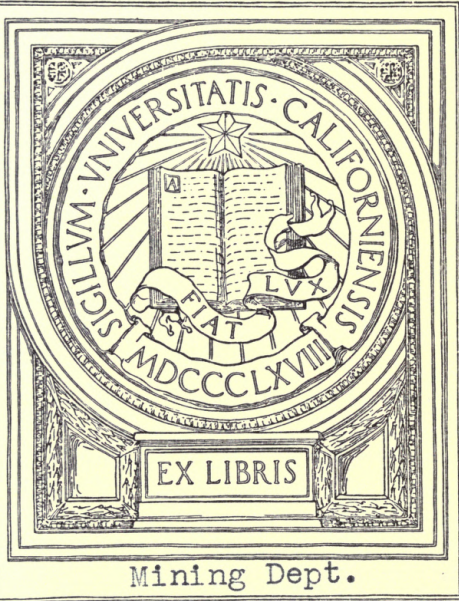


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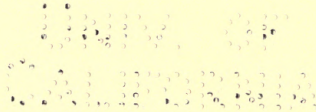
COAL

ITS COMPOSITION, ANALYSIS, UTILIZATION AND VALUATION

BY

E. E. SOMERMEIER

Professor of Metallurgy, Ohio State University



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PREFACE

THE data and descriptive matter given herein, are largely based upon private notes and upon information and material scattered through text-books, technical bulletins, and in original papers in technical and scientific journals. Much of this data is either inaccessible or in such a form as not to be readily applied or interpreted and hence is not likely to be utilized by those who have the most active interest in coal.

In the preparation and arrangement of the material, three distinct classes of readers have been to a certain extent kept in mind:

- (1) The mechanical and power plant engineer;
- (2) The chemical engineer and chemist;
- (3) The non-technically trained business man and operator who has to do with the buying and selling of the coal.

In including data which might be of interest and value to these different groups of readers a portion of the material is necessarily elementary for some and a portion is correspondingly technical for others. Good advice to each reader is to select that which may be of interest and use, and to pass over any discussion or data which may appear too elementary or too technical for his needs.

To the technical man who is familiar with much of the data and many of the formulas given, it may appear that many of the simpler illustrations and details might perhaps just as well have been omitted. However, it is the writer's experience that specific formulas and specific data are not, as a rule, likely to be given too much in detail to suit the occasional user, who may have neither the time nor the inclination to elaborate the formula or to check up the data. He wants each in a form easily understood and readily applicable to his needs.

In the effort to meet this "want" some statements are repeated, perhaps too often, some details enlarged upon a little too much and a few assumptions made which are perhaps not

strictly in accordance with facts. It is hoped, however, that any errors in this direction are of little real consequence and that the collection of material given herein may be a slight contribution toward a more general appreciation of the properties and a better utilization of one of the earth's most valuable assets—coal.

The author desires to express his appreciation to Professor E. A. Hitchcock of the Department of Mechanical Engineering, Ohio State University, and Professor D. J. Demorest of the Department of Metallurgy, for advice and suggestions.

Especial acknowledgment is due to the late Professor N. W. Lord, the able and inspiring teacher, to whom the author is indebted for much of the material given herein.

E. E. SOMERMEIER.

October, 1912.

INTRODUCTION

COAL is generally recognized as being a product of the more or less complete decomposition of vegetable matter under varying conditions of moisture, temperature and pressure. Depending upon the varying conditions and upon the completeness of the decomposition and upon the kind of vegetation from which it is derived, the resultant product as it actually occurs is far from uniform, ranging from the initial stage of woody fibrous peat through lignite (brown coal), bituminous coal high in oxygen, bituminous coal low in oxygen, semi-bituminous coal, anthracite and the final stage—graphite. For similar conditions of moisture, temperature, extent of decomposition and similar vegetable origin, the resultant coal should be uniform in composition and properties. Usually, however, other factors acting during the period of formation modify and change the final product, so that coal from different portions of the same bed or even different portions of the same mine is far from uniform in some important properties, namely, the content of sulphur and ash.

If coal contained only constituents which were present in the original vegetable matter, it would be uniformly low in both sulphur and ash, but during the early stages of its formation underneath the surface of swamps or lakes, streams or rivulets carried silt and sediment over the decomposing bed of vegetation, which sediment settled down and became an integral but varying constituent of the coal. Sulphur in solution in the water, coming in contact with salts of iron and reducing organic compounds resulted in the formation and precipitation of pyrite, while other reactions not clearly understood produced variable quantities of organic compounds of sulphur as a constituent of the coal.

Other factors or agencies may also materially affect the coal in certain portions of the seam or field. Faults and fractures in the coal and surrounding rocks are often accompanied by local variations in the nature of the coal. Weathering of the coal near

the outcrop often causes that portion to differ in quality from the more deeply covered and better protected portions. Still other factors or agencies might be enumerated as causes for local or wide-spread differences in the coal, but those already given suffice to show why variations in properties and constituents are to be expected rather than the occurrence of a material of uniformity in properties and exactness in composition.

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COAL

CHAPTER I

COMPOSITION AND HEATING VALUE

CONSIDERED from a practical point of view, coal may be described by discussing some of the more or less common terms used in connection with its composition, analysis and utilization, some of which are as follows:

- (a) Moisture.
- (b) Ash.
- (c) Sulphur.
- (d) Heating value, total and practically available.
- (e) "Residual coal," that is, coal free from the variable factors—moisture, ash and sulphur.
- (f) Proximate analysis, in which the composition is expressed as percentage of moisture, volatile matter, fixed carbon and ash present.
- (g) Ultimate analysis, in which the composition is given in percentage of carbon, hydrogen, oxygen, nitrogen, sulphur and ash.

MOISTURE

The term moisture includes only the more or less loosely held water which is driven off by heating the finely powdered coal slightly above the boiling-point of water, about 105° C. or 220° F. The residual coal substance or the mineral matter present in the ash may hold additional water which is given up on heating to higher temperatures, while still more water is produced upon the actual combustion of the coal. But in the ordinary use of the term "moisture," this more closely held water

or the water produced by burning of the fuel is never included, and if the closely held water is given at all in an analysis it is designated "combined water" or "water of combination."

The amount of moisture in coal is variable, depending upon the nature of the coal, upon its physical condition (degree of fineness) and upon weather conditions. As mined, Ohio coals contain from 4 to 10 per cent of moisture. If allowed to air dry a large portion of this moisture is expelled and well air-dried samples of Ohio coals crushed to $\frac{1}{2}$ inch and finer usually contain less than 3 per cent of moisture. On the other hand, the amount of loosely held moisture retained by fine coal (slack) may be quite large. A car of slack which has been rained upon may contain as much as 15 to 20 per cent of moisture, a large part of this, as much as 10 to 15 per cent, being what may be termed "surface" moisture or the moisture which gives the wet appearance to the slack. On the other hand, lump coal containing little or no slack retains a comparatively small amount of surface moisture. Egg and lump coal from a washer, if allowed to drain thoroughly, does not hold over 2 or 3 per cent of moisture as superficial or surface moisture.

However, apparently dry lump coal often contains a considerable amount of moisture. Lump coal gives up moisture very slowly to air, and it is probable that most shipments of lump coal from Ohio mines contain 4 or 5 per cent of moisture upon delivery even in dry summer weather, while in winter the amount in the lump coal as delivered is practically the same as when mined, which in some Ohio coals is as high as 8 or 10 per cent. Shipments of slack made in dry summer weather lose considerable moisture in transit and may contain several per cent less moisture on arrival at the point of destination than when shipped from the mine, while in wet weather the reverse is likely to be true, the shipment containing more moisture than when loaded at the mine.

The statement regarding moisture in Ohio coals applies in general to coals of intermediate moisture content. Under similar conditions, for many West Virginia coals the values are lower; for Illinois, Indiana and Iowa coals, the values are somewhat higher than those given for the Ohio coals, while in the case of lignites the moisture is very much higher, 40 per cent and over as mined, and 10 to 15 per cent in the air-dried lignite.

Unless special precautions are taken to prevent moisture loss during handling, the percentage of moisture in the sample analyzed may be considerably lower than in the coal as mined or shipped, and the specimen analyses exhibited by the operator giving the analysis of his coal are in many cases lower in moisture than the average of the coal which is received by the consumer.

ASH

The term "Ash," as commonly used, means the ignited mineral residue left after complete combustion or burning of the coal. This residue consists essentially of the mineral matter inherent in the coal and varying quantities of slate and clay from the roof or floor of the mine or from partings in the seam itself, also oxide of iron from the combustion of pyrite which may be present in the coal. If the ash contains little iron it is light colored, usually highly silicious and gives little trouble on the grate bars. If it contains much iron it is reddish and may give trouble from clinkering. As ordinarily reported the ash represents the actual weight of mineral residue after the coal is entirely burned.

Corrected ash. Some chemists report "corrected ash," which correction is based on the following points and reasoning: Iron as it occurs in coal is usually present as pyrite, a combination of iron and sulphur of which more will be said under the head of "Sulphur." In burning the coal the iron unites with oxygen from the air and remains in the ash as oxide of iron and weighs more than the iron present in the original coal. One gram of iron when oxidized to ferric oxide weighs 1.43 grams. This one gram of iron if present as pyrite is combined with 1.14 grams of sulphur, and as the chemist does not as a rule determine the iron, but does determine the sulphur in making the corrected ash reports, he bases the amount of the correction upon the amount of sulphur present and deducts three-eighths of the amount of sulphur from the weight of ash as actually weighed. A correction made on this basis is always too large and in some cases may be decidedly too high as some of the sulphur, sometimes as much as 2 per cent, is present as organic sulphur and hence has no iron combined with it. Again some of the iron may be actually present in an oxidized form and hence need no correction. Furthermore, the mineral matter in the coal present as slate or clay upon ignition loses

approximately 15 per cent of combined water, hence the weight of ash derived from this source is lower than the amount of mineral matter originally present, the amount being about 0.17 of one per cent for each per cent of ash derived from clay and shale. Hence if the object of a "corrected ash" is to obtain a correct combustible residue, the correction should also include this correction due to changes in weight in clay and shale, which is directly opposite in its effect upon ash to the corrections made for oxidation of iron. The loss in weight from the ignition of about $2\frac{1}{2}$ per cent of clay equals the increase in the weight of ash due to the oxidation of the iron equivalent to 1 per cent of sulphur present as pyrite. The amounts of clay and slate present are often two or three times as high as the amount of iron present as pyrite. Carbonate and sulphate of calcium are sometimes present as a part of the mineral constituents of the coal, and upon ignition both of these materials lose weight, and the weight of the ignited residue from these materials is less than the weight of the materials as they occur in the coal. A corrected ash which only partially corrects cannot be regarded as very satisfactory and in reporting a proximate analysis the common method of reporting the "ignited mineral residue" as the *ash* is certainly to be preferred to uncertain and possibly misleading "corrected ash" reports.

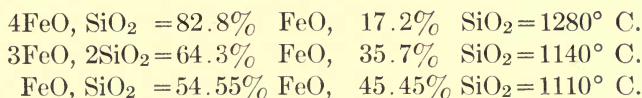
Fusibility of the ash. The fusibility of the coal ash is dependent upon the chemical composition and physical condition of the minerals present. The ash from most coals is highly silicious but the variation in the nature and amounts of the different constituents is so great that no typical composition can be given. The following analyses of ash from different coals taken from Groves and Thorpe¹ serve to illustrate this point:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
SiO ₂	64.21	45.13	31.30	15.48	3.12	1.70
Al ₂ O ₃	28.78	22.47	8.31	5.28	29.50	2.12
Fe ₂ O ₃	2.27	25.83	54.47	74.04	32.78	60.79
CaO	1.34	2.80	3.44	2.26	20.56	19.20
MgO	1.12	0.52	1.60	0.26	2.16	5.03
K ₂ O	2.28	0.60	0.07	0.53	0.99	0.35
Na ₂ O	0.28	0.29	1.72	0.08
CaSO ₄	2.37	0.52	2.17	9.17	10.71

¹ Chemical Technology.

The fusibility of the ignited and well-mixed ash is dependent upon the ratio of the silica to the bases present, upon the particular bases and upon the percentage of alumina present. Mixtures, extremely high in silica, or extremely high in bases are not readily fusible. As a rule the most readily fusible mixtures are those approximating a uni-silicate, but many silicates up to the bi-silicate or even tri-silicate composition are fusible at temperatures between 1000 and 1200° C. (1800 to 2200° F.).

According to Hofman¹, the temperature of formation of some pure ferrous silicates are as follows:



The fusion temperature after the silicate is once formed is considerably lower than the temperature of formation.

Replacing a portion of the ferrous oxide by calcium oxide, magnesium oxide, potassium oxide, etc., gives compounds having a lower formation temperature than the pure ferrous silicates. Replacing a part of the silica by alumina gives compounds having a somewhat higher temperature of formation. Ash which is low in iron is usually so highly silicious that it is not readily fusible. Ash from coals high in pyrite is necessarily high in iron and the ratio between the bases and silica is often such that easily fusible compounds may be formed.

The values given for the temperature of formation of the ferrous silicates are of interest as showing the possible fusibility of the ash, but fusibility of well-mixed ignited ash and fusibility of the ash in the coal during combustion of the coal are two entirely different things. The first is dependent upon the constitution of the ash as a whole; the second is dependent upon the nature and distribution of the different minerals in the coal acting separately or only partially mixed. An ash may form clinker during burning of the coal on account of the fusibility of a portion of the mineral matter when the chemical composition of the ash taken as a whole indicates that clinker should not form. Also some ashes may not clinker during burning of the coal when the chemical composition indicates them to be more fusible than other ashes which do clinker.

¹ Trans. A.I.M.E., Vol. 29.

In the coal the different minerals constituting the ash do not always occur mixed intimately, but lumps of minerals of different composition may be scattered irregularly through the coal. Some of these lumps in themselves may be fusible or form fusible compounds during the burning of the coal. The effect of lumps of pyrite on the clinkering of coal is discussed under "Sulphur."

On account of this irregular distribution of mineral constituents in the coal any effort to establish a close relation of the clinkering properties of the coal ash and the composition of the entire ash will always be more or less unsatisfactory and uncertain. The composition of the ash as a whole tells nothing at all as to the regularity or irregularity of distribution of the different mineral constituents in the coal.

Amount of ash in coal. The quantity of ash is so variable that no definite statement as to the percentage can be given. Clean lumps of some coals occasionally contain as low as 1 per cent of ash while dirty slack may contain as high as 25 per cent. Selected lumps of coal from Ohio seams may be as low as 2 per cent in ash, but no mine can average that figure on its actual output. The best shipments are nearer 6 per cent in ash while much of it may be 9 to 10 per cent. In shipments of slack, the ash may be as high as 14 or 15 per cent or even more. The same statement as to specimen analyses which was given under "moisture" is also applicable in regard to ash, namely, that the content of ash in picked lumps or clean coal is likely to be much lower than the average ash content of the shipment received by the consumer.

SULPHUR

Forms in which it occurs. One of the most prominent forms in which it occurs is iron pyrite (FeS_2). In some cases the pyrite is scattered in large masses or in partings and is readily recognized as such. In other cases it occurs in a very finely divided form, the separate particles being too small to be readily recognized. Another important form in which sulphur occurs is what is known as organic sulphur, or sulphur combined with carbon or carbon and hydrogen. Some Ohio coals show as much as 2 per cent of organic sulphur. Occasionally sulphur occurs in coal in the form of free sulphur but the amount of such is usually quite small. In weathered coal, such as coal near the outcrop of the seam, or the

coal in the face of an old entry or room, or in piles of slack which have been standing for some time exposed to air and moisture, some of the sulphur is present as sulphate of iron, lime and alumina, some forms of pyrite oxidizing very readily upon exposure to air.

Heating value of sulphur. The unoxidized form of sulphur on combustion of the coal is burned to sulphur dioxide, which burning is accompanied by the liberation of heat. Where it occurs as ferrous sulphate or calcium sulphate it has no heating value and during the combustion of the coal the decomposition of these sulphates absorbs heat. The amount of oxidized sulphur in unweathered coal is, however, too small to be of practical importance and for freshly mined coal sulphur may be credited with a heating value of from approximately 2250 to 2950 calories (4050 to 5300 British thermal units), the different values depending upon whether it is present as organic sulphur or as pyrite (FeS_2). If present as pyrite, the heat of its combustion which results in the formation of sulphur dioxide (SO_2) and ferric oxide (Fe_2O_3) is approximately 700 calories (1250 British thermal units) higher than the combustion of sulphur in organic form to sulphur dioxide.

Sulphur in weathered coal. In weathered coal the presence of sulphates may very decidedly affect the heating value per unit of coal, as may be shown by the following: One per cent of sulphur as pyrite in coal has a heating value of about $29\frac{1}{2}$ calories. During combustion of the coal the decomposition of the ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) corresponding to 1 per cent of sulphur absorbs about $21\frac{1}{2}$ calories of heat, which is a net loss in heating value of about 51 calories or about three-fourths of one per cent of the heating value of the coal. If this were the only effect it would not be so important as the amount of sulphur present as sulphate does not often exceed 1 per cent. However, 1 per cent of sulphur as pyrite, on oxidation, absorbs 2 per cent by weight of oxygen and absorbs and combines with about 4 per cent of water which is not given up on air drying so that the apparently air dry coal may be 6 per cent heavier on account of this oxidation of 1 per cent of sulphur, and the calorific value per unit of coal instead of being only three-fourths per cent lower, may be actually nearly 7 per cent lower in heating value.

Action of sulphur dioxide. Upon the cooling of the flue gases the sulphur dioxide formed during the combustion of the coal

unites with water and forms sulphurous acid, which as such or upon further oxidation to sulphuric acid has a corrosive effect upon metallic structures. This corrosive action takes place after cooling and the popular idea that sulphur in coal causes corrosion of boiler tubes, etc., by action of sulphur dioxide is largely without real foundation.

Relation of sulphur to clinkering of the ash. When the sulphur occurs in the coal as pyrite, as it usually does, it is objectionable for two reasons:

First, the oxide of iron produced during combustion may unite with other constituents of the ash and produce a fusible compound or clinker. Oxide of iron by itself produces no clinker, but as has been stated under "ash," the other mineral constituents of the coal are usually highly silicious and oxide of iron in contact with silica or silicates at a high temperature is very liable to result in the production of easily fusible silicates (or clinkers). The higher the temperature the more readily this fusion occurs and the operation of a furnace so as to keep the grate bars and the lower portion of the fuel bed at a relatively low temperature may result in a clean ash, when the same coal with hot grate bars and a hot bed of ash may clinker badly.

Second, pyrite (FeS_2) on being heated gives off approximately one-half of its sulphur, and a compound approximating the formula (FeS) remains. This ferrous sulphide is fusible at a red heat and in the combustion of coals containing pyrite in pieces of considerable size, lumps of this ferrous sulphide may fuse before they have had an opportunity to burn, and may be starting points for the formation of a clinker which may render it difficult to satisfactorily burn the coal. Finely disseminated pyrite will not produce this kind of trouble, but finely disseminated pyrite and a uniform distribution of highly silicious ash is a condition very favorable for the formation of clinker. Organic sulphur has no tendency to form clinker, hence high sulphur in coal is by itself not a certain index of the clinkering qualities of the ash. As a general rule, the higher the sulphur the greater the probability that the ash will clinker, but with frequent exceptions due to the presence of the sulphur in an organic form or due to the fact that the other mineral constituents of the coal are not present in forms or quantities favorable to the production of clinker.

TOTAL HEATING VALUE OF COAL

This is the total number of calories or British thermal units developed when a unit weight of the coal is burned. Expressed in a general way, it is the number of unit quantities of water which are raised one degree by the total heat from the combustion of a unit weight of coal. Expressed in calories it is the number of grams of water which can be raised one degree Centigrade by the heat from the combustion of one gram of coal. Expressed in British thermal units, it is the number of pounds of water which can be raised one degree Fahrenheit by the heat from the combustion of one pound of coal.

The specific heat of water is not uniform at different temperatures and an exact definition requires the defining of the particular temperature through which the water is raised. The temperature most usually taken is from 15 to 16° C. or 62 to 63° F. With this restriction the definition of the calorific value of a coal is the number of grams of water which can be raised from 15 to 16° C. by the heat from the combustion of one gram of coal.

