the mixture is stirred to allow the acid to make good contact with the pyrite.

A very small amount of organic sulfur possibly may be included with the extracted pyritic sulfur, particularly in certain coals. For this reason iron is commonly determined in the extract as a measure of pyritic sulfur.

Many methods are available for determining iron, but they may be divided into two types, oxidimetric and reductometric. In the oxidimetric methods the iron in the ferrous state is titrated with an oxidizing titrant such as permanganate or dichromate; in the reductometric methods the iron in the ferric state is titrated with a reducing titrant such as titanous chloride. When an oxidimetric method is used the ferric iron must first be reduced to the ferrous state. This reduction may be accomplished in several ways, all of which introduce another step into the procedure. Furthermore, it is necessary to make a blank determination for correction, and there is some evidence that such blanks may not always remain constant in the actual determination but may vary with the amount of iron present, thus introducing an error.

In the reductometric method, iron in the ferric condition is titrated directly with the reducing titrant, thus eliminating the reduction step. While a corrective blank determination should be made, it appears to remain constant in the presence of various amounts of iron. On the other hand, special precautions must be taken to preserve a titrant like titanous chloride in its reducing form. Although it is possible to obtain titanous chloride in 20 percent solution in sealed containers for making up the standard titrant, after the seal is broken the solution cannot be stored very long because exposure to air causes oxidation.

Organic Sulfur

As organic sulfur is obtained by difference, the difficulties are those involved in the determinations of the total, sulfate, and pyritic sulfur.

Uses of Data

The sulfate sulfur content in fresh coal is normally quite low, and the presence of unusually high amounts may indicate that the coal in question is weathered. Aside from this, sulfate sulfur data have very little practical significance.

The principal use for pyritic and organic sulfur data is in connection with coal cleaning. Organic sulfur cannot be removed from coal by specific gravity separation methods, but pyritic sulfur, within certain limitations, can be removed. The pyritic sulfur value may therefore be an indication of the amount of sulfur that can be eliminated by conventional cleaning processes. To remove organic sulfur it is necessary to release it from the organo-sulfur compounds by rather drastic chemical means. While various types of treatment have been tried, largely on a laboratory scale and with limited success, none of them is in use commercially as far as I am aware.

Limitations of Data

The methods commonly used for determining forms of sulfur in coal give good results when carefully followed. However, they are practical methods with tolerance limits and the data they furnish should not be interpreted beyond these limits.

The use of pyritic sulfur data as an indication of possible sulfur reduction by gravity separation is limited by the mode of occurrence of the pyrite in the coal. If it occurs as lenses or layers it usually can be removed successfully. If, however, it occurs as fine crystals widely dispersed throughout the coal substance, its removal is difficult or even impossible.

MINERAL CARBON DIOXIDE

Occurrence of Mineral Carbon Dioxide in Coal

Mineral carbon dioxide occurs in coal mineral matter as carbonates, primarily calcium carbonate. Smaller amounts may occur as carbonates of other inorganic elements, such as ferrous iron. The percentage of mineral carbon dioxide in most Illinois coals is less than 1 percent, but in a few coals the amount may be higher.

Methods for Determining Mineral Carbon Dioxide

For the determination of mineral carbon dioxide in coal, the carbon dioxide is liberated from the carbonates with acid and determined gravimetrically, volumetrically, or pressometrically. The present ASTM Standard Method (D1756-62) specifies the gravimetric procedure.

Difficulties and Precautions

The liberation and collection of carbon dioxide are accomplished in a closed gas-tight system; any leak in the system will introduce error. In the volumetric and gravimetric procedures, the liberated carbon dioxide is absorbed in an alkaline absorbent and any acid gases, such as halogen acids, sulfur oxides, or hydrogen sulfide will be absorbed and measured as carbon dioxide. Such interfering gases must be removed before absorption. Silver or anhydrous copper sulfate on pumice is used for removing them. In the pressometric method, in which the pressure of liberated carbon dioxide is measured, constant control of the temperature is essential because a change will introduce error.

Uses of Mineral Carbon Dioxide Data

The mineral carbon dioxide value is used mainly in the calculation of mineral matter of high carbonate coals. When it is high it is also used to correct volatile matter values. A high value usually indicates a high calcium carbonate content, which may cause an objectionable retention of sulfur as sulfate in the determination of ash. Such a value should alert the analyst to the need for using a modified procedure for determining ash.

Limitations of Mineral Carbon Dioxide Data

For mineral carbon dioxide contents below 1 percent, corrections for mineral matter and volatile matter are small and are not normally made. However, higher carbon dioxide contents may make corrections desirable for some purposes.

FREE-SWELLING INDEX

The free-swelling index (FSI) is a measure of the increase in volume of a coal when it is heated without restriction under specific heating conditions. This type of volume increase is associated with the plastic properties of coal, and coals exhibiting no plastic properties when heated do not show free swelling. Although the relation between swelling and plasticity appears to be complex and is difficult to study, it is believed that gas formed by thermal decomposition while the coal is in a plastic or semifluid condition is responsible for swelling in much the same way as carbon dioxide gas causes bread dough to rise. The gas forms bubbles in the more or less fluid material and the amount of swelling is influenced by the thickness of the bubble walls, the fluidity of the plastic coal, and the interfacial tension between the fluid material and the solid particles believed to be present throughout the course of the FSI test. When these factors cause many gas bubbles to be trapped, greater swelling occurs in the coal and the test buttons show a bubbly structure.

The free-swelling index of bituminous coals generally increases as the rank increases. Rees and Pierron (1954) reported average FSI values for four Illinois and three Eastern coals (table 4). Values for individual coals within a given rank may vary considerably. Anthracite does not fuse and shows no swelling index. FSI values for the lower rank coals are normally less than those of the bituminous rank coals.

Methods for Determination

The free-swelling index may be determined by either the gas or the electric heating methods. The two differ only in the kind of heating employed. Briefly, the test consists of heating the coal sample under rigidly controlled conditions to form a coke button, the size of which is indicative of the swelling characteristics of the coal being tested. Three to five buttons are made, compared with numbered profile standards, and the average of the profile numbers to which they most closely compare is taken as the free-swelling index.

TABLE 4—AVERAGE FREE-SWELLING INDEX VALUES FOR ILLINOIS AND EASTERN BITUMINOUS COALS

Rank	Coals	Free-swelling index
High-volatile C	Illinois No. 6	3.5
High-volatile B	Illinois No. 6	4.5
High-volatile B	Illinois No. 5	5.0
High-volatile A	Illinois No. 5	5.5
High-volatile A	Eastern	6.0 to 7.5
Medium-volatile	Eastern	8.5
Low-volatile	Eastern	8.5 to 9.0

Difficulties and Precautions

The free-swelling index test is quite empirical, and failure to achieve proper temperature, and particularly to achieve proper rate of temperature rise, will make results unreliable. There is also evidence that too great a heat gradient along the walls of the test crucible from bottom to top may cause erratic results. Careful standardization is therefore necessary to assure the proper temperature and rate of temperature rise for both gas and electric heating equipment. Where gas pressure may not be adequate, use of a gas pressure pump has been found helpful. Some difficulty has been experienced in obtaining burners to meet requirements. The British method specifies a Tirril burner, but it is not available in the United States and a blast type of burner is specified by ASTM. Both the gas burner and the electric heater must provide adequate heat not only to the bottom of the test crucible but also to the side walls to eliminate objectionable heat gradients. At least two electric furnaces have been developed that appear to be satisfactory. One was developed in Spain and one in the United States by Bituminous Coal Research, Inc.

Appreciable oxidation or weathering of the coal to be tested will result in a low free-swelling index. While this oxidation effect may not be as serious as once thought, it can occur, particularly if the test is delayed for some time after sampling. To eliminate possible oxidation effects, samples should be tested as soon as possible after collection and preparation. If oxidation of the coal is suspected, the test should be repeated on a known fresh sample of the same coal.