Relation of British thermal value to calorific value. In any given coal the relation between the heating value in calories and in British thermal units is as follows:

$$\begin{aligned} \text{Let the calorific value} &= a, \text{ and} \\ \text{the B.t.u. value} &= b. \end{aligned}$$

then the combustion of 1 gram of coal raises a grams of water 1° C. and the combustion of one pound of coal raises b pounds of water 1° F. Evidently as far as amounts of coal and water are concerned a and b will be numerically equal and the only thing in the two expressions which will cause them to be unequal is the difference in the unit of temperature.

$$1^{\circ} \text{ C.} = \frac{9}{5}^{\circ} \text{ F. or } 1^{\circ} \text{ F.} = \frac{5}{9}^{\circ} \text{ C.}$$

In expressing the value in British thermal units the unit of water is raised only $\frac{5}{9}$ as far as it is in expressing the value in calories, hence $\frac{9}{5}$ as many units can be raised, or numerically,

$$b = \frac{9}{5} a \text{ and conversely } a = \frac{5}{9} b.$$

or in general,

The heating value in B.t.u. = $\frac{9}{5}$ the heating value in calories.
 The heating value in calories = $\frac{5}{9}$ the heating value in B.t.u.

If it is desired to express the amount of heat in a given weight of coal in British thermal units and in calories the relation between one pound and one gram must be considered. One pound avoirdupois = 453.6 grams. Since a British thermal unit is the heat necessary to raise one pound of water one degree Fahrenheit, to express this value in calories the equivalent in grams and degrees Centigrade must be substituted, or one B.t.u. = 453.6 grams of water raised $\frac{5}{9}$ of one degree Centigrade, from which 1 B.t.u. = 252 small calories. Expressing calories in B.t.u., one small calorie = $\frac{1}{252}$ B.t.u. = 0.003967 B.t.u.

Heat producing constituents of coal. The heat of combustion of coal is due essentially to the heat produced by the oxidation of the carbon plus the heat produced by the oxidation of the hydrogen not combined with oxygen plus the oxidation of unoxidized forms of sulphur and iron. The amount of heat produced by the combustion of these elements in combination is not always exactly the same as that produced by the combustion of the free elements separately. However, the difference is not so great but that the heat can be calculated with a fair degree of accuracy from the amounts of these elements present.

Calculation of heating value from chemical composition. Many different formulas have been and are used in calculating the heating value from the chemical analysis. One of the best known and most generally used is Dulong's formula, which is commonly stated as follows:

The heating value = $(8080 \times \text{the carbon}) + [34460 \times (\text{the hydrogen} - \frac{1}{8} \text{ the oxygen})] + (2250 \times \text{the sulphur})$. The results for heating values obtained by the use of this formula are usually within less than 1½ per cent of the actual value as determined in the calorimeter. About 150 analyses of Ohio coals given in Bulletin No. 9 of the Ohio Geological Survey, show that the values by Dulong's formula range from about 30 to about 100 calories lower than the value as determined in the calorimeter. Inspection of the determined and calculated values of the coals given in Chapter X.

shows a very fair agreement between the calculated and determined values.

High oxygen coals show a calculated value considerably lower than the determined value, and the calculated values, as a whole, are lower than the determined values. Two factors may help to account for the greater part of this difference: (1) The latest value given for the heat of combustion of carbon is about 8100 instead of 8080 as used in Dulong's formula. If this higher value for carbon be used, the calculated calorific values will be raised from 10 to 15 calories on each sample. (2) The determined calorific values given were in all cases based upon the heating value of naphthalene as 9692. Later values by Atwater, Fischer and Wrede and the U. S. Bureau of Standards are considerably lower than this. If the value for naphthalene be taken as low as 9628—Atwater's value—this will lower the determined calorific values given by about 50 calories. The effect of these two causes if applied to the values given brings the calculated and determined values much nearer together with the calculated value still somewhat lower than the determined value.

Some of the differences between the calculated and determined values are very probably due to errors in the determination, while others probably correspond to actual differences in the heat developed by the combustion of the different elements in the combinations in which they exist in the coal. Some organic compounds, such as carbon bisulphide, have a decidedly higher calorific value than the calorific value of equivalent amounts of the elements present. In other words, the decomposition of the carbon bisulphide into its elements liberates heat. Such compounds are known as endothermic compounds. The low results obtained by Dulong's formula on some coals indicate the presence of endothermic compounds in the coal.

Distribution of oxygen in coal and modification of Dulong's formula. A small portion of the oxygen (in some high volatile and high moisture coals, a considerable portion) is present in coal in combination with the carbon or at least it escapes in combination with the carbon as carbon dioxide (CO_2) and as carbon monoxide (CO) instead of in combination with the hydrogen as water (H_2O), when the coal is decomposed and the volatile matter is given off. Hence Dulong's formula should be considered merely as a means of estimating heating value rather

than that the composition of the coal is in exact agreement with the formula. Any oxygen combined with carbon has a smaller effect in reducing the heating value than if it is combined with hydrogen, and some calculated heating values agree more closely with the determined ones on the assumption that carbon and oxygen are combined rather than the oxygen and the hydrogen. On this assumption, Dulong's formula would be modified to read as follows:

$$(C - \frac{3}{8}O) 8080 + H(34460) + S(2250).$$

In certain compounds the estimation of the heating value by this formula is closer to the determined value than the estimation by Dulong's formula unmodified. For example, cane sugar ($C_{12}H_{22}O_{11}$) contains 42.1 per cent carbon; 6.43 hydrogen and 51.47 oxygen.

The determined calorific value of cane sugar is 3958 calories. The calculation of the heating value by Dulong's formula is 3402 calories. By the modified formula, assuming the oxygen with the carbon = 4058 calories. Neither calculated value agrees with the determined value. The value calculated by Dulong's formula is 556 calories too low and the value calculated by the modification is 200 calories too high. For this particular material a composite formula, assigning a portion of the oxygen to the carbon and a portion to the hydrogen, is necessary to obtain a calculated result in agreement with the determined value. Many high oxygen coals give better calculated values with a slightly modified formula instead of the regular Dulong formula. However, each class of coal requires a particular modification and often the ultimate analyses themselves may be inaccurate so that special modifications to fit particular samples are to be accepted with caution.

Heat calculation formulas and actual chemical composition. The actual heating value of a fuel is the final heat evolved by complete combustion and may be and usually is the net result of a number of intermediate reactions. In such a complex substance as coal little is known as to the exact nature of the material and of these intermediate reactions and the agreement or non-agreement of the actual and calculated heating values proves nothing as to the exact chemical composition. On account of this lack of knowledge as to exactness of composition and as to the nature of the intermediate decomposition reactions it is not

possible to give an exact general formula for the heating value of coal based on its chemical composition and any and all formulas must be regarded merely as more or less exact approximations. These approximations are in general of practical value only in so far as they accord with actual determinations. However, to the chemist the calculated calorific value has a special application in that it serves as a check on the laboratory work. For any given set of samples of the same kind of coal with accurate calorimeter and ultimate determinations, the agreement or disagreement between the calculated and the determined calorific values should show considerable uniformity and any considerable error in a particular calorimeter or ultimate determination will usually be discovered upon comparing the calculated and determined calorific values.

In the past much importance and stress have been placed on calculated values but at present bomb calorimeters are in such general use that calculated values are apt to be more of special interest to the chemist than of practical importance to the consumer and discussions as to just what formulas are the most applicable are of no great practical interest to the average coal user or producer.

PRACTICALLY AVAILABLE HEATING VALUE OF A COAL

This is the amount that can be utilized, or is the total heating value less the losses necessary or incident to combustion. For a steam boiler, the losses are as follows:

(1) The latent heat in evaporating the water in the coal, including moisture, combined water and water formed during combustion.

(2) The heat carried up the stack as sensible heat by the products of combustion.

(3) The heat carried up the stack by the excess air used in burning the coal.

(4) The heat lost by incomplete combustion, as formation of carbon monoxide (CO) instead of carbon dioxide (CO₂).

(5) Heat not realized from the unburned coal in the ash pit.

(7) Radiation and other losses.

The relative amounts of these losses expressed in percentages range about as follows: Latent heat, 3 to 5 per cent; sensible

heat, 8 to 14 per cent; excess air, 8 to 25 per cent; carbon monoxide (CO), 0 to 5 per cent; unburned coal, 1 to 10 per cent; radiation and other losses, 3 to 15 per cent. The sum of all the losses is usually between 25 and 50 per cent, leaving an available value of 50 to 75 per cent. The actually available value varies with the kind of coal, the type of stoker and boiler used and the completeness of the combustion. The best boiler tests give an available heating value for the best coals as high as 75 per cent, while poor practice and inferior coals may give an available heating value as low as 50 per cent. Losses Nos. 2, 3, 4, 5 and 7 are, within limits, under control of the boiler crew and up to 15 per cent of the total heat may be saved or lost depending upon how the fire is operated. This means as high as 20 per cent of the available value and when fuel bills amount to thousands of dollars, an increase in efficiency by having at least an occasional expert inspection and test run ought to be money well spent.

When two plants operating on practically the same equipment and using the same grade of coal vary greatly in the efficiency obtained one or both of the plants need inspection. Equipment for flue-temperature measurements and adequate apparatus for making flue-gas analyses are usually profitable investments. The determinations which should be made on the flue gases are the determination of the amounts of carbon dioxide (CO₂), oxygen (O₂) and carbon monoxide (CO) present. The determination of carbon dioxide alone by mechanical devices or other means may give fairly satisfactory control if checked by properly taken Orsat determinations. Mechanical or automatic devices left to take care of themselves may be worse than useless. For details and discussion of flue gas sampling and analysis, see Chapter XI.

DETERMINATION OF THE HEAT LOSSES

An illustration of the values and methods of obtaining these losses is as follows:

(1) *Latent heat.*—The amount of this loss is dependent upon the coal used and is not subject to control by the firemen operating the furnace unless the coal is wet down intentionally by the firemen, in which case the latent heat loss is greater than the amount calculated from the analysis. The amount of hydrogen in the coal as determined by analysis multiplied by 9 equals the amount

of water present in the coal together with that formed during combustion. This amount of water multiplied by $539.1 + 0.52(100 - t)$ equals the calories of heat lost. Where 539.1 is the latent heat in evaporating the water at $100^{\circ}\text{C}.$; t is the boiler room temperature in degrees Centigrade and $0.52(100 - t)$ equals the difference between the specific heat of water and the specific heat of water vapor for the range $100 - t$ degrees. The other portion $0.48(100 - t)$ is taken care of under sensible heat carried off by the products of combustion where it is assumed that the water is evaporated at the boiler room temperature and the sensible heat of water vapor calculated from that temperature. The above value for latent heat of water at $212^{\circ}\text{F}.$ is that given by Marks and Davis¹ and is based upon the work of Joly and Henning. The above formula for British thermal units is,

$$\text{B.t.u.} = 970.4 + 0.52(212 - t),$$

with t = boiler room temperature in degrees Fahrenheit.

(2) *Products of combustion.* The products of complete combustion are carbon dioxide, water vapor, sulphur dioxide, nitrogen and ash. The amounts of these obtained from the unit weight of coal are $3\frac{2}{3}$ times the carbon for the carbon dioxide; nine times the hydrogen for the water vapor; two times the sulphur for the sulphur dioxide, and the ash and nitrogen as shown by the analysis. The water equivalent of the products of combustion is obtained by multiplying each of these items by its specific heat and adding the products.

The weight of the nitrogen in the air used for combustion is equal to very nearly 3.33 times the weight of the oxygen required for combustion. This oxygen is equal to $2\frac{2}{3}$ times the carbon, plus eight times the hydrogen, plus the sulphur minus the oxygen contained in the coal. The nitrogen thus obtained multiplied by the specific heat of nitrogen gives the water equivalent of the nitrogen from the air. Similarly the amount of ash multiplied by its specific heat gives the water equivalent of this item.

The sum of all the water equivalents obtained as above multiplied by the difference between the temperature at which the products escape and the temperature of the air supplied for com-

¹ Tables and Diagrams of Thermal Properties of Saturated and Super-saturated Steam.

bustion gives the heat carried off in the products of combustion.

(3) *Excess air.* The excess air present is equal to the amount of air required for combustion multiplied by the ratio of the excess air to that required. The weight of air required for combustion is 4.33 times the oxygen required for combustion, or 4.33 times the sum of $\frac{8}{3}$ of the carbon, plus 8 times the hydrogen plus the sulphur minus the oxygen in the coal. The ratio of the excess air present to that used for combustion is obtained from the analysis of the gases passing out of the chimney. If the small amount of nitrogen present in coal be neglected the ratio of the air present in the chimney gases to the air used in combustion is equal to

$$\frac{\text{Oxygen}}{0.3 \text{ Nitrogen} - \text{Oxygen}}$$

in which the oxygen and nitrogen are percentages by weight of the gases. Where the percentages are given by volume the formula becomes:

$$\frac{\text{Oxygen}}{\frac{\text{Nitrogen}}{3.8} - \text{Oxygen}}$$

Calculation of the excess air. The derivation of the above formula for excess air is as follows:

$$\text{The ratio of the excess air} = \frac{\text{the excess air}}{\text{the air required for combustion}}$$

In the flue gas the oxygen present is that which is in the excess air. The nitrogen present is the nitrogen from the air required plus the nitrogen in the excess air. The required air equals the total air minus the excess air. By volume, air is composed of 20.8 parts oxygen and 79.2 parts nitrogen or for every 4.8 parts of air there are 3.8 parts of nitrogen and one part of oxygen. The excess air is found from the amount of oxygen present and is equal to 4.8 times the oxygen present. The total air is determined from the total nitrogen present and is equal to $\frac{4.8}{3.8}$ times the total nitrogen. Subtracting the excess air (4.8 times the oxygen) from

the total air $\left(\frac{4.8}{3.8} \text{ times the nitrogen}\right)$ gives the air required for combustion as

$$\frac{4.8}{3.8} \text{ nitrogen} - 4.8 \text{ oxygen.}$$

Substituting these values for the excess air and the required air, the ratio of the excess air equals

$$\frac{4.8 \text{ Oxygen}}{\frac{4.8}{3.8} \text{ Nitrogen} - 4.8 \text{ Oxygen}},$$

and dividing by 4.8 gives the formula in the form as given above:

$$\frac{\text{Oxygen}}{\frac{\text{Nitrogen}}{3.8} - \text{Oxygen}}.$$

The formula by weight is obtained in a similar manner.

As an illustration, when the flue gas by volume analyzes as follows:

CO ₂	9.2 per cent
O ₂	10.9 per cent
CO.....	0.0 per cent
N ₂	79.9 per cent
Total.....	100.0 per cent

the excess air, by substituting these values in the formula, is

$$\frac{10.9}{\frac{79.9}{3.8} - 10.9} = 1.08$$

or 108 per cent of the air required for combustion.

These formulas are applicable only where the amount of nitrogen in the fuel is so small as to be neglected as in the case of coals. If, however, the fuel contains nitrogen in considerable quantity, which is the case with some gaseous fuels, the formula

is modified to allow for the nitrogen present in the fuel. The formula where the percentages are given by volume becomes

$$\frac{\text{Oxygen}}{\text{Nitrogen} - \frac{V'E}{V}} - \text{Oxygen}$$

$$\frac{\quad}{3.8}$$

where V' is the volume of gaseous carbon in 100 volumes of flue gas and V the volume of gaseous carbon in 100 volumes of fuel gas and E is the percentage by volume of nitrogen in the fuel gas.

The derivation of this modified formula is as follows: For convenience in calculation, the molecule of carbon in a gaseous state is usually considered as composed of two atoms. As all the carbon in the fuel is present in the products of combustion the relation of the volume of the fuel gas to the volume of the flue gas is obtained by comparison of the ratio of the volumes of the carbon present in the two gases, from which the volume of nitrogen in the fuel gas can be determined in terms of the volume of the flue gas. This is

$$\frac{V'E}{V}$$

The nitrogen in the total air required for combustion is accordingly the total nitrogen in the flue gas minus the nitrogen in the fuel gas or

$$\text{Nitrogen} - \frac{V'E}{V}.$$

To make this clearer by a special example, suppose the fuel gas and the flue gas by volume to have the following composition:

	Fuel Gas.	Flue Gas.
Carbon dioxide (CO ₂)	4.5	14.5
Oxygen (O ₂)	0.5	2.9
Ethylene (C ₂ H ₄)	1.0	
Carbon monoxide (CO)	22.0	
Hydrogen (H ₂)	9.5	
Methane (CH ₄)	3.5	
Nitrogen (N ₂)	59.0	82.6
	100.0	100.0

The volume of carbon molecules in the fuel gas is as follows:

$$\begin{array}{r}
 \frac{1}{2} \times \text{CO}_2 = 2.25 \\
 1 \times \text{C}_2\text{H}_4 = 1.00 \\
 \frac{1}{2} \times \text{CO} = 11.00 \\
 \frac{1}{2} \times \text{CH}_4 = 1.75 \\
 \hline
 \text{Total} = 16.00
 \end{array}$$

In the flue gas the volume of the carbon molecules equals $\frac{1}{2}$ the $\text{CO}_2 = 7.25$. Substituting these values in the formula, it becomes:

$$82.6 - \frac{2.9}{7.25 (59)} = 0.24, \\
 \frac{16}{3.8} - 2.9$$

or 24 per cent of the air required for combustion.

These calculations may be made if desired on the assumption of one atom in the gaseous carbon molecule in which case the volume of the carbon molecules in each gas will be twice as great, but they will have the same ratio to each other and the same numerical result is obtained.

(4) *Incomplete combustion.* The heat lost by incomplete combustion or formation of CO instead of CO_2 is determined as follows: One gram of carbon burned to $\text{CO}_2 = 8080$ calories. One gram of carbon burned to CO = 2430 calories, or the heat loss due to the formation of CO instead of CO_2 is $8080 - 2430 = 5650$ calories. The amount of carbon which is burned to CO instead of CO_2 is determined from the flue gas analysis and the amount of carbon present in a unit of coal. Since equal volumes of CO and CO_2 contain equal amounts of carbon, the ratio of carbon burned to CO instead of CO_2 is equal to the

$$\frac{\text{CO by volume}}{\text{CO}_2 \text{ by volume} + \text{CO by volume}}$$

Multiplying the percentage of carbon present in the coal by this ratio gives the actual amount of carbon burned to CO per unit of coal fired. This multiplied by 5650, equals the calories of heat lost.

(5) *Unburned coal.* The heat not realized from unburned coal in the ash pit is also a large loss in many cases. The total calories of heat lost is the amount of unburned coal times the calorific value of the coal.

Calculation of amount of unburned coal. The amount of unburned coal is determined from the analysis of the refuse taken from the ash pit and the analysis of the coal as fired.

Let the ash in the coal by analysis = a . Then the total volatile and combustible matter including moisture and fixed carbon in the coal by analysis = $1 - a$.

Let the volatile and combustible matter or ignition loss in the refuse = c .

Let the incombustible matter in the refuse = r , all of these values being decimals.

The unburned coal in the refuse expressed in terms of the refuse = $\frac{c}{1-a}$.

The ash in this unburned coal in the refuse expressed in terms of the refuse is

$$a\left(\frac{c}{1-a}\right) = \frac{ca}{1-a}$$

The ash in the unburned coal : total ash :: the unburned coal : total coal. Substituting the above values, this proportion becomes:

$$\frac{ca}{1-a} : r :: x : 1,$$

where x is the unburned coal, from which

$$x = \frac{ca}{(1-a)r}.$$

As a particular example suppose the ash in the coal = 10 per cent. The refuse by analysis = volatile and combustible 30 per cent, incombustible 70 per cent. Substituting these values,

$$\frac{ca}{(1-a)r} = \frac{0.3 (0.10)}{(0.9)(0.7)} = \frac{0.03}{0.63} = 0.049.$$

In which case the loss due to unburned coal equals the calorific value of the coal times 0.049.

(7) *Radiation.* The radiation and other losses. The sum of 1, 2, 3, 4 and 5 plus the heat in the water evaporated subtracted from the total calorific value of the coal gives the radiation and other unaccounted for losses.

Unaccounted losses. Some of the unaccounted losses are as follows:

- (a) Traces of hydrogen and hydrocarbons in the flue gas.
- (b) Unburned carbon in soot and smoke.
- (c) Latent and sensible heat due to water used to wet down the coal or added to the ash pit.
- (d) Sensible heat in flue gas due to the moisture in the air.

The heat losses due to the presence of traces of unburned hydrogen or methane or ethylene in the flue gas are usually considered as small. Certainly no large amounts of these gases are found in the escaping flue gas but the presence of undetermined traces of any of these gases may help to account for some of the unaccounted-for losses. As an example, in the combustion of No. 6 coal with 100 per cent excess air and a flue-gas analysis of CO₂, 9.3; O₂, 10.6; CO, 0.0 and N₂ 80.1 per cent, the presence of $\frac{1}{100}$ per cent of hydrogen (H₂) or of methane (CH₄) or of ethylene (C₂H₄) would represent a heating loss approximately as follows: On the assumption that practically all of the 0.66 gram of carbon in one gram of coal fired is contained in the 9.3 per cent of CO₂ in the flue gas, a molecular volume 22.4 liters of CO₂=44 grams of CO₂=12 grams of carbon. A molecular volume of hydrogen=2 grams of hydrogen, from which 1 cubic centimeter of hydrogen contains by weight one-sixth as much hydrogen as the weight of the carbon in 1 cubic centimeter of CO₂. The relative volumes of hydrogen and CO₂ in the gas on the assumption of $\frac{1}{100}$ per cent of hydrogen present is as 1:930. Hence the weight of hydrogen in the gas corresponding to 1 gram of coal fired is $\frac{1}{3} \times \frac{1}{930} \times 0.66 = \frac{1}{85100}$ gram. The calorific value of $\frac{1}{85100}$ of a gram of hydrogen is $\frac{1}{85100}$ of 34460=4 calories.

One cubic centimeter of methane (CH₄) has approximately 3 times the heating value of 1 cubic centimeter of hydrogen=12 calories. One cubic centimeter of ethylene (C₂H₄) has approximately 5 times the heating value of 1 cubic centimeter of hydro-

gen = 20 calories. Hence for this condition of 100 per cent excess air the losses expressed in percentage of the total calorific value of a fuel are as follows:

- $\frac{1}{100}$ per cent of hydrogen in the flue gas = $\frac{1}{17}$ per cent loss.
- $\frac{1}{100}$ per cent of methane in the flue gas = $\frac{1}{8}$ per cent loss.
- $\frac{1}{100}$ per cent of ethylene in the flue gas = $\frac{2}{7}$ per cent loss.

The determination of hydrogen, methane and ethylene in the flue gas to $\frac{1}{100}$ per cent is not at all easy, and the unaccounted-for losses due to traces of these gases in some cases might have appreciable effects on the heat balances without the chemist in charge being able to determine with certainty the quantities of these gases present.

The heat loss due to the unburned coal in the soot and smoke usually does not exceed a few tenths of one per cent, and any serious effect due to this cause must be due to poor absorption of heat by the boilers as a result of deposition of soot on or in the tubes, or on the heating surfaces.

Water added to dry dusty coal to wet it down just previous to firing may, by securing more favorable conditions of firing, increase the available heating value more than enough to counteract the heat lost by the evaporation of this water and the sensible heat in the water vapor. However, the addition of any water after the coal is actually weighed, in so far as the heat balance is concerned, simply contributes so much more heat as latent and sensible heat to the unaccounted for heat losses. Likewise water added to the ash pit may by its cooling action on the grate bars and lower part of the fuel bed tend to improve the combustion of the coal and make it more efficient. In so far as the heat balance is concerned this sensible and latent heat is also included in the unaccounted-for losses.

The sensible heat carried off by the moisture in the air used varies with the excess air and with the temperature and humidity of the air ranging from less than 0.1 per cent in cold dry weather to upwards of 1 per cent of the total heating value of the coal in warm rainy weather. For example, 1 gram of Ohio No. 6 coal (assuming 100 per cent excess of air) requires:

$$4\frac{1}{3} \times [(0.6903 \times \frac{8}{3}) + (0.0543 \times 8) + (0.0330 \times 1) - 0.1362] = 9.41$$

grams or allowing the 100 per cent excess air = approximately 19 grams of air per gram of coal fired.

19 grams of dry air = 14.7 liters of moist air at 0° C. (32° F) 760 mm. or = 17.0 liters of moist air at 30° C. (86° F) 760 mm.

One liter of saturated air at 0° C. contains 4.8 mg. of water vapor.
One liter of saturated air at 30° C. contains 30 mg. of water vapor.

14.7 liters at 0° C. contains 70 mg. of water vapor
and

17.0 liters at 30° C. contains 510 mg. of water vapor.

The sensible heat of the water vapor at 300° C. (572° F.) for the two conditions is,

$$0.070 \times 0.48 \times 300 = 10 \text{ calories}$$

$$0.510 \times 0.48 \times 270 = 66 \text{ calories}$$

a loss from about 0.14 per cent to about 1 per cent, from which it is apparent that in cold or dry weather the loss is quite small, but that in warm rainy weather it may be very appreciable.

Specific heat of products of combustion. The exactness of the above formulas for determining the available heat depends upon the exactness of the values for the specific heats. The specific heats of the gases were formerly regarded as being practically constant for all temperatures, but more recent researches have shown that changes in the temperatures of the gases are accompanied by changes in the specific heats.

The mean specific heats in small calories per gram molecular volume of gases under constant pressure from 0° Centigrade to temperature (t) based upon the results of Le Chatelier and Mallard are given by Damour¹ substantially as follows:

Diatomic gases (O_2 , N_2 , H_2 and CO) = $6.83 + 0.0006 t$.

Water vapor (H_2O) = $8.08 + 0.0029 t$.

Carbon dioxide (CO_2) = $8.52 + 0.0037 t$.

Methane (CH_4) = $9.78 + 0.006 t$.

The values in small calories per gram of gas or in kilograms calculated per kilogram of gas under constant pressure as given by Richards² and as figured from the formulas given above are as follows:

¹ Industrial Furnaces.

² Metallurgical Calculations, Vol. I.

	RICHARDS.	DAMOUR.
Nitrogen	=0.2405+0.0000214 <i>t</i>	0.2438+0.0000214 <i>t</i>
Oxygen	=0.2104+0.0000187 <i>t</i>	0.2135+0.0000187 <i>t</i>
Water vapor	=0.42 +0.000185 <i>t</i>	0.447 +0.000162 <i>t</i>
Carbon dioxide	=0.19 +0.00011 <i>t</i>	0.194 +0.000084 <i>t</i>
Sulphur dioxide	=0.125 +0.0001 <i>t</i>
Carbon monoxide	=0.2405+0.0000214 <i>t</i>	0.2438+0.0000214 <i>t</i>
Hydrogen	=3.37 +0.0003 <i>t</i>	3.412 +0.000300 <i>t</i>
Methane	0.611 +0.000375 <i>t</i>

The most recent values for specific heats of the common gases are given by Lewis and Randall¹ and are based mainly upon the work of Holborn and Austin, Holborn and Henning and of Pier. The values for specific heats in small calories per gram molecular volume of gas under constant pressure, for absolute temperatures are as follows:

Nitrogen	=6.50+0.0010 <i>T</i> ;
Oxygen	=6.50+0.0010 <i>T</i> ;
Carbon monoxide	=6.50+0.0010 <i>T</i> ;
Hydrogen	=6.50+0.0009 <i>T</i> ;
Water vapor	=8.81-0.0019 <i>T</i> +0.00000222 <i>T</i> ² ;
Carbon dioxide	=7.0+0.0071 <i>T</i> -0.00000186 <i>T</i> ² ;
Sulphur dioxide	=7.0+0.0071 <i>T</i> -0.00000186 <i>T</i> ² .

According to these different authorities the mean specific heats from 0 to 300° Centigrade (572° Fahrenheit) and from 0 to 1000° Centigrade (1832° Fahrenheit) for these different gases are as follows:

	Richards		Damour		Lewis and Randall	
	0 to 300	0 to 1000	0 to 300	0 to 1000	0 to 300	0 to 1000
Nitrogen.....	0.247	0.262	0.250	0.265	0.247	0.259
Oxygen.....	0.216	0.229	0.219	0.232	0.216	0.227
Carbon dioxide.....	0.223	0.300	0.219	0.278	0.219	0.248
Water vapor.....	0.476	0.605	0.497	0.610	0.469	0.512
Carbon monoxide.....	0.247	0.262	0.250	0.265	0.247	0.260
Air.....	0.240	0.257	0.243	0.258	0.240	0.252
Sulphur dioxide.....	0.155	0.225	0.150	0.170
Hydrogen.....	3.460	3.670	3.502	3.712	3.41	3.57
Methane.....	0.723	0.986

The specific heat of ash may be taken as about 0.16.

¹ Jr. Am. Chem. Soc. Vol. XXXIV, page 1128, Sept. 1912.

Calculation of the available heating power of Hocking or Ohio No. 6 coal. As an illustration of the foregoing calculations, the available calorific value of this coal based on the average analysis of the seam and under conditions corresponding to the use of the coal in a steam boiler of the best type working under the best conditions is calculated as follows: The excess of air under the conditions assumed is taken at 50 per cent, flue temperature at 300° C., temperature of the air at zero and the temperature at which the ash is withdrawn from the furnace the same as the temperature of the air. The composition and the calorific value of the coal are:

Carbon.....	0.6903
Hydrogen.....	0.0543
Nitrogen.....	0.0126
Oxygen.....	0.1362
Sulphur.....	0.0330
Ash.....	0.0736
Calorific value.....	6980 Calories

The latent heat equals $9 \times 0.0543 \times (539.1 + 0.52(100)) = 288.7$

The water equivalent of the products of combustion exclusive of the nitrogen in the air equals:

Carbon dioxide	$= 0.6903 \times \frac{11}{3} \times 0.223 = 0.5644$
Water	$= 0.0543 \times 9 \times 0.476 = 0.2326$
Sulphur dioxide	$= 0.0330 \times 2 \times 0.155 = 0.0102$
Nitrogen	$= 0.0126 \times 0.247 = 0.0031$
	<hr/> 0.8103

The oxygen in the air used in combustion equals:

For carbon	$= \frac{8}{3} \times 0.6903 = 1.8408$
For hydrogen	$= 8 \times 0.0543 = 0.4344$
For sulphur	$= 0.0330$
	<hr/> 2.3082
Deducting the oxygen in the fuel	0.1362
	<hr/> 2.1720

The water equivalent of the nitrogen in the air corresponding to the oxygen equals $3.33 \times 0.247 \times 2.1720 = 1.7865$.

The water equivalent of the products of combustion, 0.8103, plus the water equivalent of the nitrogen from the air, 1.7865,

equals 2.5968, which multiplied by 300° , the flue temperature—equals 779.0, the sensible heat carried off in the products of combustion.

The excess air equals the oxygen (2.1720) multiplied by 4.33 and by 0.5 (the ratio of excess air), or $2.1720 \times 4.33 \times 0.5 = 4.7024$. The heat carried off in the excess air equals:

$$4.7024 \times 0.24 \times 300^{\circ} = 338.6 \text{ heat units.}$$

Writing these various values together and adding them, gives the following:

Latent heat	= 288.7
Heat lost in products of combustion (including nitrogen from air used)	= 779.0
Heat lost in excess air in flue gas	= 338.6
Total	= <u>1406.3</u>

Deducting the sum (1406.3) from the calorific value of the fuel (6980) leaves 5573.7 as the heat theoretically available per unit of fuel and under the conditions assumed. This is equal to about 80 per cent of the total calorific value.

This value is higher than the actual available value as any heat loss due to unburned coal in the ash pit or the formation of CO instead of CO_2 and the radiation losses are included in the 80 per cent. Also the assumed value of 50 per cent for the excess air is much lower than is usually found, 100 per cent excess being a closer approximation to common practice. With 100 per cent excess air and the same flue temperature, 300°C. , (572°F.) the heat loss due to excess air is 338.6 calories higher or approximately 4.8 per cent of the total heating value. Assuming 5 per cent for unburned coal remaining in the ash pit, or that the coal actually burned equals 95 per cent of the coal fired then the heat lost in the excess air and in the products of combustion with 100 per cent excess air is 0.95 of $(1406.3 + 338.6) = 1657.6$ calories or 23.8 per cent of the total heating value. To this add 5 per cent, the heat in the unburned coal, = $23.8 + 5 = 28.8$ per cent. Then $100 - 28.8 = 71.2$ per cent for evaporation of water and radiation and unaccounted-for losses. If the radiation and unaccounted for losses be taken as 10 per cent the remainder available for actual evaporation of water =

61.2 per cent of the total heating value. 61.2 per cent of 6980 calories = 4272 calories. Dividing this number by 539.1, the latent heat of evaporation of water into steam at 100° C., gives 7.92 as the number of grams of water that can be evaporated by one gram of coal, or expressed in pounds as the number of pounds of water that can be evaporated by one pound of coal.

Printed forms for calculating the heat balance. The calculation of the heat balance can be shortened and made much easier by the use of a printed form for entering the various values as determined or as calculated. Such a form using logarithms with the logarithms of the constants printed on the form saves much labor in multiplying and dividing and once familiar with the routine the calculation is comparatively simple.

On pages 28-29 are given the calculation of the Ohio No. 6 coal together with data on the flue-gas and refuse and assuming that the refuse is removed from the ash pit at 300° C. The values for the specific heats corresponding to the logarithms used are as follows: Nitrogen, 0.246; oxygen, 0.215; water vapor, 0.48; carbon dioxide, 0.217; carbon monoxide, 0.220; air, 0.238; sulphur dioxide, 0.15; ash, 0.16.

THE USE OF THERMAL CAPACITY TABLES FOR HEAT CALCULATIONS

The use of thermal capacity tables to determine the sensible heat carried off in the flue gas considerably shortens heat balance calculations.

By thermal capacity of a gas is meant the heat necessary to raise a definite quantity of the gas from 0° C. to the temperature (t). The tables may be figured on any basis desired, as the thermal capacity per liter, per molecular volume or per cubic foot, or the thermal capacity per kilogram, gram or pound, or as in the table given the thermal capacity of the gas corresponding to a gram of one of the elementary constituents of the gas, as the thermal capacity of carbon dioxide per gram of carbon, from which the carbon dioxide is derived. The table which follows is on the basis of the thermal capacity of the several gases, produced during combustion, corresponding to one gram of the elements—carbon—hydrogen—sulphur and nitrogen in the coal. The value for air is per gram of air.

HEAT BALANCE FOR BOILER TEST WITH COAL

Analysis of Coal		C' = Carbon in coal burned H' = Hydrogen in coal burned O' = Oxygen in coal burned S' = Sulphur in coal burned N' = Nitrogen in coal burned C'' = Carbon burned to CO C''' = Carbon burned to CO ₂ C' = C'' + C'''	Unburned Coal = D		Carbon as CO	
Moisture	5.56		C' = Carbon burned to CO C''' = Carbon burned to CO ₂ C' = C'' + C'''	= ac r(1 - a)		Log. C' =
Vol. Combustible	38.11	a = Ash in coal by analysis		c = Combustible in refuse	r = Incombustible in refuse	Log. C'' =
Fixed Carbon	48.96	C'' = Carbon burned to CO C''' = Carbon burned to CO ₂ C' = C'' + C'''	(All decimals)		C'' =	Log. C'' = Log. $\frac{1}{3}$ = 0.3680
Ash	7.36		Log. a = $\bar{2}.8669$	Log. c = $\bar{1}.6010$	Log. CO =	
Total	100.00	C'' = Carbon burned to CO C''' = Carbon burned to CO ₂ C' = C'' + C'''	Log. ac = $\bar{2}.4679$	Log. r = $\bar{1}.7789$	Log. CO =	Log. Sp. ht. = $\bar{1}.3424$ Σ Log. =
Hydrogen (H)	5.43		Log. r(1 - a) = $\bar{1}.9668$	Log. r(1 - a) = $\bar{1}.7457$	Log. Sp. ht. = $\bar{1}.3424$	
Carbon (C)	69.03	ΣO - O' = Oxygen from air used 3½(ΣO - O') = N'' = Nitrogen from air used	Log. ac = $\bar{2}.4679$	Log. r(1 - a) = $\bar{1}.7457$	W. E. CO = 0	
Nitrogen (N)	1.26		Log. (-) Log. r(1 - a) = $\bar{1}.7457$	Log. D = $\bar{2}.7222$	Heat Loss Due to Formation of CO	
Oxygen (O)	13.62	Excess Air = $\frac{O}{3.8} - O$ $\frac{N}{3.8} - O = 21.08$ $\frac{N}{3.8} - O = 10.60$ $\frac{N}{3.8} - O = 10.48$	D = 0.0527	Log. C'' =	Log. 5650 = 3.7520 Σ Log. =	
Sulphur (S)	3.30		Log. (1 - D) = $\bar{1}.9765$	1 - D = 0.9473		Σ Log. =
Ash (a)	7.36	Log. Xs Air = 0.0049	Log. (1 - D) = $\bar{1}.9765$	No. Calories = 0		
Total	100.00		Loss Due to Unburned Coal	Log. D = $\bar{2}.7222$	Oxygen in CO	
Calorific Value		Log. Xs Air = 0.0049	Log. cal. value = $\bar{3}.8439$	Log. C'' =	Log. $\frac{1}{3}$ = 0.1249	
Calories	6980		Σ Log. = $\bar{2}.5661$	No. Calories = 268		Log. O'' =
B.T.U.	12564	Log. Xs Air = 0.0049	Log. (1 - D) = $\bar{1}.9765$	O'' = 0		
Analysis of Refuse			Ash	Ash(1 - D) = 0.0697	Carbon as CO ₂	
Combustible (c)	39.9	Log. Xs Air = 0.0049	D = 0.0527	C''' = C' - C''	Log. C''' = $\bar{1}.8155$ Log. $\frac{1}{3}$ = 0.5643	
Refuse (r)	60.1		Ash(1 - D) + D = $\bar{0}.1224$	Ash(1 - D) + D = $\bar{1}.0878$		Log. Sp. ht. = $\bar{1}.3365$
Total	100.0	Log. Xs Air = 0.0049	Log. Sp. ht. = $\bar{1}.2041$	Σ Log. = $\bar{1}.7163$		
Analysis of Flue Gas			W. E. Ash = 0.0197	Σ Log. = $\bar{2}.2919$	W. E. CO ₂ = 0.524	
By Vol.		Log. Xs Air = 0.0049	W. E. Ash = 0.0197	Oxygen in CO ₂		
CO ₂	9.4		Carbon	Log. Carbon(C) = $\bar{1}.8390$	Log. C''' = $\bar{1}.8155$ Log. $\frac{1}{3}$ = 0.4259	
O ₂	10.6	Log. Xs Air = 0.0049	Log. (1 - D) = $\bar{1}.9765$	Log. O'' = 0.2414		
CO	0.0		Log. C' = $\bar{1}.8155$	O''' = 1.744		
N ₂	80.1	Log. Xs Air = 0.0049	Log. C' = $\bar{1}.8155$			
Total	100.0					
Temperature		Log. Xs Air = 0.0049				
Flue Gases (t') = 300						
Boiler Room (t) = 0		Log. Xs Air = 0.0049				
t' - t = 300						
Water Evaporated		Log. Xs Air = 0.0049				
per lb. coal = 7.96						
Water Evaporated = W = 7.96		Log. Xs Air = 0.0049				
CO (by vol.) = Q		Log. Xs Air = 0.0049				
CO + CO ₂ (by vol.) = Q						
No. Calories = 4270						

Note.—Where the amount of CO present in the flue gas is small, the calculation of the sensible heat carried off by CO may be omitted, and in calculating the heat carried off as CO₂, C' taken as = C'''.

TEST NO.

DATE.