Ample evidence shows that the size consist of the test sample may influence the free-swelling index values of some coals. More specifically, for many coals, an excess of fine coal (minus 100- or 200-mesh) may cause values to be as much as two index numbers high. The Illinois Geological Survey has found that for high-volatile C and B bituminous coals of Illinois the amount of minus 100-mesh coal should not exceed 60 to 65 percent of the test sample. For medium- and low-volatile bituminous coals, the size consist of the test sample has been found to have less effect on index values.

The ASTM method specifies a test sample pulverized to minus 60-mesh. Ideally, the size consist of the test sample should be specified exactly. However, this does not seem practical in view of the wide range of grindability of coals. It would be simple to specify a proper size consist, but if this were done an adequate pulverizing procedure should be specified. Such a pulverizing procedure might be worked out for one coal but it is probable that it would not be suitable for other coals. About the only recommendation I can offer is to keep the amount of very fine coal in the test sample to a minimum. To accomplish this a stage pulverization procedure should be used.

In some cases test buttons of irregular shape may be formed that do not compare well with the standard profiles. They may sometimes be evaluated, within significance limits, by rotating them while they are being compared to standard profiles. If more precise values are required, the cross-sectional area of the button may be determined and converted to swelling index numbers by comparison with the curve provided for this purpose in the ASTM method. It is possible that formation of buttons of irregular shape may be due, in some cases, to improper temperature gradient in the walls of the test crucible. If this is the case it should be checked and corrected.

Uses of Free-Swelling Index

The free-swelling index test has been considered useful in evaluating coking properties of coals. It also has been used as an indication of the tendency of coals to form coke trees when burned in certain types of equipment, particularly underfeed stokers.

The suitability of coals for use in coal-burning railroad locomotives has also been so evaluated, and the test has been used to detect oxidation of coal by comparing the determined value with that of a fresh sample of the same coal.

The crucible swelling test (in general the same as the free-swelling index test) is one of two recognized by the Classification Working Party of the Economic Commission for Europe for obtaining caking property data used in the International Classification System. The free-swelling index test has also been suggested as a means of assessing agglomerating properties of coals in the ASTM rank classification system.

Limitations of Free-Swelling Index Values

While free-swelling index values may have some significance in assessing coking properties of coals, they should not be relied on too closely. Qualitatively, a coal showing a free-swelling index of 2 or less probably will not be a good coking coal, whereas one showing an index of 4 or above may have good coking properties. Actually, the relation of the determined value to the normal value for the fresh coal is of more importance. For example, several years ago a coke plant was experiencing difficulty in pushing charges from ovens. A Pocahontas coal that had been in storage for an extended period of time was being used in the coking blend. The normal swelling index of this coal in a fresh state was 9, but the coal in use was found to have an index of 5.5 to 6.0, indicating deterioration that was probably due to weathering. When the weathered coal was replaced in the blend with fresh coal of the same kind, the pushing difficulties disappeared. Furthermore, a coal with a swelling index of 4.5 that appeared to be satisfactory in a specific coking blend was not satisfactory in the same blend when its swelling index dropped to 2.5.

When underfeed stokers were widely used for domestic and small commercial plant heating, the free-swelling index test was used to assess the tendency of a coal to form objectionable coke trees. Pre-oxidizing units were developed to lessen coke-tree formation, and the free-swelling index test was used to determine the amount of pre-oxida-

tion needed and to gauge whether pre-oxidation had been accomplished. The usefulness of the test has diminished as the use of underfeed stokers has declined, and as combustion conditions have been adjusted to minimize difficulties due to coke-tree formation. The extensive replacement of coal-fired locomotives by diesel fueled units also has helped to eliminate the need for the test.

Although the free-swelling index test has been used to detect oxidation or weathering of coal, it appears to be less sensitive to weathering effects than once thought. For example, Rees et al. (1961) used it in studying the effects of outdoor storage on an Illinois steam coal. The free-swelling index value dropped little, if any, up to about 48 weeks of storage. Calorific value dropped long before this, indicating that deterioration, which was probably due to oxidation or weathering, had occurred. The same lack of sensitivity has been detected when the test is used in following the progress of weathering in coking coals.