COAL "OHIO No. 6"

<p>Hydrogen</p> <p>Log. H = 2.7348 Log. (1 - D) = 1.9765</p> <p>Log. H' = 2.7113</p> <p>Log. H'' = 2.7113 Log. 9 = 0.9542 Log. Sp. h. = 1.6812</p> <p>Σ Log. = 1.3467</p> <p>W. E. H₂O = 0.222</p> <p>Oxygen in H₂O</p> <p>Log. H' = 2.7113 Log. 8 = 0.9031</p> <p>Log. O'v = 1.6114</p> <p>O'v = 0.4116</p> <p>Latent Heat</p> <p>Log. H₂O = 1.6655 Log. (591.1 - 0.52t) = 2.7717</p> <p>Σ Log. = 2.4372</p> <p>Latent Heat = 274</p> <p>Sulphur</p> <p>Log. S = 2.5185 Log. (1 - D) = 1.9765</p> <p>Log. S' = 2.4950</p> <p>Log. S'' = 2.4950 Log. 2 = 0.3010 Log. Sp. ht. = 1.1761</p> <p>Σ Log. = 3.9721</p> <p>W. E. SO₂ = 0.0094 Ov = S' = 0.0312</p> <p>Nitrogen</p> <p>Log. N = 2.1004 Log. (1 - D) = 1.9765</p> <p>Log. N' = 2.0769</p> <p>N'' = 0.0119 N''' = 6.86</p> <p>Σ = 6.872</p> <p>Log. Σ = 0.8371 Log. Sp. ht. = 1.3909</p> <p>Σ Log. = 0.2280</p> <p>W. E. N₂ = 1.69</p>	<p>Oxygen</p> <p>Log. O = 1.1341 Log. (1 - D) = 1.9765</p> <p>Log. O' = 1.1106</p> <p>O'' = 0.1290</p> <p>O''' = 1.7440 O'v = 0.4116 Ov = 0.0312</p> <p>Σ O = 2.1868</p> <p>Σ O - O' = 2.0578</p> <p>3½ (Σ O - O') = N'' = 0.3134 Log. (Σ O - O') = 0.3134 Log. 3½ = 0.5229</p> <p>Log. N'' = 0.8363</p> <p>N'' = 6.86</p> <p>Heat in Excess Air</p> <p>Log. (Σ O - O') = 0.3134 Log. 4½ = 0.6368</p> <p>Log. Air = 0.9502</p> <p>Log. Air = 0.9502 Log. Xs Air = 0.0049 Log. Sp. ht. = 1.3766</p> <p>Log. (t' - t) = 2.4771</p> <p>Σ Log. = 2.8088</p> <p>No. Calories = 644</p>	<p>Water Equivalent of Products of Combustion</p> <p>W. E. CO₂ = 0.524 W. E. CO = 0.000 W. E. H₂O = 0.222 W. E. N₂ = 1.690 W. E. SO₂ = 0.009 W. E. Ash = 0.020</p> <p>Σ = 2.465</p> <p>Log. Σ = 0.3918 Log. (t' - t) = 2.4771</p> <p>Σ Log. = 2.8689</p> <p>No. Calories = 740</p> <p>Heat Balance</p> <table border="1" style="width:100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th>Calories</th> <th>%</th> </tr> </thead> <tbody> <tr> <td>Latent Heat</td> <td>274</td> <td>3.9</td> </tr> <tr> <td>Products of combustion</td> <td>740</td> <td>10.6</td> </tr> <tr> <td>Excess Air</td> <td>644</td> <td>9.3</td> </tr> <tr> <td>CO</td> <td>0</td> <td>0.0</td> </tr> <tr> <td>Unburned coal</td> <td>368</td> <td>5.3</td> </tr> <tr> <td>Water evaporated</td> <td>4270</td> <td>61.2</td> </tr> <tr> <td>Loss</td> <td>684</td> <td>9.7</td> </tr> <tr> <td>Total</td> <td>6980</td> <td>100.0</td> </tr> </tbody> </table> <p>Total heat carried off by H₂O in gases =</p> <p>{ (100 - t) = the heat required to raise water to 100° C. { 539.1 = the latent heat of vaporization at 100° C. { 0.48(t' - 100) = the sensible heat in water vapor from 100° to t'.</p> <p>This may be written</p> <p>0.52(100 - t) + 0.48(100 - t) + 539.1 + 0.48(t' - 100) = 539.1 + 0.52(100 - t) + 0.48(t' - t) = 591.1 - 0.52t (the latent heat) + 0.48(t' - t) the sensible heat in water vapor from t up to t'.</p>		Calories	%	Latent Heat	274	3.9	Products of combustion	740	10.6	Excess Air	644	9.3	CO	0	0.0	Unburned coal	368	5.3	Water evaporated	4270	61.2	Loss	684	9.7	Total	6980	100.0
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If 0.01 of the carbon burns to CO and is calculated to CO₂ instead, the error introduced in sensible heat is about 5.6 cal. where flue gas is 200° C. above boiler-room temperature.

THERMAL CAPACITY FROM 0° C. TO TEMPERATURE (*t*)

VALUES IN SMALL CALORIES

° F.	Temper- ature, ° C.	Air per Gram of Air.	Dif. per 1° C.	Nitrogen per Gram of Nitrogen.	Dif. per 1° C.	CO ₂ per Gram of Carbon.	Dif. per 1° C.	CO per Gram of Carbon.	Dif. per 1° C.	SO ₂ per Gram of Sulphur.	Dif. per 1° C.	H ₂ O per Gram of Hydrogen.	Dif. per 1° C.
32	0												
50	10	2.37		2.44	0.244	7.1	0.72	5.7	0.55	2.5	0.26	40.6	4.08
68	20	4.74	0.237	4.88	0.244	14.3	0.73	11.6	0.55	5.1	0.26	81.4	4.11
86	30	7.12	0.238	7.33	0.245	21.6	0.73	17.1	0.56	7.7	0.27	122.5	4.14
104	40	9.50	0.239	9.78	0.246	28.9	0.74	22.9	0.57	10.4	0.27	163.9	4.17
122	50	11.89	0.239	12.24	0.246	36.3	0.74	28.6	0.57	13.1	0.27	205.6	4.20
140	60	14.28	0.239	14.70	0.247	43.7	0.75	34.3	0.58	15.8	0.28	247.6	4.23
158	70	16.67	0.240	17.17	0.247	51.2	0.76	40.1	0.58	18.6	0.29	289.9	4.26
176	80	19.07	0.241	19.64	0.247	58.8	0.76	45.9	0.58	21.5	0.29	332.5	4.28
194	90	21.48	0.241	22.11	0.248	66.4	0.77	51.6	0.58	24.4	0.29	375.3	4.32
212	100	23.88	0.242	24.59	0.248	74.1	0.77	57.4	0.58	27.3	0.29	418.5	4.35
230	110	26.30	0.242	27.07	0.249	81.8	0.78	63.2	0.58	30.2	0.30	462.0	4.36
248	120	28.71	0.242	29.56	0.249	89.6	0.78	69.0	0.58	33.2	0.31	505.6	4.41
266	130	31.13	0.242	32.05	0.249	97.5	0.79	74.8	0.58	36.3	0.31	549.7	4.43
284	140	33.56	0.243	34.55	0.250	105.4	0.79	80.6	0.58	39.4	0.31	594.0	4.44
302	150	35.98	0.243	37.05	0.250	113.4	0.80	86.5	0.59	42.5	0.31	638.6	4.46
320	160	38.42	0.244	39.55	0.250	121.5	0.81	92.4	0.59	45.6	0.32	683.8	4.49
338	170	40.85	0.244	42.06	0.251	129.6	0.82	98.2	0.59	48.8	0.33	728.7	4.52
356	180	43.29	0.244	44.57	0.251	137.8	0.82	104.1	0.59	52.1	0.33	774.1	4.54
374	190	45.73	0.245	47.08	0.252	146.0	0.83	110.0	0.59	55.4	0.33	819.9	4.58
392	200	48.19	0.245	49.61	0.252	154.3	0.83	115.8	0.59	58.7	0.33	866.0	4.61
410	210	50.64	0.247	52.13	0.252	162.7	0.84	121.7	0.59	62.1	0.34	912.3	4.63
428	220	53.09	0.245	54.66	0.253	171.1	0.84	127.6	0.59	65.5	0.34	958.9	4.66
446	230	55.55	0.246	57.20	0.254	179.6	0.85	133.6	0.59	69.0	0.35	1005.9	4.70
464	240	58.02	0.247	59.74	0.254	188.1	0.85	139.5	0.59	72.6	0.35	1053.1	4.72
482	250	60.49	0.247	62.28	0.255	196.9	0.87	145.4	0.59	76.0	0.35	1100.6	4.74
500	260	62.97	0.248	64.83	0.255	205.6	0.87	151.4	0.60	79.6	0.36	1148.4	4.78
518	270	65.44	0.248	67.37	0.255	214.2	0.87	157.3	0.60	83.2	0.36	1196.5	4.81
536	280	67.92	0.248	69.93	0.256	222.9	0.87	163.3	0.60	86.9	0.37	1244.9	4.84
554	290	70.41	0.249	72.48	0.256	231.8	0.89	169.3	0.60	90.6	0.37	1293.5	4.86
572	300	72.90	0.249	75.05	0.257	240.7	0.89	175.3	0.60	94.4	0.38	1342.5	4.90
590	310	75.40	0.250	77.62	0.257	249.7	0.90	181.3	0.60	98.2	0.38	1391.7	4.92
608	320	77.89	0.250	80.19	0.257	258.8	0.91	187.3	0.60	102.0	0.38	1441.2	4.95
626	330	80.39	0.250	82.77	0.258	267.9	0.91	193.3	0.60	105.9	0.39	1491.1	4.99
644	340	82.90	0.251	85.35	0.258	277.0	0.91	199.3	0.60	109.8	0.39	1541.2	5.01
662	350	85.42	0.251	87.94	0.259	286.3	0.92	205.3	0.60	113.8	0.40	1591.6	5.04
680	360	87.93	0.251	90.53	0.259	295.5	0.92	211.4	0.61	117.8	0.40	1642.3	5.07

$$1^{\circ} \text{ F.} = \frac{5}{9}^{\circ} \text{ C.} \quad (^{\circ} \text{ C.} \times \frac{9}{5}) + 32 = ^{\circ} \text{ F.}$$

$$1^{\circ} \text{ C.} = \frac{9}{5}^{\circ} \text{ F.} \quad (^{\circ} \text{ F.} - 32) \times \frac{5}{9} = ^{\circ} \text{ C.}$$

To determine the heat necessary to raise a gas from temperature *t* to *t'* by means of a thermal capacity table, the thermal capacity of the gas at *t* is subtracted from the thermal capacity of the gas at *t'*. For example, the heat required to raise 1 gram of air from 20° C. to 320° C. is the difference between the thermal capacity at 320° C. and the thermal capacity at 20° C. = 77.89 - 4.74 = 73.15 calories. In ordinary boiler test calculations his value can be obtained with sufficient accuracy by simply

taking the thermal capacity of the gas corresponding to the difference in temperature. 320°C. minus $20^{\circ}\text{C.} = 300^{\circ}\text{C.}$, and the thermal capacity of the gas at 300°C. by the table is 72.90 as against the more exact figure 73.15, an agreement sufficiently close to warrant the use of the abbreviated method in most calculations.

The calculation of No. 6 coal using the data on the logarithmic form and the thermal values using the table of thermal capacities is as follows:

The unburned coal is 0.0527 from which $1-d=0.9473$. The values of the different constituents in the coal burned for a unit of coal as fired are as follows:

$$\left. \begin{array}{l} \text{Carbon} \dots\dots\dots 0.6903 \\ \text{Hydrogen} \dots\dots\dots 0.0543 \\ \text{Nitrogen} \dots\dots\dots 0.0126 \\ \text{Oxygen} \dots\dots\dots 0.1362 \\ \text{Sulphur} \dots\dots\dots 0.3330 \\ \text{Ash} \dots\dots\dots 0.0736 \end{array} \right\} \times (1-d) \text{ or } 0.9473 = \left\{ \begin{array}{l} C' = 0.6539 \\ H' = 0.0514 \\ N' = 0.0119 \\ O' = 0.1290 \\ S' = 0.0312 \\ A' = 0.0697 \end{array} \right.$$

The latent heat $= 9 \times 0.0514 \times (539.1 + 0.52 (100)) = 274.$

The sensible heat of the products of combustion using the thermal capacity values of the gases for 300° equals:

For carbon dioxide	$= 0.6539 \times 240.7$	$= 157.0$
For carbon monoxide	$= 0.0000 \times$	$=$
For water	$= 0.0514 \times 1342$	$= 69.0$
For sulphur dioxide	$= 0.0312 \times 94.4$	$= 3.0$
For nitrogen	$= 0.0119.$ (See below)	

The sum $= 229.0$

The oxygen required for carbon dioxide $= 0.6539 \times \frac{8}{3} = 1.7437$

The oxygen required for water $= 0.0514 \times 8 = 0.4112$

The oxygen required for sulphur dioxide $= 0.0312 \times 1 = 0.0312$

Total $= 2.1861$

Deducting the oxygen in the fuel 0.1290

The oxygen from the air required $= 2.0571$

The nitrogen corresponding to the oxygen $= 3.33 \times 2.057 = 6.85$. To this add the nitrogen in the coal, $0.0119 = 6.862$. The

sensible heat in the nitrogen using the thermal value for 300°
 $= 6.862 \times 75.05 = 515.0$.

The excess air $= 4.33 \times$ oxygen required $(2.057) \times 1.01$, the ratio of the excess air $= 8.996$.

The sensible heat in the excess air $= 8.996 \times$ thermal capacity of air for 300° $= 8.996 \times 72.90 = 656$.

The sensible heat of the refuse $=$ [the ash (0.0697) + the unburned coal (0.0527)] $\times 0.16$ (the specific heat) $\times 300 = 5.9$

The heat lost due to the formation of

$$CO = C' \times \frac{CO}{CO + CO_2} \times 5650 = 000.0$$

The heat lost in unburned coal $= 0.0527 \times 6980 = 368.0$.

The heat of the water evaporated $= 7.92 \times 539.1 = 4270.0$

The summary of the heat balance is as follows:

	Calories.	Per Cent.
Latent heat	274	3.9
Products of combustion (including refuse)	747	10.7
Excess air	656	9.4
Carbon monoxide	000	0.0
Unburned coal	368	5.3
Water evaporated	4270	61.2
Radiation, etc.	665	9.5
Total	6980	100.0

The values obtained for the losses in the products of combustion and in the excess air are 7 and 12 calories higher than those obtained by use of the logarithmic form. A portion of this difference is due to the use of the log tables but the greater portion is due to the differences in the values taken for specific heats, the values used on the logarithmic form differing somewhat from Damour's values which are used in the thermal capacity table. The differences are not large, but are sufficient to call attention to the fact that the actual results obtained depend upon the particular constants used.

To change calories into B.t.u., it is only necessary to multiply each item in calories by $\frac{9}{5}$ to obtain the equivalent value in B.t.u. The percentage relations are unchanged.

Balance on basis of coal fired. The heat balance as given is based on the amount of coal actually fired under the boiler. From this balance the calculation to any basis desired is comparatively easy.

(1) *Per pound of dry coal fired.* To obtain the values per pound of dry coal fired, divide the values per pound of coal fired by $(1 - \text{the moisture in the coal})$.

(2) *Per pound of combustible fired.* (Combustible by the Mechanical Engineering Code definition = $1 - (\text{moisture} + \text{ash})$). To obtain the values per pound of combustible fired, divide the values per pound of coal fired by $1 - (\text{moisture} + \text{ash})$.

(3) *Per pound of coal burned.* To obtain the values per pound of coal burned omit the item of unburned coal and divide the remaining items per pound of coal fired by $(1 - \text{the unburned coal})$. Reduce to a basis of 100 per cent.

(4) *Per pound of dry coal burned.* Omit the item of unburned coal and divide the remaining items per pound of coal fired by $[(1 - \text{the moisture}) \times (1 - \text{the unburned coal})]$. Reduce to a basis of 100 per cent.

(5) *Per pound of combustible burned.* Omit the item of unburned coal and divide the other values per pound of coal fired by $[(1 - (\text{moisture} + \text{ash})) \times (1 - \text{the unburned coal})]$. Reduce to a basis of 100 per cent.

For purposes of comparing different values, or comparing boiler efficiency, some of these modified forms are desirable, but there appears no valid reason for not making the "coal as fired" the primary basis. Certainly the consumer testing out two coals needs this basis as he pays for the coal in the ash pit just the same as for that which is burned and a report of a balance omitting the item of unburned coal is hardly to be considered as complete.

The foregoing heat balance in its essential details has been used in the Departments of Metallurgy and Mechanical Engineering at the Ohio State University for the past fifteen years and graduates of these departments who conduct boiler tests are consistently using heat balance forms based on these principles. The mechanical engineering profession, in general, has not given this basis of calculation the consideration that it deserves, but has continued to use the older code form.

The Code balance recommended by the American Society of Mechanical Engineers is based on the combustible actually burned. The distribution of the items is as follows:

HEAT BALANCE OR DISTRIBUTION OF THE HEATING VALUE OF THE
COMBUSTIBLE

Total Heat Value of 1 Pound of Combustible	B.t.u.	Per Cent.
1. Heat absorbed by the boiler = evaporation from and at 212° per pound of combustible $\times 965.7$
2. Loss due to moisture in coal = per cent of moisture referred to combustible divided by $100 \times [(212 - t + 966 + 0.48(T - 212))]$ (t = temperature of air in the boiler room, T = that of the flue gases.)
3. Loss due to moisture formed by the burning of hydrogen = per cent of hydrogen to combustible divided by $100 \times 9 \times [(212 - t) + 966 + 0.48(T - 212)]$
4. Loss due to heat carried away in the dry chimney gases = weight of gas per pound of combustible $\times 0.24(T - t)$
5. Loss due to incomplete combustion of carbon = $\frac{\text{CO}}{\text{CO}_2 + \text{CO}} \times \frac{\text{per cent C in combustible}}{100} \times 10150$
6. Loss due to unconsumed hydrogen and hydrocarbons, to heating the moisture in the air, to radiation, and unaccounted for
Totals	100.00

A comparison of the items given in the heat balance of the coal as fired with the items of the Code balance is as follows:

Item.	Balance Coal as Fired.	Code Balance.
No. 1. Latent heat		corresponds to Nos. 2 and 3
No. 2. Sensible heat in products of combustion		corresponds to part of Nos. 2, 3, and 4
No. 3. Heat in the excess air		corresponds to remainder of No. 4
No. 4. Heat lost due to CO		corresponds to No. 5
No. 5. Loss due to unburned coal		not included
No. 6. Heat in the water evaporated		corresponds to No. 1
No. 7. Radiation and other losses		corresponds to part of No. 6

A balance to be satisfactory should show where all the heat goes and should separate the variable heat losses into separate items in order that the magnitude of each can be readily appreciated. In this respect the enumeration of the heat lost in the unburned coal and the heat lost in the excess air as separate

items is a decided improvement over the code form. The separation of relatively fixed losses from the more variable ones is certainly desirable in order to more clearly appreciate the magnitude of the variable losses, as loss due to too much air compared to the loss from formation of CO due to too little air or the losses in sensible heat for different temperatures of the flue gases and different percentages of excess air. For example, what are the losses in burning Ohio No. 6 (Hocking) Coal with 50 per cent excess air and 0.2 per cent of CO in the flue gas and a flue temperature of 350° C.; or with 150 per cent excess air and no CO in the flue gas at temperatures of 200 and 300° compared with the given conditions of 100 per cent excess air, no CO and a temperature of 300° C? These conditions as to excess air correspond to flue gas analyses as follows:

ANALYSIS OF FLUE GASES WITH VARYING EXCESS AIR

	50 Per Cent.	100 Per Cent.	150 Per Cent.
CO ₂	12.7	9.5	7.4
O ₂	7.0	10.4	12.5
CO.....	0.2	0.0	0.0
N ₂	80.1	80.1	80.1
	100.0	100.0	100.0

The carbon burned to CO with 50 per cent excess air is $\frac{CO}{CO_2 + CO} = \frac{2}{129} = 1.55$. 1.55 of 0.6538 (the carbon burned per unit of coal fired) = 0.01 gram per gram of coal fired.

The calculated losses with the different conditions are as follows:

100 per cent excess air, 300° C., 0 per cent CO

Products of combustion = (as already calculated)	740
Excess air..... = (in the heat balance.)	644
CO..... = (See log sheet.)	0
Total.....	<hr/> 1384

50 per cent excess air, 350° C., 0.2 per cent CO

$$\text{Products of combustion} = 740 \times \frac{350}{300} = 863$$

$$\text{Excess air} \dots\dots\dots = 644 \times \frac{1}{2} \times \frac{350}{300} = 376$$

$$\text{CO} \dots\dots\dots = 0.01 \times 0.5650 = 57$$

$$\text{Total} \dots\dots\dots 1296$$

150 per cent excess air, 200° C., 0 per cent CO

$$\text{Products of combustion} = 740 \times \frac{200}{300} = 493$$

$$\text{Excess air} \dots\dots\dots = 644 \times \frac{3}{2} \times \frac{200}{300} = 644$$

$$\text{CO} \dots\dots\dots = 0$$

$$\text{Total} \dots\dots\dots 1147$$

150 per cent excess air, 300° C., 0 per cent CO

$$\text{Products of combustion} = 740 \times \frac{300}{300} = 740$$

$$\text{Excess air} \dots\dots\dots = 644 \times \frac{3}{2} = \frac{300}{300} = 966$$

$$\text{CO} \dots\dots\dots = 0$$

$$\text{Total} \dots\dots\dots 1706$$

These widely divergent values serve to show the importance of a proper relation of excess air to flue temperature and the importance of having the heat balance stated in such a form as to admit of a ready comparison of these losses.

Variation of available heating power. The available heating power of a coal as used under a boiler is greatly modified by the adaptability of the coal to burn on the particular grate and in the particular furnace used. Coals differ in the percentage of the excess of air required for their complete combustion and it is well known that experience in the use of any coal is necessary to use it to the best advantage. Coals which contain, or furnish on burning, large percentages of water will show low percentages

of available heat calculated on their total calorific value on account of the large amount of the latent heat and the large quantity of sensible heat carried off by the water vapor in the products of combustion. As has just been shown, the amount of sensible heat carried off in the products of combustion increases directly with the temperature of the escaping gas and the best results for available heating power are usually not secured where the flue temperature is excessive. This is especially true where the amount of moisture in the coal is large. The amount of ash present in the coal has an important effect on the available heating power realizable as complete combustion and low excess air are hard to obtain with high ash or where the ash clinkers badly. Aside from its effect on the excess air and complete combustion, large amounts of ash involve extra expense in handling and on this account have a negative heating value. The loss of heat due to formation of smoke and soot varies with the coal used and also with the type of furnace, but the actual loss from this cause is in no case very large and coals which have a tendency to form large amounts of smoke and soot are objectionable, more on account of being a nuisance and a menace to public health, or because the deposition of soot on the heat absorbing surfaces of the boiler prevents the ready absorption of heat by the boiler rather than on account of the loss of heat due to failure of the smoke and soot to burn.

COMMERCIAL VALUE OF COAL

For most purposes the relative commercial value of a coal is dependent upon the amount of heat or power which can be obtained from a given amount of the coal, or in other words is dependent upon the available heating value of the coal. In most cases the available heating value varies directly with the total heating value, and, other things being equal, the value of a coal is dependent upon the total number of heat units it contains. This is however not always the case. A number of factors, some of which have already been mentioned, as clinkering of ash, adaptability of one coal rather than another to the furnace and stokers in use, etc., may cause the total value, if considered alone, to be somewhat misleading and some coals having a lower total calorific value may under certain conditions of practice give

a higher actual available value than other coals showing a greater total value.

In general, however, the coal having higher total heating value is the better coal and the seller of the coal having the lower heating value should show under what special conditions an inherently inferior coal may actually be the superior coal in production of heat or power, or if not actually superior, show that it actually is the more desirable coal under the conditions where it is to be used.

Actual testing under average working conditions is sometimes necessary to prove or disprove the claim of any certain coal. A comparison of the results of a boiler test made by experts under the best obtainable conditions with the every-day results of the ordinary boiler crew is not the way to prove or disprove it, but only shows that the average conditions may be far from satisfactory. The boiler tests if taken as a guide should be made on both coals and under similar working conditions. The average results for a considerable period of time on one coal compared with the average results on another coal for the same length of time, if conditions of firing, weather conditions, etc., are similar ought, to be conclusive as to which coal is better under the same conditions. This does not necessarily show how much better either coal might be if the firing and regulations were as good as they should be. Boiler tests with expert handling should show what may be done; how nearly every-day results can come to this is largely dependent upon the efficiency of the boiler crew.

RESIDUAL COAL

If the variable factors of coal, moisture, ash and sulphur, be removed the remainder may be considered as consisting of a practically uniform residual coal substance which while complex in its nature is fairly uniform in composition and heating value. The value of the coal actually bought and sold is largely dependent upon the actual percentage of residual coal present. In any given seam the heating value of a unit amount of the residual coal is fairly constant and different samples of coal from the same bench or seam will differ from one another in heating value according as they differ in the amounts of moisture, ash and sulphur present, or stated in another way, as they differ in the amount of actual "residual coal" present in a unit amount of each.

Heating value of residual coal, H. The heating value of a unit weight of the residual coal was designated by the late Professor N. W. Lord as H and is found as follows:

From the total heating value of the sample subtract that due to the sulphur present which equals the amount of sulphur times 2250 calories or times 4050 British thermal units. Divide the remainder by 1 minus the sum of the amount of moisture, ash and sulphur present. The product is the heating value per unit of residual coal, or

$$H = \frac{\text{calorific value} - 2250 (\text{sulphur})}{1 - (\text{moisture} + \text{ash} + \text{sulphur})}$$

The average of 65 samples of Ohio No. 6 coal as given in *Bulletin* No. 9 of the Ohio Geological Survey is as follows:

Moisture.....	0.0556
Ash.....	0.0736
Sulphur.....	0.0330
Calorific value.....	6980 calories

from which,

$$H = \frac{6980 - 0.0330 \times 2250}{1 - (0.0556 + 0.0736 + 0.0330)} = 8243 \text{ calories,}$$

or expressed in British thermal units,

$$8243 \times \frac{9}{5} = 14837.$$

Calculation of heating value from proximate analysis and from H. Since the heating value of the coal is due to the residual coal and sulphur present, the heating value of one sample may be calculated from the determined heating value of another sample if the moisture, ash and sulphur in both samples are known. For example, to calculate the heating value of a sample of Ohio No. 6 coal, Sample No. 115 of *Bulletin* No. 9 of the Ohio Geological Survey contains,

Moisture.....	0.0472
Ash.....	0.0547
Sulphur.....	0.0405

The amount of residual coal

$$= 1 - (0.0472 + 0.0547 + 0.0405) = 0.8576.$$

Multiplying the value of H above—8243—by this value $=8243 \times 0.8576 = 7069$ which is the heat of the residual coal. To this add the heat due to the sulphur $=0.0405 \times 2250 = 91$ calories. The total heating value $=7069 + 91 = 7160$. The calorific value as actually determined was 7199 or a difference of 39 calories.

Accuracy of calculated heating value. Where the samples from which H is determined are from the same portion of the seam as the sample, the heating value of which is to be determined, and where the variations in moisture, ash and sulphur are not too large the calculated results agree fairly well with actual determinations.

Results for heating value calculated on oxidized and weathered samples are likely to be much too high, and it is unsafe to apply this calculation to such samples.

Results on widely different samples. As it is difficult or impossible to determine the exact relation of the ash obtained to the amount of mineral matter as it occurs in the coal where the variations in ash and sulphur are large, the results by this formula may be considerably in error.

Effect of changes in ash on accuracy of calculation. As previously stated under the subject of "Ash," the ash as actually weighed is too high by $\frac{3}{8}$ of 1 per cent for each per cent of sulphur in the coal as pyrite, and too low by about 0.17 of 1 per cent for each per cent of ash originally present in the coal as clay or shale. Where the differences in ash and sulphur in the different samples are due to differences in amounts of clay and pyrite, application of this formula in a modified form, using a "corrected ash" for the *difference in ash* in the two samples, gives more concordant results. Designating the amounts of ash and sulphur in the samples from which H has been determined as A and S and the amounts of ash and sulphur in the samples the calorific value of which is to be determined by A' and S' , then the ash corrected or A' (corrected) =

$$A' - \left[\frac{3}{8}(S' - S)\right] + .17[A' - A - \frac{3}{8}(S' - S)]$$

from which the corrected ash in Sample No. 115 corresponding to $0.0547 = 0.0547 - \frac{3}{8}(0.0405 - 0.0330) + .17[0.0547 - 0.0736 - \frac{3}{8}(0.0405$

-0.0330)] = 0.0482 or 0.0065 less ash than the amount as actually weighed up. Using this corrected value gives,

$$1 - (0.0472 + 0.0482 + 0.0405) = 0.8641$$

as the amount of residual coal as against 0.8576 by the first calculation. The calorific value of the sample is therefore,

$$0.8641 \times 8243 + 0.0405 \times 2250 = 7214 \text{ calories}$$

as against 7160 calories with the uncorrected ash and 7199 calories as actually determined in a bomb calorimeter. The calculated value with the uncorrected ash is 39 calories lower than the value determined in the calorimeter while the calculated value with the corrected ash is 15 calories higher or a difference of 24 calories in favor of the result by the corrected ash.

As further illustration, samples of Ohio No. 6 coal, samples Nos. 92 and 93 in *Bulletin* No. 9 of the Ohio Geological Survey contain nearly the same amount of ash but differ in sulphur by 1.53 per cent. The moisture, ash and sulphur and determined calorific values are as follows:

	Sample No. 92.	Sample No. 93.
Moisture.....	5.25	5.90
Ash.....	9.86	10.10
Sulphur.....	3.43	4.96
Determined calorific value	6773	6686

The value obtained for *H* in sample No. 92 is 8220. The calculated calorific value of Sample No. 93, using this value for *H* and making no corrections for the ash is 6609. Assuming that the difference in sulphur is due to a difference in the amount of pyrite present, and correcting the ash by subtracting $\frac{3}{8}$ of this sulphur difference and using this corrected ash, the calculated value obtained is 6656. With the uncorrected ash the calculated value is 77 calories lower than the actually determined value. With the corrected ash it is only 30 calories lower for this sample, a difference of 47 calories in favor of a corrected ash.

Comparison of samples with the same sulphur content. Two other samples of Ohio No. 6 coal, Samples Nos. 99 and 104, in

Bulletin No. 9 of the Ohio Geological Survey, have essentially the same sulphur content but differ in ash. The moisture, ash, sulphur and determined calorific value of the samples are as follows:

	Sample No. 99.	Sample No. 104.
Moisture.....	5.44	5.55
Ash.....	9.28	5.23
Sulphur.....	3.77	3.63
Calorific value.....	6822	7191

The value obtained for H in Sample No. 99 is 8265. Calculating the calorific value of 104 from this value for H and making no correction for the ash gives 7156 as the calorific value. Assuming that the difference in ash is due to differences in amount of slate or clay in the sample, and correcting the ash and calculating the calorific value with corrected ash, the value obtained is 7213 as against 7191 as actually determined in a calorimeter. The uncorrected ash result is 35 calories too low, the corrected ash is 22 calories too high or a difference of 13 calories in favor of the corrected ash.

The use of this "corrected ash" should be restricted to comparisons of the ash in the two samples, which is practically limiting it to the ash difference. It cannot be used in the formula for obtaining the value for H , as much of the sulphur present in the sample may be present as organic sulphur, also a portion of the ash is present in other forms, as clay and shale. A failure to correct for the amounts of clay and pyrite means that the actual value for H is too low or too high. This is however of little importance as in obtaining the calculated calorific value of another sample, approximately the same error is present as in the sample from which H is derived and in the calculation one error practically eliminates the other and only the difference in amounts of clay and pyrite need be allowed for. Since in most samples of the same coal the difference in ash and sulphur is largely due to differences in amount of clay and pyrite present, this corrected formula should in most cases give somewhat more accurate results.

CHAPTER II

CHEMICAL ANALYSIS OF COAL

PROXIMATE ANALYSIS

THIS analysis gives the composition of the coal under four headings as follows: moisture, volatile matter, fixed carbon, and ash.

The results obtained are more or less dependent upon the exact process used and small variations in working out the details of the process may make a considerable difference in the results actually obtained, while a distinctly different process gives radically different values for some of the determinations. Hence the results are relative and not absolute and should be so regarded by both the chemist and the user of the coal. The efforts of some chemists to find a method of determining the "true moisture" in coal might better be spent in trying to simplify and improve the method already in use for obtaining the comparative value.

Moisture. As has already been stated, the term moisture includes only the more or less loosely held water which is driven off by heating 1 gram of the finely ground sample for 1 hour at 105° C. A finely ground sample of coal during the operation undergoes changes due to oxidation and escape of gases, hence the actual value obtained for moisture is the amount of water driven off plus or minus any oxidation changes. In most coals if not ground excessively fine these oxidation changes are of minor importance compared to the moisture loss so that the reporting of this net loss as moisture does not lead to any serious errors although it practically never represents the exact amount of water expelled. A sample of coal which has been heated for 1 hour at 105° will give off more moisture and undergo further oxidation changes if heated to a still higher temperature, the

amount of moisture given off depending upon the kind of coal and upon the increase in temperature. The extent of the oxidation also increases with the temperature and varies with the kind of coal and fineness of the sample. While it is true that the results for moisture obtained by heating the sample to 105° have no absolute value but merely a relative one, it is equally true when two samples of approximately the same kind of coal are treated in the same way for moisture by heating to 105° , the difference in the results obtained show very closely the difference in the amount of loosely held moisture in the coal. Usually this is what the user of the coal wishes to know and on this account the moisture determination has importance and value.

Volatile matter. The determination of volatile matter is an arbitrary one and the results are obtained by following a certain prescribed procedure, which is essentially to heat 1 gram of the finely ground sample in a covered platinum crucible over the full flame of a Bunsen burner for seven minutes. The loss in weight represents moisture plus volatile matter. Subtracting the value for moisture from this result gives the amount of volatile matter in the coal. This determination cannot be regarded as entirely satisfactory as the result obtained is to a considerable degree dependent upon the particular conditions under which the sample was run and two different chemists in two different laboratories both trying to follow out the same method of procedure may easily obtain results for volatile matter upon the same sample of coal which may differ by 2 or 3 per cent. Furthermore, some high moisture coals suffer mechanical losses during the heating to drive off the volatile matter. Such samples require special treatment to insure results of even approximate accuracy. On account of such possible differences and errors this determination cannot be regarded as very exact. It is, however, true that the same chemist working in the same way with the same crucibles, the same height of gas flame, the same Bunsen burner, etc., can obtain results which will duplicate within a few tenths of 1 per cent, and in control work the same chemist's results on approximately the same coals ought to be comparable among themselves to within less than 1 per cent. The amount of volatile matter in itself gives very little idea of the coal, as two coals with approximately the same amount of volatile matter may differ very greatly in heating value, physical properties, etc.,

and any significance which the determination of volatile matter actually has is largely a relative one which may be of value when the same or similar coals are compared with one another.

The volatile matter consists essentially of any combined water in the coal plus a portion of the sulphur, on an average probably about one-half of the total sulphur present in the coal, plus the nitrogen in the coal, plus hydrocarbons of unknown and varying composition. The nitrogen and combined water in the volatile matter have no heating value and, if present large amounts, the heating value of the combustible will be correspondingly lower.

Fixed carbon. Fixed carbon represents the difference obtained by subtracting the percentage of moisture, volatile matter and ash from 100. The fixed carbon as its name indicates is mostly carbon. Approximately one-half the sulphur in the coal present in the form of pyrite and a variable portion of that present as organic sulphur remains with the fixed carbon and the heating value of the fixed carbon is, on this account, somewhat lower than that of pure carbon. On the other hand, small amounts of hydrogen may be retained in the fixed carbon which would slightly increase its heating value. In most coals the heating value per unit of the fixed carbon is not far from that of carbon—8080—and this value may be used in estimating heat values without any great error. With high sulphur coals, a somewhat lower value, approximately 30 calories lower for each per cent of sulphur in the coal, is probably more nearly a correct value. This is based on the assumption that one-half of the sulphur remains with the fixed carbon and that not more than traces of hydrogen are retained in the fixed carbon.

Ash. As ordinarily reported this is the weight of ignited mineral matter in the coal. The relation of this ignited mineral matter to the mineral matter in the coal has already been discussed in detail and no especial points need repeating here.

Comparison of proximate analyses of certain coals. As illustrations of the proximate analyses of widely different coals the following determinations including sulphur and calorific value are taken from *Professional Paper* No. 48 and *Bulletin* No. 290 of the U. S. Geological Survey:

	North D. No. 1.	Wyo. No. 1.	Colorado No. 1.	Mon. No. 1.	Illinois No. 4.	Indiana No. 1.	Ohio No. 8.
Moisture.....	35.38	22.63	18.68	11.05	12.91	11.40	7.55
Volatile matter..	29.59	35.68	34.88	35.90	31.90	33.81	38.00
Fixed carbon...	25.68	37.19	40.45	42.08	43.55	41.39	46.08
Ash.....	9.35	4.50	5.99	10.97	11.64	13.40	8.37
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulphur.....	1.55	0.59	0.55	1.73	1.32	2.50	2.84
Calories.....	3846	5408	5635	5855	6002	6145	6738

	Alabama No. 2.	Indian Territory No. 2.	Alabama No. 1.	Kentucky No. 1.	West Virginia No. 1	Arkansas No. 5.	West Virginia No. 10.	West Virginia No. 12.
Moisture.....	3.36	4.45	2.34	3.10	1.75	2.36	1.75	1.72
Volatile matter..	32.88	36.15	31.84	36.12	36.77	12.68	18.59	17.85
Fixed carbon...	51.33	48.40	53.28	56.39	55.14	72.88	75.08	73.56
Ash.....	12.43	11.00	12.54	4.39	6.34	12.08	4.58	6.87
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulphur.....	1.01	1.52	0.72	1.22	0.90	1.99	0.56	0.68
Calories.....	6861	7004	7142	7860	7837	7366	8346	8095

This series of samples was selected not as representing the coals of these regions but to show the wide variation in moisture and volatile matter and fixed carbon in different coals and the variable heating value of the volatile matter. The variable heating value of the volatile matter can be most strikingly seen by comparing the different values for H in these different coals. H , as has already been explained, is the heating value per unit of "residual coal" and is obtained by dividing the total calorific value less the calorific value of the sulphur present by one minus the sum of the moisture, ash and sulphur. The values for H for the different samples are as follows:

VALUE FOR *H*

	Calories.	Nitrogen, Per Cent.
North Dakota, No. 1.....	7094	0.54
Wyoming, No. 1.....	7464	1.02
Colorado, No. 1.....	7519	1.15
Montana No. 1.....	7627	1.33
Illinois, No. 4.....	8056	1.15
Indiana, No. 1.....	8375	1.18
Ohio, No. 8.....	8216	1.29
Alabama, No. 2.....	8219	1.54
Indian Territory, No. 2.....	8395	1.67
Alabama, No. 1.....	8443	1.65
Kentucky, No. 1.....	8580	1.83
West Virginia, No. 1.....	8589	1.54
Arkansas, No. 5.....	8760	1.37
West Virginia, No. 10.....	8950	1.06
West Virginia, No. 12.....	8905	1.33

The value ranges from about 7100 to over 8900, an extreme difference of nearly 1900 calories. As the moisture and ash in the samples have no heating value and the value of the fixed carbon is approximately the same per unit of fixed carbon in all the samples, the great difference in the value of *H* is due to the variable composition of this volatile matter. The inert constituents of the volatile matter are nitrogen and combined water. The amount of nitrogen in the different samples is given in the foregoing table.

The extreme difference is less than $1\frac{1}{2}$ per cent and the effect of nitrogen on the value for *H* is of minor importance.