The empirical nature of the free-swelling index or crucible swelling test makes it not entirely dependable for assessing caking properties of coals for use as parameters in a classification system.

PLASTICITY OF COAL (GIESELER PLASTICITY)

Plasticity in coal is its tendency to fuse or soften and become more or less fluid when heated. The chemical nature of the constituents that account for coal's plastic properties is not known. Considerable work has been done on this problem, but the complex nature of coal seriously complicates such studies. Some investigators have succeeded in removing material from coal by solvent extraction, leaving a nonplastic residue. The extracted material has variously been termed "bitumen," "coking principle," and "metaplast," a polymerized unstable intermediate product. This extract was considered responsible for plastic properties. Pierron and Rees (1960), using pyridine as the solvent, attempted to relate the amount of extract obtained to the plastic properties of certain coals, and more specifically to fluidities as determined with the Gieseler plastometer. They found that as the amount of extract increased the fluidity increased, but the relation was not exact and did not appear to be a reliable way to make accurate estimates of plastic properties of coals. Nonplastic residues were obtained that could be rendered plastic by returning to them the extracts obtained by the solvent extraction. Their Gieseler fluidities were found to be even greater than those of the original coals.

Methods for Determining Plastic Properties of Coal

Several laboratory methods have been suggested for measuring coal plasticity. Used to some extent but largely discarded for one reason or another are the Layng-Hawthorne test, in which the resistance to passage of a gas though heated coal was measured; the Agde Damm test, which was a dilatometer type of test; and the Davis plastometer test, which measured the resistance that heated coal developed to a rotating horizontal shaft with rabble arms.

Some of the methods receiving current attention are the Audibert-Arnu and Hoffman tests, both dilatometer types of tests; the Saposnikoff test, which is a penetrometer type of test; and the Gieseler plastometer test, which might be described as a viscosity type of test. The Gieseler test is the one in use at the Illinois Geological Survey.

Briefly, the Gieseler plastometer is a vertical instrument consisting of a sample holder, a stirrer with four small rabble arms attached at its lower end, a means of applying a known torque to the stirrer, a means of heating the sample that includes provision for controlling temperature and rate of temperature rise, and a way to measure the rate of turning of the stirrer. A sample of minus-60 mesh coal is packed in the sample holder, with the stirrer in place, in such a way that the holder is completely filled and the rabble arms of the stirrer are all in contact with the coal. The apparatus is then assembled, immersed in the heating bath, and a known torque applied to the stirrer. During early heating no movement of the stirrer occurs, but as the temperature is raised it begins to turn and its speed increases as the temperature rises. Throughout the test the temperature and the rate of stirrer movement are observed and recorded.

There are two types of the Gieseler plastometer, the manual and the constant torque. They differ mainly in the methods used for controlling temperature rise, for applying torque, and for measuring rate of turning of the stirrer.

The present ASTM tentative standard specifies the manual unit, in which temperature and rate of temperature rise are controlled by a manually operated rheostat or variable transformer. Torque is applied by a known weight suspended at the end of a cord, which passes over a dial pulley and is wound around a small drum that is engaged with the upper end of the stirrer. A pointer attached to the dial pulley moves in reference to a fixed graduated dial mounted directly behind it. Rate of movement is determined by observing the number of dial divisions the pointer moves past in a given time, and it is expressed as dial divisions per minute.

In the constant torque Gieseler plastometer, sometimes referred to as the automatic Gieseler, an electric device provides automatic control of temperature and rate of temperature rise. Torque is applied continuously and automatically by a magnetic brake system. A photo-electric counter measures stirrer movement.

Values normally determined with the Gieseler plastometer are (1) initial softening temperature—the temperature at which stirrer movement is equal to 0.5 dial divisions per minute (it may be characterized by other rates but if so the rate must be reported); (2) maximum fluid temperature—the temperature at which stirrer movement reaches maximum rate in terms of dial divisions per minute; (3) solidification temperature—the temperature at which stirrer movement stops; and (4) maximum fluidity—the maximum rate of stirrer movement in dial divisions per minute.