As has been mentioned in connection with Dulong's formula and its modifications, a greater part but not all of the oxygen in the coal appears in the form of water. The exact relation between the small amount properly belonging with carbon and that present as water varies with each coal, but for purposes of comparison all of it can be assumed as present as water without serious error, bearing in mind however, that the values for combined water on this assumption are all somewhat high. On this assumption the combined water in the samples is as follows:

	Oxygen.	Total Water.	Moisture.	Combined Water.
North Dakota, No. 1	41.72	46.93	35.38	11.55
Wyoming, No. 1	32.59	36.66	22.63	14.03
Colorado, No. 1	28.78	32.38	18.68	13.70
Montana, No. 1	21.52	24.21	11.05	13.16
Illinois, No. 4	19.72	22.18	12.91	9.27
Indiana, No. 1	17.21	19.36	11.40	7.96
Ohio, No. 8	15.00	16.87	7.55	9.32
Alabama, No. 2	11.49	12.93	3.36	9.57
Indian Territory, No. 2	11.15	12.54	4.45	8.09
Alabama, No. 1	8.50	9.56	2.34	7.22
Kentucky, No. 1	9.76	10.98	3.10	7.88
West Virginia, No. 1	7.94	8.93	1.75	7.18
Arkansas, No. 5	4.30	4.84	2.36	2.48
West Virginia, No. 10	4.18	4.70	1.75	2.95
West Virginia, No. 12	3.98	4.48	1.72	2.76

An inspection of the values for combined water shows a variation of from 14 per cent in the highest to $2\frac{1}{2}$ per cent in the lowest, or a variation of about 12 per cent. The highest combined water however is not found in the sample having the lowest value for *H* so that the variable composition of the volatile hydrocarbons must be compared in order to more completely explain the variation in *H*. The total hydrogen in these samples as shown by the ultimate analysis and the available hydrogen which is the amount left after subtracting that as combined water are as follows:

	Total Hydrogen.	Available Hydrogen.
North Dakota, No. 1	6.61	1.40
Wyoming, No. 1	6.39	2.32
Colorado, No. 1	6.07	2.47
Montana, No. 1	5.37	2.68
Illinois, No. 4	5.43	2.97
Indiana, No. 1	5.37	3.22
Ohio, No. 8	5.48	3.60
Alabama, No. 2	4.84	3.40
Indian Territory, No. 2	5.17	3.78
Alabama, No. 1	5.01	3.95
Kentucky, No. 1	5.43	4.21
West Virginia, No. 1	5.28	4.29
Arkansas, No. 5	3.82	3.28
West Virginia, No. 10	4.65	4.13
West Virginia, No. 12	4.43	3.93

Listing the volatile constituents under the following headings: combined water, nitrogen, sulphur, available hydrogen and carbon, the following values are obtained for the different samples:

	Total Volatile.	Com- bined Water.	Nitrogen.	Sulphur.	Avail- able Hydro- gen.	Carbon.
North Dakota, No. 1.	29.59	11.55	0.54	0.78	1.40	15.32
Wyoming, No. 1.	35.58	14.03	1.02	0.30	2.32	17.91
Colorado, No. 1.	34.88	13.70	1.15	0.28	2.47	17.28
Montana, No. 1.	35.90	13.16	1.33	0.86	2.68	17.87
Illinois, No. 4.	31.90	9.27	1.15	0.66	2.97	17.85
Indiana, No. 1.	33.81	7.96	1.18	1.25	3.22	20.20
Ohio, No. 8.	38.00	9.32	1.29	1.90	3.60	21.89
Alabama, No. 2.	32.88	9.57	1.54	0.50	3.40	17.87
Indian Territory, No. 2.	36.15	8.09	1.67	0.51	3.78	22.10
Alabama, No. 1.	31.84	7.22	1.65	0.36	3.95	18.66
Kentucky, No. 1.	36.12	7.88	1.83	0.72	4.21	21.48
West Virginia, No. 1.	36.77	7.18	1.54	0.30	4.29	23.46
Arkansas, No. 5.	12.68	2.48	1.37	1.00	3.28	4.55
West Virginia, No. 10.	18.59	2.95	1.06	0.19	4.13	10.26
West Virginia, No. 12.	17.85	2.76	1.33	0.28	3.93	9.55

The amount of sulphur in the volatile matter varies with the nature of the occurrence of the sulphur from as low as $\frac{1}{3}$ to as high as $\frac{2}{3}$ of the total sulphur present. On the following samples the amount of sulphur in the volatile matter is calculated from the results on the coke tests given in *Professional Paper* No. 48 and in *Bulletin* No. 290 of the U. S. Geological Survey. The approximate percentages of the total sulphur in the coke and in the volatile matter are as follows:

	Coke.	Volatile Matter.
	Per Cent.	Per Cent.
Indian Territory, No. 2.	67	33
Kentucky, No. 1.	40	60
Ohio, No. 8.	33	67
West Virginia, No. 1.	67	33
West Virginia, No. 10.	67	33
West Virginia, No. 12.	60	40

On the remaining samples on which no coke tests were made, the amount of sulphur in the volatile matter is estimated as 50 per cent of the total amount present. This is of course an assumption but the error introduced by it can in no case be very large, not large enough to materially change the final findings as to the nature and heating value of the volatile matter.

The carbon values are obtained by subtracting the sum of the combined water plus the nitrogen plus the sulphur plus the available hydrogen from the total volatile matter. The heat per unit of volatile matter may be calculated by Dulong's formula and is equal to:

$$\frac{(8080 \times \text{Carbon}) + (34460 \times \text{available Hydrogen}) + (2250 \times \text{Sulphur})}{\text{Volatile matter}}$$

The results for each of the samples are as follows:

North Dakota, No. 1	5874
Wyoming, No. 1	6332
Colorado, No. 1	6459
Montana, No. 1	6649
Illinois, No. 4	7774
Indiana, No. 1	8193
Ohio, No. 8	8034
Alabama, No. 2	7989
Indian Territory, No. 2	8575
Alabama, No. 1	9036
Kentucky, No. 1	8868
West Virginia, No. 1	9195
Arkansas, No. 5	11995
West Virginia, No. 10	12135
West Virginia, No. 12	11944

These results show a range for the heating value of the volatile matter of from about 5900 to over 12,000 calories or a difference of over 100 per cent in heating value per unit of volatile matter. The highest heating value is found in those coals which are relatively high in available hydrogen, and at the same time are low in combined water. West Virginia No. 10 with a value of 8950 for *H* has over 4 per cent of available hydrogen and less than 3 per cent of combined water, while North Dakota No. 1 has only 1.4 per cent available hydrogen and 11.55 per cent of combined

water. These values make clear that in order to determine anything very definite about the actual heating value of the coal, something more than the proximate analysis is required. The value of this determination is merely a relative one and should be restricted to a comparison of different samples of the same bed, or at most to different coals known to be somewhat similar in the relative amounts of oxygen and available hydrogen which are contained in a unit amount of the "residual coal." This term "residual coal," from what has been given above, is less misleading than the more commonly used term "combustible," since in many of the samples a large part of the volatile matter is non-combustible.

ULTIMATE ANALYSIS

This analysis gives the composition of the coal under the following headings: percentages of carbon, hydrogen, nitrogen, sulphur, oxygen and ash. The percentage of oxygen is obtained by subtracting the sum of the other percentages from 100. Hence the algebraic sum of all the errors in the other determinations appears in the value obtained for oxygen which makes the accuracy of the obtained value for oxygen somewhat uncertain. Corrections in the ash may improve the oxygen value somewhat, but as has been discussed under "Ash" this correction is not entirely satisfactory. As the errors in the oxygen are dependent upon the errors in the other determinations the approximate limits of the accuracy of these determinations must be considered in order to obtain an idea of the probable accuracy of the oxygen determination.

The determination of the carbon and hydrogen requires a high degree of skill and care in order to secure satisfactory results. The results of determinations made by poor manipulators or under unfavorable conditions may easily be 1 or 2 per cent in error for carbon and 0.4 or 0.5 of 1 per cent in error for hydrogen. With careful manipulation and proper conditions the carbon and hydrogen results in most samples should be accurate to within 0.2 of 1 per cent for carbon and within about 0.05 or 0.06 of 1 per cent for hydrogen, provided that the laboratory sample of coal has been previously reduced to approximately an air dry condition. Unless the latter has been done, the errors incident to weighing out small

amounts of sample for ultimate analysis makes a high degree of accuracy practically impossible. The question of air drying of the samples is discussed in detail under the head of "Sampling." The results for sulphur, nitrogen and ash should be accurate within 0.05 of 1 per cent and the value obtained for oxygen can be duplicated to within 0.25 of 1 per cent on coals which are fairly low in oxygen. Whether it is within 0.25 of 1 per cent for the oxygen as it actually occurs in the sample is not so certain, since in high ash coals the possible corrections to the ash are several times this amount. The actual value obtained for oxygen for small differences has a relative value rather than an absolute one. Large differences, such as are shown in the list of samples given, have an absolute value in indicating the nature of the coal, the errors in the determination or corrections for the ash being of minor importance compared to the total difference in the oxygen value.

While the results for the ultimate analysis should be accurate to within about the limits given for the sample as analyzed, it does not necessarily follow that these results actually come this near to representing the original coal, as this is dependent upon whether the sample itself is representative of the coal. This is another question in itself and is discussed in detail under the head of "Sampling."

The complete ultimate analyses and the determined and calculated heating values expressed in calories and British thermal units on the different coals, the proximate analyses of which have already been given are given on page 53, the calculated values being based on Dulong's formula:

$$8080C + 34460(H - \frac{1}{8}O) + 2250S.$$

Some of the variations in the results are as follows: total hydrogen 3.82 to 6.61; carbon 40.23 to 84.97; oxygen 3.98 to 41.72, and nitrogen 0.54 to 1.83. Such wide variations in the ultimate composition make it easy to understand why the heating values likewise have such a wide range, from 3767 to 8346 calories, and help to make more clear the statement that "coal as it actually occurs in nature differs widely in physical and chemical properties."

	North Dakota No. 1.	Wyoming No. 1.	Colorado No. 1.	Montana No. 1.	Illinois No. 4.	Indiana No. 1.	Ohio No. 8.	Alabama No. 2.
Hydrogen.....	6.61	6.39	6.07	5.37	5.43	5.37	5.48	4.84
Carbon.....	40.23	54.91	57.46	59.08	60.74	60.34	67.02	68.69
Nitrogen.....	0.54	1.02	1.15	1.33	1.15	1.18	1.29	1.54
Oxygen.....	41.72	32.59	28.78	21.52	19.72	17.21	15.00	11.49
Sulphur.....	1.55	0.59	0.55	1.73	1.32	2.50	2.84	1.01
Ash.....	9.35	4.50	5.99	10.97	11.64	13.40	8.37	12.43
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Heating value determined:								
Calories.....	3846	5408	5635	5855	6002	6145	6738	6861
B.t.u.....	6923	9734	10143	10539	10804	11061	12128	12350
Heating value calculated:								
Calories.....	3767	5247	5508	5739	5959	6044	6718	6745
B.t.u.....	6781	9445	9913	10330	10726	10880	12092	12140

	Indian Territory No. 2.	Alabama No. 1.	Kentucky No. 1.	West Virginia No. 1.	Arkansas No. 5.	West Virginia No. 10.	West Virginia No. 12.
Hydrogen.....	5.17	5.01	5.43	5.28	3.82	4.65	4.43
Carbon.....	69.49	71.58	77.37	78.00	76.44	84.97	82.71
Nitrogen.....	1.67	1.65	1.83	1.54	1.37	1.06	1.33
Oxygen.....	11.15	8.50	9.76	7.94	4.30	4.18	3.98
Sulphur.....	1.52	0.72	1.22	0.90	1.99	0.56	0.68
Ash.....	11.00	12.54	4.39	6.34	12.08	4.58	6.87
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Heating value determined:							
Calories.....	7004	7142	7860	7837	7366	8346	8095
B.t.u.....	12607	12856	14148	14107	13259	15023	14751
Heating value calculated:							
Calories.....	6952	7160	7729	7801	7353	8299	8054
B.t.u.....	12514	12888	13912	14042	13235	14938	14498

Calculating an ultimate analysis. From what has been stated concerning the difficulties in the carbon and hydrogen determinations, it may rightfully be inferred that the ultimate analysis is a somewhat troublesome and expensive determination and for most purposes where an ultimate analysis is required, as in a boiler-test heat balance, a calculated ultimate analysis, based on an actual ultimate analysis of a similar sample of the same coal, is fairly satisfactory. If the percentage of moisture, ash and sulphur in each sample be subtracted from 100 the remainder is the per cent of residual coal in each sample and the calculation of the derived ultimate, based on the assumption that the residual coal in each sample has approximately the same percentage composition, is as follows: The determined ultimate analysis is given in per cent of carbon, hydrogen, nitrogen, oxygen, sulphur and ash per unit of coal. Representing these percentages by C, H, N, O, S, and A and the percentages of the derived samples by C', H', N', O', S', and A' and the moisture, ash and sulphur in the two samples by M, A, and S and M', A', and S' respectively, then the procedure is as follows:

Subtract the hydrogen, H, and oxygen, O, corresponding to the moisture, M, from the total hydrogen and oxygen as given in the ultimate analysis. The remainder will be the hydrogen and oxygen in the residual coal. Represent the residual coal $(100 - (M + A + S))$, in the sample by R and the residual coal $(100 - (M' + A' + S'))$, in the sample to be calculated by R'. The carbon, hydrogen, oxygen, and nitrogen in a unit of residual coal =

$$\left. \begin{array}{l} C \\ H - \frac{1}{8}M \\ O - \frac{8}{8}M \\ N \end{array} \right\} \text{divided by R.}$$

Multiplying these values by R' gives the amount of carbon, hydrogen, oxygen and nitrogen in the residual coal, R'. To get the ultimate composition of the coal corresponding to R', the hydrogen and oxygen must be corrected by adding to these obtained values the correction corresponding to the moisture, M'. For hydrogen this correction = $\frac{1}{8}M'$, for oxygen $\frac{8}{8}M'$.

If $\frac{100 - (M' + A' + S')}{100 - (M + A + S)}$ or $\frac{R'}{R}$ be represented by K the ultimate analysis of the derived sample is as follows:

$$\begin{aligned}
 C' &= CK \\
 H' &= (H - \frac{1}{8}M)K + \frac{1}{8}M' \\
 O' &= (O - \frac{8}{8}M)K + \frac{8}{8}M' \\
 N' &= NK \\
 A' &= A' \\
 S' &= S'
 \end{aligned}$$

Total 100

The agreement between the calculated and determined ultimates is shown by determinations on samples Nos. 1061 and and 1157, *Professional Paper*, No. 48, U. S. Geological Survey, the moisture, ash and sulphur in which are as follows:

	Sample No. 1157.	Sample No. 1061.
Moisture.....	2.56	2.03
Ash.....	13.92	13.46
Sulphur.....	0.78	5.39

Sample No. 1157 is a portion of Alabama No. 1 and Sample No. 1061 is a portion of Kansas No. 3 coal. The determined and calculated values for carbon and hydrogen on these two samples are as follows:

Sample No.	Determined Hydrogen.	Calculated Hydrogen.	Determined Carbon.	Calculated Carbon.
1157	4.82	4.94	70.00	70.19
1061	4.77	4.84	68.94	68.85

The proximate and ultimate analysis of the car samples from which the ultimates are derived are given in the analytical tables in Chapter X.

The derived results for carbon differ from the actually determined results by an amount within the limit of variation of duplicate determinations of carbon. The variations between the determined and derived hydrogen—0.07 and 0.12—are not much greater than the errors in the actual hydrogen determinations and a calculated ultimate based on a carefully run ultimate of a similar

sample of coal is in the opinion of the author likely to be as reliable as an actual determination made by an average manipulator under ordinary working conditions. Certainly the error introduced is usually not large enough to have any great effect upon the calculations which are affected by it.

Effect of errors in the ultimate analysis on the heat balance.

For illustration, assume a maximum error of 1 per cent in the calculated value for carbon and 0.2 per cent in the calculated value for hydrogen. Then 0.01 gram of carbon is equivalent to 0.0367 gram of CO_2 . The nitrogen equivalent to the oxygen from the air required to produce this amount of $\text{CO}_2=0.10$ gram; allowing 100 per cent excess air= 0.128 gram of air. On the boiler test with the products of combustion escaping at 300°C . (572°F .) the sensible heat carried off in these products is about 19 calories. 0.2 per cent of hydrogen= 0.018 gram of H_2O . The latent heat of this amount of water equals 10.6 calories. The sensible heat, assuming the gases escaping at 300°C ., in this amount of water is 2.7 calories. The nitrogen equivalent to the oxygen required to combine with this amount of hydrogen equals 0.053 gram. Allowing 100 per cent excess air, the amount of air required for the excess is 0.069 gram. The sensible heat carried off at 300°C . by this amount of air and nitrogen equals about 8 calories, making the total heat carried off about 21 calories. If the errors in carbon and hydrogen are both high or both low at the same time, the total error in the distribution of the heat loss amounts to about 40 calories or about $\frac{1}{2}$ per cent of the total heat produced; as the radiation and unaccounted-for losses in a boiler test are frequently 20 times this large, it is apparent that the error from the use of a calculated ultimate of approximate accuracy has little effect upon the actual results of the boiler test.

CHAPTER III

SAMPLING

THE old saying that a chain is only as strong as its weakest link may well be applied to the valuation of the results of chemical tests and many times the weakest link is the sampling. This may be due to one or more of several reasons:

(1) Failure to secure a representative sample due to the faulty method of sampling, as for example the sampling of a car of coal by merely taking several lumps or shovel fulls from the top of the car.

(2) Difficulty in securing a representative sample due to the occurrence and the irregular distribution of materials of different composition, as the irregular distribution of pyrite in coal or the irregular distribution of gold in gold ores.

(3) Alterations or changes in the sample during handling or before it is analyzed, as changes due to gain or loss of moisture or changes due to oxidation.

Failure to secure a representative sample due to any or all of these causes may result in errors ten times as large as any of the probable chemical errors and too much emphasis cannot be laid on the importance of care and thoroughness in taking and handling the sample on which the chemical results are to be obtained. If necessary as much or more time and money should be expended in securing a sample as is expended in having it analyzed, as the determinations of the chemist if properly made represent only the sample as received and if made on improperly taken samples they may be so far from representing the actual material as to be worse than useless. The practice of entrusting sampling to ignorant laborers or mere boys having little or no idea of what they are doing deserves to be strongly condemned, as skill and training are as essential in taking and handling a sample as in making the chemical determinations. It is indeed true that an ordinary laborer can be trained to the work and can take the samples

properly but the training should be thorough as to details and strict observance of details insisted upon if the results are to be of value and too often the persons giving instructions in sampling do not themselves appreciate the importance of some of the necessary precautions.

In sampling coal the effect upon the sample of the three variable factors, moisture, ash and sulphur, should be considered separately and collectively. The amounts of these constituents vary in the different materials composing the coal (i.e., in the coal, slate, pyrite, etc.) and also in different parts of these separate constituents, as in the lump and fine coal. Hence to secure a representative sample, it is essential that the amount of lump coal, fine coal, slate, clay and pyrite in the sample be proportionate to that in the entire lot of coal sampled. The problem of the sampler therefore is to endeavor to get this proportionate amount for each of the samples taken.

The details of handling and taking the sample are dependent upon what it is desired that the sample shall represent. For example, when sampling coal in the mine what the operator often desires especially to find out are the variations in ash and sulphur in order that the average ash and sulphur of the coal shipped from the different parts of the mine may be estimated.

The moisture variations in the samples in this particular case are of minor importance and the moisture content in such mine samples when analyzed may differ by several per cent from the amount of moisture that the coal actually contains in the mine. However, this difference has very little effect upon the percentages obtained for ash and sulphur. For illustration, suppose that the sample taken in the mine analyzed as follows: Moisture 5 per cent, ash 7 per cent and sulphur 2 per cent and that the true moisture content of the coal in the mine is 10 per cent. Then the analysis of this sample reduced to mine conditions is moisture 10 per cent, ash 6.75 per cent and sulphur 1.90 per cent. The effect of variation in moisture on the ash percentage is as a rule of minor importance to the operator. On the other hand, if the sample is to represent the coal as fired under a boiler any failure to secure the proper result in moisture is simply an error proportionate to the amount of moisture gain or loss. In the illustration just given the 5 per cent difference in moisture means a 5 per cent difference in the heating value of the coal and approximately

a 5 per cent difference in the value of the coal in dollars and cents.

The sampling of coal may be considered under two general heads: Sampling of coal as it occurs in the mine and sampling of lots of coal as bought and sold or as used.