Difficulties and Precautions

Many factors and difficulties influence the Gieseler plastometer test and must be reckoned with. Some of these are discussed in the following paragraphs.

Oxidation

Plastic properties of coal, as determined by the Gieseler plastometer, appear to be sensitive to oxidation. The effect of oxidation on the various temperature values may not be beyond repeatability, but its effect in lessening maximum fluidity may be appreciable. In fact, extended oxidation may completely destroy the fluidity of a coal. To reduce oxidation, samples should be tested soon after collection. Where delay is unavoidable, storage under water or in a nonoxidizing atmosphere such as nitrogen is advisable.

Swelling

Some coals swell considerably when heated and extrude from the sample cup into the barrel of the plastometer where they exert some resistance to the stirrer well above the rabble arms. In extreme cases most of the coal may be extruded and the rabble arms left exposed. The results, of course, would be unreliable.

For coals that swell excessively, a washer on top of the coal sample may be helpful. Because the size of the washer hole through which the stirring shaft extends is most important, close adherence to specifications for the washer should be observed. It has been suggested that specific amounts of inerts be added to coals that swell too much. However, Rees and Pierron (1955) found that, although the inerts did reduce swelling, the effect of a specific inert on maximum fluidity was not the same for different coals and that different inerts had different effects on the same coal.

In some cases the periphery of the coal sample appears to soften before the remainder of the sample, permitting the whole sample to turn more or less freely in the sample holder. As no actual stirring occurs under these circumstances no measurement of fluidity is attained. One means of preventing such slippage is to provide, in the side of the sample holder, a pin that can be pushed into the coal sample to hold it in place.

Packing of Sample

Difficulty may be experienced in packing certain coals, especially weathered coals, satisfactorily in the sample holder. For a successful Gieseler test, the coal sample must be so packed that the stirrer, with torque applied, will not turn until the coal softens. There is some evidence that an excess of very

fine coal may make the test sample hard to pack. The addition of a few drops of benzene or toluene may be helpful. Control of the size consist of the sample also may help.

Rate of Heating

The rate of heating, from the softening temperature to the end of the test, influences values obtained in the Gieseler test. Maximum fluidity appears to be influenced most by changes in the rate of heating. The standard rate specified for the test is 3° C per minute. When this rate was doubled, in a test of Illinois coal of low fluidity, the maximum fluidity value was approximately doubled. Other studies have shown that reducing the heating rate to 1° C per minute resulted in lower maximum fluidity values than were obtained at 3° C. When the rate was increased to 5° C per minute the fluidity value was definitely higher. However, the percentage change in maximum fluidity per degree of change in heating rate was not the same for different coals.

Rate of heating also appears to influence some of the temperature values commonly determined in the Gieseler test. For example, the maximum fluidity temperature for a low-volatile bituminous coal decreased when the heating rate was reduced to 1° C per minute. When the heating rate was increased to 5° C, both the final, or setting, temperature and the maximum fluidity temperature were higher. In testing a high-volatile coal of high fluidity, both the setting and maximum fluidity temperatures were found to be lower when the heating rate was reduced from the standard 3° C to 1° C per minute; increasing the heating rate to 5° C per minute produced higher values. Obviously the rate of heating must be carefully controlled to comply with the specified rate. This may be accomplished fairly well by manual control but good automatic program control is preferable.

Friction in the Plastometer

Variations in friction from one instrument to another, or even in the same instrument, may cause nonconcordant results. The total friction of the plastometer comprises the frictions of the various moving parts. For example, there is friction between the lower end of the stirrer and the inside bottom of the sample container, although it is only a small part of the total friction, particularly in the manual instrument. Specifications call for the lower end of the stirrer to be tapered so that it will fit into a conical bearing in the bottom of the sample holder. The angle of taper of the stirrer is greater than that of the bearing so that it rides on the angle of taper rather than fitting closely, thus reducing friction. Other components contribute more friction, such as the bearings in the plastometer head and the lubricant used in the bearings. The balance and weight of the pointer may contribute to erratic movement.