Sampling coal in the mine. In sampling coal in the mine a number of factors are to be considered, as the number of samples to be taken, their location and the method of taking them. For a mine shipping coal the directions of the Bureau of Mines specify not less than 4 samples for a daily production of 200 tons or less, with an additional sample for each additional 200 tons of coal mined per day. The number should be greater from mines in which the quality of the coal varies greatly. The location of the samples taken should be such as to fairly represent the coal being worked. Other samples in head entries or in the deepest portions of the mine may be taken if desired in order to indicate the character of the future output.

In selecting the exact place to take a sample, care should be taken to avoid exceptional features, such as faults or irregular patches or partings or veins of pyrite. A freshly exposed face of the coal should be selected and before taking the sample the face should be freed or cleaned from any dirt or loose coal from roof to floor for a width of 5 or 6 feet. This is done in order to prevent fragments of foreign matter from falling off the face and becoming mixed with the sample. For the same reason, insecure portions of the roof should also be carefully taken down. The face, where the sample is to be cut, should be squared up and an inch or so of the surface cut away with the pick before actually cutting the channel sample. In cutting the sample a uniform cut should be made across the face of the seam including in the sample all that portion that is included in the coal as mined and rejecting any portions which would be rejected in good mining practice. The amount of coal taken for a sample should be sufficient to reasonably insure a fair representation. The sample obtained from a channel 1 inch wide and 1 inch deep if strictly uniform in width and depth is satisfactory but no sampler can cut such a channel and a channel 4 to 8 inches wide by 2 to 4 inches deep should be cut, the errors in width and depth being relatively much less with a wide and deep cut than with a narrow and shallow one.

In collecting the sample a large canvas or oil cloth about 7 ft. square should be spread on the floor, care being taken that mud and dirt are not introduced into the sample from the boots or shoes of the sampler. With a uniform depth and width of cut the amount of the sample cut varies with the height of the seam. The directions of the United States Government for sampling are to take at least 6 pounds for each foot of thickness. This amount corresponds approximately to a channel 2x6 or 3x4 inches. After cutting the sample it should be either shipped entire or if a sampling outfit is available it may be broken down till the coarsest particles pass through a $\frac{1}{2}$ -inch screen, especial care being taken to crush all lumps of slate and pyrite quite fine. The sample may then be reduced after thorough mixing by quartering and rejecting the opposite quarters, taking care to brush away the entire part of the rejected portions. The two remaining quarters may be again mixed and quartered until the final product amounts to not less than 8 or 10 pounds. If a $\frac{3}{8}$ -inch sieve is available this 10-pound portion may be crushed until the largest particles pass this sieve after which it may be quartered down to 4 or 5 pounds.

A careful and painstaking sampler with a keen eye for slate and pyrite may if all such particles are finely crushed quarter this $\frac{3}{8}$ -inch portion down to 2 or 3 pounds without introducing any error of consequence since portions of clean coal $\frac{3}{8}$ -inch in size or larger have little influence on the ash and sulphur content. This item is discussed more in detail under "Car sampling."

Working down the sample in the mine is however too often done in a dim light and hurriedly, rather than under favorable conditions and the author strongly favors a minimum division of the sample in the mine rather than the division to the smaller amounts. The 10-pound portion of the $\frac{1}{2}$ -inch size or the 5-pound portion of the $\frac{3}{8}$ -inch size, or better still the entire sample if not reduced should be sent to the chemical laboratory. If the moisture result is unimportant the shipment may be made in a closely woven canvas bag. If, however, the moisture is of importance the shipment must be made in a closed metal or glass container. A half gallon fruit jar suffices for the smaller sample but a metal container is to be preferred as being less liable to breakage, in which case a $\frac{1}{2}$ -gallon galvanized or tin container with a screw top for the small sample or a one- to four-gallon

container with screw top for the larger sample is satisfactory, the screw top being sealed by means of adhesive tape to prevent moisture loss.

The shipments of samples by the Ohio Geological Survey are made in galvanized iron cans 10x10x10 inches, fitted with 3½-inch screw caps or tops. One of these cans hold about 40 pounds of sample and allows for the shipment either of all or of one-half of the sample cut. Well-constructed wooden cases built to hold four of these cans are used in shipping the samples to the laboratory.

If nothing better is at hand tall tin pails or cans with well-fitting lids may be used, care being taken to tie the lids very securely on to the pails or cans. If not well secured they may loosen in transit and where several samples are shipped together in the same box all may be spoiled by an accident of this kind. In shipping glass cans or metal containers they should be well packed with burlap, paper or excelsior in order to lessen danger of breakage in transit.

Portable sampling outfit. Where much mine sampling is to be done a portable sampling outfit is almost a necessity. The essential articles comprising such an outfit are as follows:

Carrying bag or container, sampling cloth or canvas, mortar and pestle, sieves, sampling scoop, brush or whisk broom, sampling cans, adhesive tape, measuring tape. A pick and shovel are a necessary part of the equipment but these can usually be obtained at the mine and are not included as such as a part of the portable outfit.

Carrying bag or container. Any container which will hold the outfit will do and the simpler the better. An ordinary canvas sack is very satisfactory and the outfit can be carried either in the hand or thrown over the shoulder.

Sampling cloth. This should be of durable material and impervious to water. Closely woven 16 to 20 oz. duck or heavy enamelled buggy cloth is satisfactory. If the enamelled cloth is used it should be used enamelled side down. The cloth must not be too small. The author prefers a cloth about 7 feet square.

Portable mortar. The mortar at present used by the Departments of Metallurgy and Mining Engineering at the Ohio State University is constructed as follows: The mortar block consists of a $\frac{1}{16}$ -inch steel plate 10 inches in diameter on which is mounted a wooden block 1½ inches thick and to this is attached the mortar

plate proper of $\frac{1}{8}$ -inch steel. Each plate is secured to the wooden block by countersunk screws. The lower portion of the sides of the mortar are formed by a heavy circular piece of sole leather $2\frac{1}{2}$ inches wide which is firmly secured by screws to the wooden block. To prevent escape of coal the ends of the leather are tapered, lapped and glued together with waterproof leather cement. To the upper portion of the leather is attached a circular piece of 16-ounce canvas, $7\frac{1}{2}$ inches wide, which forms the upper portions of the sides of the mortar. The upper edge of the canvas is attached to a flat steel ring, this ring being connected to the mortar base by collapsible spring steel supports held in position

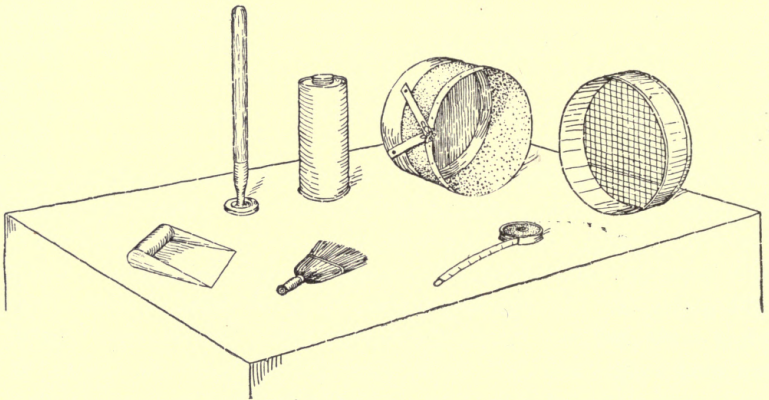


FIG. 1.—Portable Sampling Outfit.

by set screws. When the set screws are loosened the supports and canvas fold down out of the way, the loose ends of the spring steel supports being secured by spring clips on the sides of the mortar block.

Pestle. A common molder's tamping iron $3\frac{3}{4}$ inches in diameter and fitted with a handle 12 inches long is used.

Sieve. This consists of a galvanized iron frame 11 inches in diameter by 5 inches high, into which are fitted removable screens of different sizes, as $\frac{3}{4}$, $\frac{1}{2}$, $\frac{3}{8}$ and $\frac{1}{4}$ inch. The $\frac{1}{2}$ - and $\frac{3}{8}$ -inch screens are the two usually used. This sieve is large enough to hold the mortar when the outfit is packed together.

Sampling scoop. This is merely a heavy piece of galvanized iron resembling a small dustpan but having no handle. It is

used for quartering down and mixing and also for scooping up the reserve portion of the sample.

Broom. A small 6-inch whisk broom is very satisfactory.

Sampling cans. The cans at present used by the Departments of Metallurgy and Mining Engineering are 5 inches in diameter by $11\frac{3}{4}$ inches high and hold from 8 to 10 pounds of sample. They are constructed of 22 gauge galvanized iron and the dimensions are such that two cans fit end to end in an ordinary 24-inch trunk.

Adhesive tape. Ordinary electrical or bicycle tape is used for sealing the lid after the sample has been put into the can.

Measuring tape. A 25-ft. metallic tape graduated to fractions of an inch is useful in measuring sections, etc. Fig. 1 is an illustration of portions of the above described outfit.

The outfit used by the U. S. Bureau of Mines is similar to the one described except that smaller sampling cans are used and a spring balance is included as a part of the outfit. An experienced sampler has little use for a spring balance and with the large sample cans the amount of sample cut can be checked up in the laboratory from the weight of the sample and from the data given in the collector's notes as to what aliquot portion of the sample is represented by the final sample.

For details of the Government sampling outfit, see *Technical Paper* No. 1, Bureau of Mines, Department of the Interior.

Car sampling and sampling coal as used. Directions for sampling coal in a car, sampling a coal as unloaded or sampling coal as used are hard to formulate owing to the great difference in moisture, ash and sulphur and in the physical conditions of different lots of coal. The amount of sample to be taken depends upon the variations in these factors and upon the amount of coal sampled and a set of directions which might give satisfactory results on one coal if used on an entirely different coal might be very unsatisfactory; and a set of directions for sampling a bad lot of coal would be unnecessarily expensive if used to sample a comparatively uniform coal.

The common method of obtaining a sample of coal during a boiler test is as follows: As each lot of coal is weighed, portions taken from various parts are put into a closed barrel, box or a metal container with a closely fitting cover, an effort being made to get an average of fine and lump coal. The amount of sample taken in this way in a day's run where 5 or 6 tons of coal are

fired should be from 100 to 300 pounds, depending upon the coal. If clean slack or washed nut coal, the smaller amount may be satisfactory. If ash and sulphur are present in considerable amounts and especially if in the form of slate and pyrite, the larger quantity should be taken. In sampling a car as unloaded the same method should be used, small portions being taken at regular intervals during the unloading, the amount taken varying with the coal, 500 or 600 pounds, if the coal is run-of-mine to as low as 200 pounds if fine slack or clean nut.

Reduction of the large sample. The entire sample taken (200 to 600 pounds) should be spread upon a clean floor, the large pieces of coal, slate and pyrite crushed with a hammer and a heavy iron plate till the largest particles of slate and pyrite do not exceed $\frac{1}{2}$ inch. This requires that the sample be gone over repeatedly with a shovel so as to bring all portions to the view of the sampler. It should then be thoroughly mixed and divided into quarters. The two opposite quarters should be brushed to one side with a broom. The two remaining quarters should be again mixed, any chunks of slate and pyrite crushed still finer and the sample again divided by quartering. With careful crushing of slate and pyrite this quartering can be repeated a third time if desired. The last portion of sample amounting to 60 to 80 pounds, should be sent to the chemical laboratory for further treatment. If a power crusher or pulverizer is available—and where much sampling is to be done such a machine is almost a necessity—the entire 600 pounds should be put through this pulverizer which can be set to reduce it to a fineness of about $\frac{1}{8}$ inch and finer, in which case the sample can be quartered down repeatedly and the sample sent to the laboratory need not exceed 4 or 5 pounds.

The chute through which the crushed sample passes after being put through the pulverizer may easily be arranged to mechanically divide the sample by an arrangement of partitions to successively divert aliquot parts, so that the final portion diverted is small enough to be sent to the laboratory without further handling. (See Fig. 2.) The space below the end of the chute must of course be sufficient to accommodate a container for holding the portion of the sample which passes through. For example, with samples up to 600 pounds and $\frac{1}{8}$ passing through the chute the receiving bucket should hold not less than

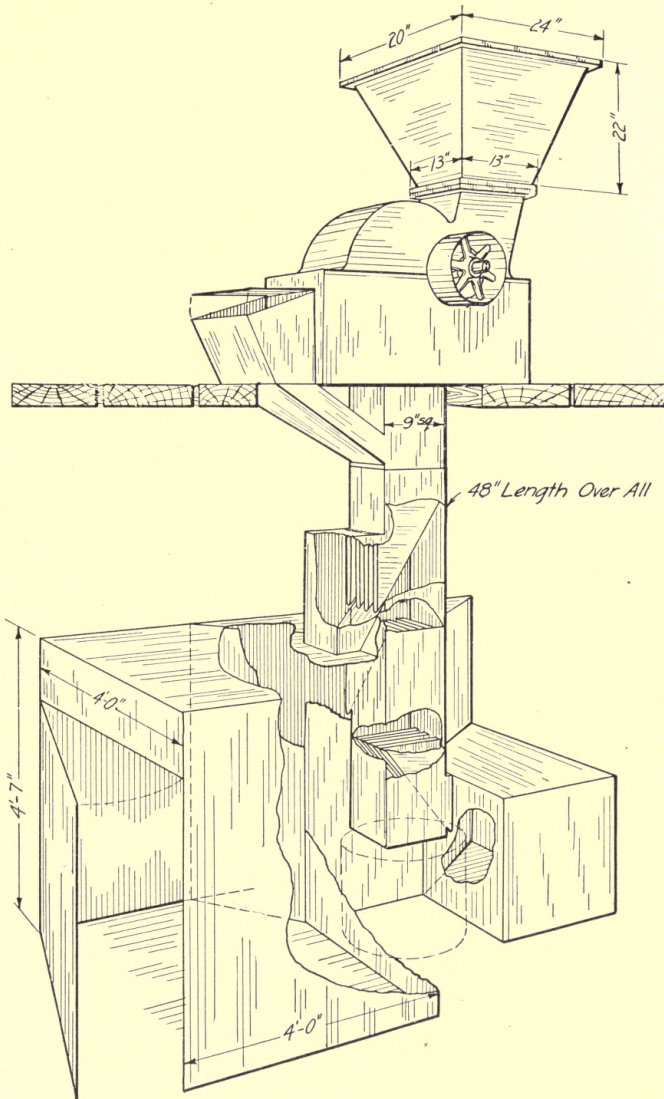


FIG. 2.—Sampling Chute.

80 pounds of coal. In order to further divide this 80-pound sample, an auxiliary hopper may be connected to the top of the chute and the sample again divided by passing through the chute a second time. If desired the divisions in the chute can be arranged so that only $\frac{1}{16}$ of the sample passes through and for large samples—1000 pounds or more—this is desirable in that it avoids the handling of excessively heavy samples in the second subdivision. One laboratory fitted with a sampling chute similar to the one described has a revolving cylindrical mixer between the pulverizer and the sampling chute. The author doubts that this is any decided real improvement as the mixing in the pulverizer is certainly thorough. With the pulverizer fitted with a bar screen, the usual equipment, the pulverized sample escapes from the crusher evenly across the face of the screen and in turn is distributed uniformly in the top of the chute.

In the arrangement shown in Fig. 2 the discarded portions of the sample are collected in the small bins and must be removed with a shovel by hand. When the elevation of the pulverizer is sufficient the chutes may be arranged to deliver into a common bin of larger capacity which need be emptied only occasionally. A still more efficient arrangement, where the amount of sampling to be done warrants the installation, is to have these discarded portions of the samples removed mechanically by having the chutes deliver them on to a belt conveyor. Mechanical arrangements for conveying the sample to the pulverizer are likewise desirable when large amounts of sample are to be handled.

In quartering down by hand the work should be done as rapidly as is consistent with good work and should be done preferably in a cool room so as to make the moisture losses as small as possible and the portion of the sample sent to the chemical laboratory should be sent in a closed container. Reduction of the sample in a power pulverizer is not only more satisfactory on account of the finer reduction of the coarse sample but the crushing being done rapidly the chances of moisture loss are likewise reduced.

The effects of particles of slate and pyrite upon the sample. These may be perhaps best shown in tabular form and serve to emphasize and make clear the precautions to be observed in sampling. Pyrite has a specific gravity of about 5, contains about 53 per cent of sulphur and on burning forms the equiv-

alent of 65 per cent of ash. Slate and shale have a specific gravity of about $2\frac{1}{2}$ and the ash may run as high as 80 per cent. A piece of pyrite one inch each way weighs approximately 80 grams (3 oz.) and contains the equivalent of 42 grams (1.6 oz.) of sulphur and the equivalent of 52 grams (1.9 oz.) of ash, the weight and equivalent amounts of sulphur and ash in pieces of pyrite equivalent to cubes of varying sizes larger and smaller than one inch are as follows:

Size in Inches.	Pyrite Weight in Grams.	Sulphur Weight in Grams.	Ash Weight in Grams.
2	640	336	416
1	80	42	52
$\frac{1}{2}$	10	5.25	6.5
$\frac{3}{8}$	4.22	2.21	2.7
$\frac{1}{4}$	1.25	0.656	0.81
$\frac{1}{8}$	0.156	0.082	0.10
$\frac{1}{16}$	0.0195	0.0103	0.012
$\frac{1}{32}$	0.00244	0.0013	0.0015
$\frac{1}{64}$	0.00031	0.00016	0.00019

On a one-gram sample reduced to such a size that the largest single particle of pyrite does not exceed $\frac{1}{64}$ inch the weight of sulphur and ash equivalent to a single particle is 0.00019 ash and 0.00016 sulphur. Hence the results on a one-gram sample containing particles of this size will be too high or too low by 0.016 per cent on sulphur and 0.019 per cent on ash for each particle more or less than the true average which is contained in the sample as weighed.

If this proportionate weight of the largest size pieces to the total amount of sample be observed for pieces of pyrite equivalent to cubes of different sizes, approximately the following amounts of sample must be taken for each size:

Size in Inches.	Sample Weight in Grams.	Sample Weight.
$\frac{1}{64}$	1	$\frac{1}{28}$ ounces
$\frac{1}{32}$	8	$\frac{3}{7}$ "
$\frac{1}{16}$	64	$2\frac{2}{7}$ "
$\frac{1}{8}$	510	$1\frac{1}{8}$ pounds
$\frac{1}{4}$	4090	.9 "
$\frac{3}{8}$	13700	30 "
$\frac{1}{2}$	32700	72 "
1	260000	570 "
2	2100000	4600 "
3	16800000	37000 "

The preservation of this ratio on the basis of the largest pieces of pyrite being three inches in size means that practically the whole car has to be taken as the sample and in those cases where pyrite occurs as sulphur balls several inches in diameter or the slate occurs in great chunks it is impossible to secure a representative sample by taking only a small amount of sample from the car. Fortunately, however, the slate and pyrite present in the coal as marketed usually occur in smaller particles and a 500- or 600-pound sample with care being observed that no large lumps of slate and pyrite are present ought to be satisfactory for most coal samples as far as slate and ash are concerned.

It must not be assumed that this possible accuracy in sampling of only one piece too many or too few will be actually obtained in practice. Working down the large sample to the small laboratory sample requires that the quartering operation be performed 8 or 10 times and the composition of the reserve portion at each operation is somewhat different from the true average of the whole sample taken. If the quartering is properly done these variations from the true average ought to be both higher and lower and hence tend to partially eliminate each other and the composition of the final portion should approximate that of the original sample. Failure to properly mix and quarter the sample may, however, result in the accumulation of these errors in one direction. For example, a failure to carefully sweep away the heavy particles of the rejected portions would tend to produce a final sample containing more than its share of heavy particles.

The diameter of the wires composing the sieves cuts down the actual size of the openings from 10 to 15 per cent on the larger sizes to as much as 50 per cent on the fine sieves and the actual volume of particles passing through the different mesh sieves (if the mesh is uniform) compared to the volume calculated is only $\frac{3}{4}$ to $\frac{1}{2}$ for the larger sizes down to as low as $\frac{1}{8}$ for the finer sieves, hence the sampling conditions are actually more favorable than is shown by the calculation. However, this is much more than offset by the fact that in practice a variation of only one particle from the true average cannot be obtained and in actual sampling an accuracy varying with the coal and with the skill and care of the sampler of from 0.03 to 0.20 per cent on sulphur and from 0.05 to 0.5 per cent on ash is to be regarded as good

sampling. The lower values apply to clean coal low in ash and low in sulphur. The higher values apply to coal high in slate and pyrite and with improper mixing and failure to crush the slate and pyrite the actual errors on such coals may be much greater, errors of 1 to 3 per cent for ash and 0.3 to 0.5 per cent for sulphur being far too common in ordinary sampling practice.