Close adherence to specifications is necessary in constructing the plastometer so that comparison of results from different instruments will be reliable. Properly lubricated ball bearings should be used.

Surface or Contact Area of Rabble Arms

The surface area of the four rabble arms on the stirrer may affect the maximum fluidity value obtained. A brief study was made at the Illinois Geological Survey in which three stirrers were used in making Gieseler tests on the same coal. Surface areas of the rabble arms of the stirrers were measured and related to maximum fluidities obtained. The results were:

Surface area (sq. in.)	Maximum fluidity (dial div./min.)
0.2020	72
0.1808	72
0.1084	97

The first stirrer was new, the second had been used and cleaned for 30 determinations, and the third had been used and cleaned for approximately 100 determinations. The surface area was reduced by increased usage and necessary cleaning. While these data are inadequate for firm conclusions, it appears that a rather large reduction in surface area of the rabble arms may lead to high maximum fluidity values and that stirrers should not be used for more than 30 or 40 determinations.

Torque Applied

Studies have been made on the effect of applying different torques to the stirrer in

both manual and automatic instruments. Results have shown that the amount of torque definitely influences Gieseler values, particularly maximum fluidity values. A study of this factor was conducted in the Illinois Geological Survey laboratory several years ago with the manual plastometer. Three coals, Pocahontas No. 4, Illinois No. 6, and Eagle seam coal, were tested with various torques applied. The results of this study are shown in figure 2. Maximum fluidity values increased for all three coals as the torque was increased. A similar study was made later in the same laboratory with the automatic Gieseler plastometer. Six coals of different ranks and different levels of fluidity were tested at different torques. Results showed the same trend as those of the manual study. The relationship between torque and maximum fluidity did not appear to be linear. To secure comparable results the same torque must be used in all tests.
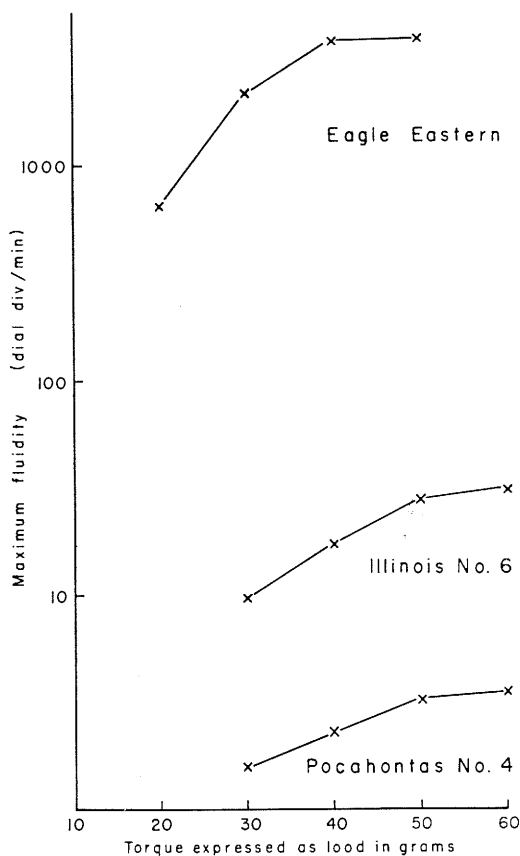

FIG. 2—Maximum fluidity versus torque for one Illinois coal and two Eastern coals.

The manner in which torque is applied in the manual Gieseler is not entirely satisfactory. During the course of the manual test on a highly fluid coal it is necessary to stop the stirrer in order to rewind the weight-supporting cord on the stirrer pulley. The interruptions may affect results. In the constant torque instrument, torque is applied constantly throughout the test. While results obtained with the two instruments are usually in fair agreement, there is some evidence that average results obtained with the automatic unit are somewhat higher.

Uses of Gieseler Data

Gieseler data are used primarily for assessing coking properties of coals. Maximum fluidity values are used most in this connection, and plastic range (the temperature range between softening and final or setting temperatures) has been used to some extent as a guide in blending coals for carbonization. Some technical men believe the plastic ranges of individual coals in a blend must overlap appreciably to insure production of good coke. Maximum fluidity values are used also in choosing coals for blending for production of satisfactory metallurgical coke. For example, if a coal of low maximum fluidity is to be used for making coke, it may be necessary to blend with it a coal of higher fluidity.

Attempts have been made to use the Gieseler test as a guide to the behavior of coal burned in an underfeed stoker by relating maximum fluidity to resistance to air-flow during combustion, but not much success has been achieved.

The fact that the Gieseler test is sensitive to oxidation or weathering of coal has led to its use in detecting oxidation. Yohe (1965) used Gieseler data to detect oxidative deterioration of coal treated with various antioxidants. Maximum fluidity values of stored coal are useful in detecting oxidation or weathering, particularly that of coking coals, when compared to known values for fresh coal.

Limitations of Gieseler Data

The present ASTM "Tentative Method of Test for Plastic Properties of Coal by Gieseler Plastometer" states that, for reproducibility,

all characteristic temperature points for duplicate tests should agree within 5° C, and maximum rates of pointer movement (maximum fluidity) should agree within 20 percent. In studying the effect of diluents (inerts) on Gieseler data, Rees and Pierron (1955) evaluated their data for duplicability. They found that duplicate determinations of characteristic temperature values (in degrees centigrade) showed an average difference of approximately 0.5 percent for all samples tested. The average difference for maximum fluidity values was 15.9 percent, but the spread was even wider, ranging from 0.0 to 100 percent. These deviations applied to all samples tested, including original coals and their mixtures with various diluents or inerts. When the individual coals were tested without diluents, the average difference between temperature values obtained in duplicate determinations was about the same (0.5 percent) as for the coals mixed with diluents. However, for maximum fluidity, duplicability was better, being 6.9 percent with a range of from 0.0 to 13.3 percent.

It would seem logical to calculate Gieseler data for blends of coals from determined values for the individual coals and the percentage of each coal in the blends. When such calculation was attempted in the Survey laboratory, characteristic temperature values were found to agree reasonably well with determined values, but maximum fluidity values did not. Each blend appeared to be distinct and required direct determination of maximum fluidity.

Earlier in this discussion the Gieseler plastometer test was described as a viscosity type of test. It is true that some of the fundamental factors, such as torsion and shear, involved in a measurement of true or absolute viscosity are involved in the Gieseler test for coal. However, as the test is conducted and results reported, we are dealing with fluidity, which may be described as the opposite of viscosity. Continuing on the premise that the Gieseler test is a viscosity type of test, it must be remembered that it is impossible to determine the true viscosity of a multiphase system. Inasmuch as there are probably three phases — solid, liquid, and gas — present at all times throughout the plastic range of coal, we must conclude that we are measuring apparent viscosity, not true viscosity, or, to be more exact, its apparent fluidity. Because of these facts it is not proper to calibrate the Gieseler plastometer in terms of true or absolute viscosity units nor to report results in such units. It seems more logical to use dial divisions per minute, although they are arbitrary units.

In my opinion the Gieseler test is qualitative, or at best semiquantitative, when it is used for assessing coking properties of coals. It is empirical in nature and is subject to the influence of variables, many of which are not well understood and not amenable to adequate control. Until more information is available concerning the fundamental constitution of coal, the test will probably remain in the empirical category. This does not necessarily mean that the test is useless. On the contrary, Gieseler data, even though only qualitative, are useful as a guide in blending coals for the production of satisfactory coke. Such data are probably more useful when applied to low-fluid, less strongly coking coals than in assessing differences in coking characteristics of highly fluid, more strongly coking coals. Gieseler data should not be interpreted too closely. Their limitations must be realized and it must be remembered that plastic properties, as measured in the Gieseler plastometer, are not the only factors involved in successful carbonization of coal.

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