The passing of the final laboratory sample through a 60-mesh sieve insures a fineness of this final product which in proportion to the sample weighed out is greater than for the larger bulk samples, as with a uniform 60-mesh sieve the largest particles passing through probably do not exceed $\frac{1}{80}$ to $\frac{1}{100}$ inch in diameter, and the ratio of the largest particle of this size to a one-gram sample is 2 or 3 times the calculated ratio of a $\frac{1}{64}$ -inch particle. Hence as far as duplicate determinations on the actual laboratory samples are concerned, results ought to be and are much closer than can be expected on duplicates of the larger samples.

Effect of large pieces of clean coal upon the sample. Large lumps of clean coal will not seriously affect the average of the ash and sulphur in the sample and while it certainly is not advisable to include without breaking down lumps of clean coal 8 inches in diameter in a sample, the effect of such a lump of clean coal on a 600-pound sample would not be very serious. For example, a lump of coal 8 inches each way weighs about 20 pounds. Assuming that this lump analyzes 5 per cent ash and 1 per cent sulphur and that the true average of the shipment is 10 per cent ash and 2 per cent sulphur, then this lump will affect the true ash percentage as follows: 10 per cent on 600 pounds=60 pounds of ash—the correct amount; 10 per cent of ash on 580 pounds =58 pounds of ash and 5 per cent of ash on 20 pounds=1 pound of ash or a total of 59 pounds of ash for the 600 pounds of sample containing the large lump of clean coal, a percentage of 9.83 instead of 10—the correct percentage. On the other hand, a piece of shale 8 inches each way containing 75 per cent ash and weighing 40 pounds would affect the true result as follows: 560 pounds of coal with 10 per cent ash=56 pounds; 40 pounds of shale with 75 per cent of ash=30 pounds of ash or a total of 86 pounds of ash in the 600-pound sample containing the large lump of shale, a percentage of 14.3 ash instead of 10—the correct percentage.

The sampler must, therefore, use common sense and discre-

tion in sampling rather than to sample by a rigid rule. Common sense and discretion mean to guard against moisture losses and to look out for large pieces of slate and pyrite, to break them down fine and to try to get as near as possible a fair proportion of each in the sample.

Relation of amount of car sample to the number of cars sampled. Where a number of cars are sampled and the results of the analysis of the mixed samples is the basis of settlement for the entire shipment, the amount of coal taken from each individual car may be considerably less than where only one car is sampled as the errors in the different samples will to a considerable extent tend to balance each other provided a proper method of sampling is used. For example, if 500 pounds is required to secure a representative sample from a single car, to secure an equally representative sample from 10 cars, it is not necessary to take 500 pounds from each car. The average of samples of 200 pounds from each car should be as close to the true composition of the coal in the 10 cars as the analysis of 500 pounds from any single car is to the true composition of the coal in the single car, since the errors in the ten samples will to a large degree counter-balance each other. This is true, however, provided that the sampling is properly done. If the sampling is improperly done the errors in the individual samples are all liable to be in the same direction and hence the average of any number of such samples will not represent a true average of the shipment. The taking of samples from the top of a car only is to be strictly avoided as almost certain to introduce systematic errors.

TREATMENT OF THE SAMPLE IN THE CHEMICAL LABORATORY

Air drying. Upon arrival at the laboratory, if necessary, the sample should be reduced by crushing to about $\frac{1}{4}$ inch and finer and quartered down to 4 to 6 pounds. This portion should then be weighed and allowed to thoroughly air dry by standing exposed to the air of the room for 36 hours or longer or by putting in a drier heated to a temperature of 10 or 15 degrees above the room temperature and having adequate circulation of air, in which case the drying can usually be completed in six to eight hours. (See Fig. 3.) This air drying should be continued until two weigh-

ings made at intervals of $\frac{1}{2}$ day or so if dried in the laboratory or two hours or more if dried in the drier show less than $\frac{1}{2}$ per cent loss in weight. The more thorough by the air drying is done the less the finely ground laboratory sample is liable to change. The total loss in weight is reported as air drying loss.

Reduction of sample. After air drying, the sample should be reduced by passing through crushing rolls or by means of a

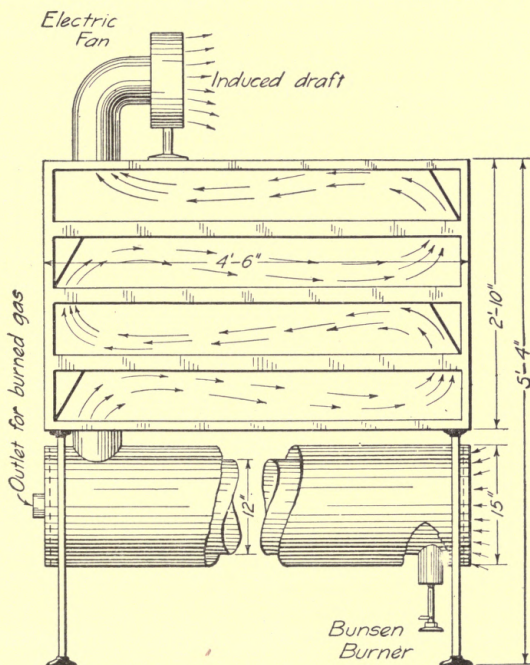


FIG. 3.—Drier for Coarse Samples.

bucking board until it passes an 8-mesh sieve at which point it may be quartered down to about 1 pound. This should be still further reduced, if necessary, until it will pass a 10-mesh sieve. It may then be quartered down to $\frac{1}{2}$ to $\frac{3}{4}$ pound and reduced to a powder in a pebble mill or in the absence of a pebble mill bucked down on a bucking board until a 1- or 2-ounce sample is obtained which will pass a 60-mesh sieve. This bucking board sample, or about a 2-ounce portion of the well-mixed sample from the pebble mill, should be placed in a wide-mouth 4-ounce

bottle and well stoppered. This constitutes the laboratory sample.

For the fine grinding the author prefers a pebble mill, for coals containing much moisture. The jars used are 7 inches in diameter by 7 inches high inside. The pebbles used are about 1 inch in diameter. For this size jar a speed of from 55 to 60 revolutions a minute gives good results, a three-fourth-pound sample being reduced from one-eighth inch to one-sixtieth inch in from 30 to 35 minutes. At the end of the grinding operation the jar is opened and the sample is separated from the pebbles by pouring the contents of the jar upon a coarse sieve.

The fine sample of coal is divided down to about 2 ounces by passing through a small riffle sampler or the sample is thoroughly mixed by hand with a spatula and about 2 ounces taken with a sampling spoon from various parts of the material. This 2-ounce portion is then put through the 60-mesh sieve and kept well covered during the sifting to prevent moisture changes. A light flat brass ring (about 2 inches in diameter and weighing about 4 ounces) placed in the sieve, is of very great assistance in sifting the sample, preventing caking of the material and clogging of the meshes of the sieve. Usually a few coarse particles, amounting to from one-fourth to one-half per cent of the sample, remain upon the sieve. These are bucked down by hand on a bucking board and thoroughly mixed with the sifted portion of the sample. The whole is then put in a glass bottle and securely stoppered and constitutes the laboratory sample for analysis.

The jars and pebbles after being cleaned by brushing with a stiff brush (this part of the operation requiring only a minute or so) are ready for the grinding of another sample of coal. When samples of entirely materials are ground, the jars and pebbles may require more thorough cleansing with water and scrub brush, but, as a rule, in their use for coal, dry cleansing is sufficient.

The riffle sampler used in reducing the sample is shown in figure 4. Two sizes of sampler are used in the laboratory. The larger size has one-inch subdivisions and is used in reducing the sample from 25 pounds down to the amount to be ground in the ball mill (about three-fourths pound). The sample, after grinding in the ball mill, is divided down to about 2 ounces by

means of the smaller sampler having one-half inch subdivisions.

The sampler is essentially a metal box mounted on legs and fitted with a number of equidistant vertical parallel partitions, the alternate bottoms of the spaces between the partitions sloping in opposite directions. The angle of slope should be about 60° from the horizontal. If much less than this the coal will not run freely and may clog the sampler.

The lower portions of the sides of the sampler are open and

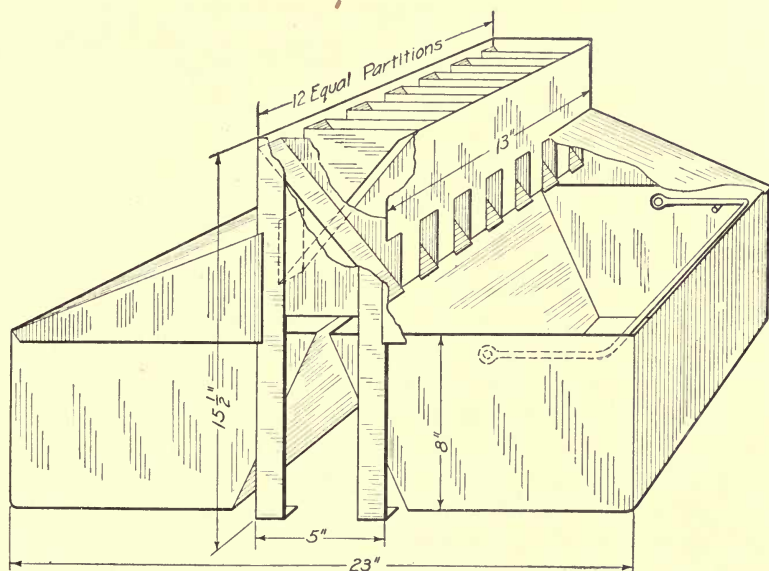


FIG. 4.—Riffle Sampler.

the coal emptied in the top of the sampler runs down the sloping bottoms of the subdivisions and is caught in two buckets below, one-half of the sample being caught in each bucket. To keep down dust the space above the receiving buckets is covered with a metal hood or shield. Three buckets are necessary for convenience in sampling, two to set under the sampler and the third to contain the portion of the sample to be subdivided. After pouring the material through the sampler one of the buckets containing one-half of that poured through is removed and the empty bucket set in its place. The one-half portion is then

poured through in turn. The bucket last set under containing one quarter of the original sample is removed and the empty one again set in its place, the subdivision of the sample being continued till the sample is reduced to the amount desired.

After dividing a sample, the sampler is most conveniently cleaned by directing a blast of air from a handbellows through the subdivisions and any particles of material clinging to the sides or the bottoms of the divisions removed before the apparatus is used for dividing another sample.

SPECIAL NOTES ON SAMPLING

Fineness of final sample. Coals unusually high in pyrite and slate should perhaps preferably be put through an 80-mesh sieve rather than through the 60-mesh but the author is of the opinion that the 60-mesh is amply fine for nearly all samples. Grinding to 100-mesh and finer is to be avoided as the more rapid oxidation of the fine sample may and in some samples certainly does affect the results obtained for calorific value and the ultimate composition. Where the sample is ground in a ball-mill the grinding should be continued only long enough to insure the desired fineness of 60-mesh and finer. If left in a longer time the sample will be ground excessively fine and subject to the larger oxidation changes mentioned.

Grinding of coals containing appreciable amounts of moisture. With coals containing appreciable amounts of moisture it is safer in case the sampling is done on the bucking board to reserve a 2-ounce portion of the 10-mesh size for the moisture determination. Plenty of time may then be taken for sampling the bucking board sample and in fact it is a better laboratory sample if spread out and dried for a considerable period of time before being put into the sample bottle. The analytical results obtained upon this sample must be reduced to the moisture content in the coarse sample obtained by determining the moisture on a 5- or 10-gram portion of the 10- or 20-mesh sample.

It is often assumed with a well air dried coarse sample that there is no danger from moisture changes in bucking down the fine sample on the bucking board. This, however, is a false assumption as the results of numerous experiments on different coals have shown that fine samples of coal give up or take up considerable

moisture with changes in the humidity and temperature of the sampling room. A large number of experiments on this point are given in *Bulletin* No. 323 of the U. S. Geological Survey which is published as a reprint by the Bureau of Mines as *Bulletin* No. 28. A large number of comparisons of the bucking board samples and the ball-mill samples, sampled under observed conditions of temperature and humidity are recorded. These comparisons show losses in the bucking board samples in some cases as great as 2 per cent. In other cases where the air drying of the coarse samples had been a little too thorough the bucking board samples showed increases in moisture, in some cases amounting to 0.6 per cent. These results are all upon the air dried samples which were presumably close to an air-dry condition.

The moisture losses upon bucking board samples of undried coal may easily be 4 to 5 per cent with coals at all high in moisture. Laboratory experiments on a fine sample of Illinois coal containing 12.4 per cent moisture showed for a one-gram sample spread on a watch glass and exposed to the laboratory air a loss of 2 per cent in 5 minutes. As the time required to buck down a fine sample on a bucking board is often several times 5 minutes the moisture losses on such samples cannot be otherwise than of considerable magnitude. A sample of Illinois coal, the coarse sample of which had previously been well air-dried, showed a loss of 0.93 per cent after 5 minutes' exposure to the laboratory air with a total moisture content of only 4.12 per cent in the sample, from which the conclusion that bucking board samples even on well air-dried samples are not entirely satisfactory seems to be if anything conservative. With low moisture coals such as some of the Arkansas and West Virginia coals the moisture losses on bucking board samples from the well air-dried samples are not likely to be very large, the experiments recorded showing moisture losses or changes of only 0.1 or 0.2 per cent; but in higher moisture coals such as Illinois, Indiana, or Ohio the bucking board samples cannot be regarded as entirely satisfactory.

Omitting the air-drying on the coarse sample. When this is done the reservation of a portion of the 10-mesh sample for the moisture determination is essential if the moisture percentage and the calorific value are desired. If only ash and sulphur results are desired, in many coals, failure to correct to "moisture as received" may not be important. When preliminary air

drying of the coarse sample is omitted the weighing of the fine sample in the laboratory must be done quickly as serious moisture losses may occur and mixing of such a sample on paper previous to weighing should be strictly prohibited as moisture losses are sure to result.

Bucking board grinding. While slower than power grinding, if used in connection with power crushing and the crushing rolls, the reduction of the sample is not excessively tedious, but if the bucking board is used to grind down a sample from $\frac{1}{4}$ inch or larger, it is considerably slower on account of the much larger amount of sample to be reduced, and a great danger of bucking board sampling is too much quartering down of the rather coarse sample. The crushing rolls and ball-mill avoid this tendency entirely and are to be preferred on this account as well as on account of smaller moisture changes.

Necessity of making analytical determinations on the fine sample without undue delay. The analytical work upon the laboratory sample should be done promptly as fine samples of coal are known to undergo considerable oxidation changes. Experiments recorded in the bulletin just referred to show oxidation changes amounting to as much as $2\frac{1}{2}$ per cent of the original weight of the coal during a period of eight months. These oxidation changes took place on samples well stoppered with rubber stoppers. Where the sample has more or less free exposure to air the oxidation changes are almost certain to be of considerable magnitude. Certainly reliable results cannot be obtained upon a sample which have stood around the laboratory for any great length of time.

Equipment for reduction of samples. The equipment used by the author, some of which has already been described and which he has found satisfactory, is as follows:

(1) A swing hammer pulverizer equipped with a chute for mechanically dividing the samples. Such a pulverizer readily reduces large samples to $\frac{1}{4}$ inch and the samples can be divided down to 4 or 5 pounds without further treatment.

(2) A hand or power jaw crusher for reducing coal samples to $\frac{1}{4}$ inch is very satisfactory, but for rapid reduction of large samples of coal the author prefers the pulverizer. For small samples—25 pounds or less—a hand jaw crusher is satisfactory but for large samples power crushers of larger capacity are pref-

erable. It is hardly necessary to state that an ordinary laboratory does not need a power equipment of both crusher and pulverizer.

(3) For crushing the $\frac{1}{4}$ -inch samples to 10-mesh a pair of 6-inch power rolls are efficient, rapid and satisfactory.

(4) For reduction of the 10-mesh samples to 60-mesh and finer a pebble mill is very efficient and prevents moisture changes during pulverizing.

(5) For occasional sampling an ordinary bucking board with a rather heavy muller answers the purpose.

(6) For air drying of coarse samples previous to pulverizing a drying oven similar to the one shown in figure 3 is very satisfactory. The trays of this drier are of galvanized iron 1 inch deep by 24 by 24 inches.

(7) In weighing up the air-dried samples on the large trays a Troemner solution scale No. 80 is very satisfactory.

(8) For mechanical dividing of the samples, riffle samplers similar to that shown in figure 4 are satisfactory.

(9) Coarse wooden frame sieves from one inch to $\frac{1}{4}$ -inch and brass sieves from 10-mesh to 80-mesh are a necessary part of the equipment.

The particular machines used by the author are as follows and have proven satisfactory. Similar machines of other makes are doubtless equally as efficient.

(1) Jeffrey "baby pulverizer" manufactured by the Jeffrey Manufacturing Company, of Columbus, Ohio. Horse-power required 6 to 8. The "baby pulverizer" easily has a capacity of over 1000 pounds per hour.

(2) Chipmunk jaw crusher, manufactured by F. W. Braun & Co., Los Angeles, California. Horse-power required 1 to 2. The jaw crushers have a capacity per hour of about 200 pounds for the smaller size to about 1000 pounds for the larger size.

(3) Six-inch crushing rolls manufactured by the American Concentrator Company, Joplin, Mo. The crushing rolls have ample daily capacity for any ordinary requirement. Allowing time for cleaning between grinding of samples if run to capacity 50 to 100 samples of four or five pounds each can easily be reduced by the rolls from $\frac{1}{4}$ inch to 10-mesh and finer.

(4) Four-jar ball-mill manufactured by the Abbé Engineering Company, New York. The four-jar ball-mill if provided with

an extra set of jars and kept running to capacity will grind 40 to 50 samples per day.

(5) The drier, riffle sampler, etc., can readily be constructed by local tinsmiths. The drier described, see figure 3, holds only eight large samples but if supplemented by air drying of samples over night 15 to 20 samples per day can be dried ready for final grinding. If a larger number of samples are to be handled a larger drier should be provided.

CHAPTER IV

METHODS OF ANALYSIS

THE samples from the sampling room or laboratory should be sent to the chemical laboratory in wide-mouth bottles securely closed with rubber stoppers. Ordinary 4-ounce wide-mouth bottles are very convenient for coal samples.

Weighing out a Sample for a Determination. In weighing out portions of the laboratory sample for a determination, the sample should be well mixed. An efficient method of mixing is as follows: The material is thoroughly mixed by giving the bottle 15 to 20 rotations with an upending and tilting movement of the bottle to insure mixing of the top and bottom portions of the sample. For satisfactory mixing in this way the sample should not fill the bottle more than half full. After the mixing in the bottle the stopper is removed and the sample still further mixed by means of a sampling spoon and successive small portions taken until the amount required for the determination is secured, especial care being taken to again securely stopper the bottle before setting it aside for other determinations. If the sample more than half fills the bottle it should be emptied out on paper, well mixed and a sufficient amount discarded until the remainder is small enough to be properly handled in the sampling bottle.

Moisture. A one-gram portion of the well-mixed 60-mesh sample is weighed into an empty capsule or crucible and heated for an hour at 105° C. in a constant-temperature oven. The capsule is then removed from the oven, covered and cooled in a desiccator over sulphuric acid. The loss in weight times 100 is considered as the percentage of moisture. The writer prefers, for moisture determinations, porcelain capsules about 1 inch high by 1 $\frac{5}{8}$ inches in diameter at the top. The particular kind used has been obtained from The Henry Heil Chemical Co., of St. Louis, and are designated as porcelain-moisture capsules No.

2. They are much more substantial and satisfactory than the ordinary porcelain crucible.

The lids used in connection with the capsules are stamped from sheet aluminium. They are light and unbreakable and much more convenient to handle than the ordinary covers used with porcelain crucibles. In weighing out the sample at the beginning of the determination the lid is placed upon the balance pan under the empty capsule in which the sample is weighed.

The oven used for a number of years by the author is a double-

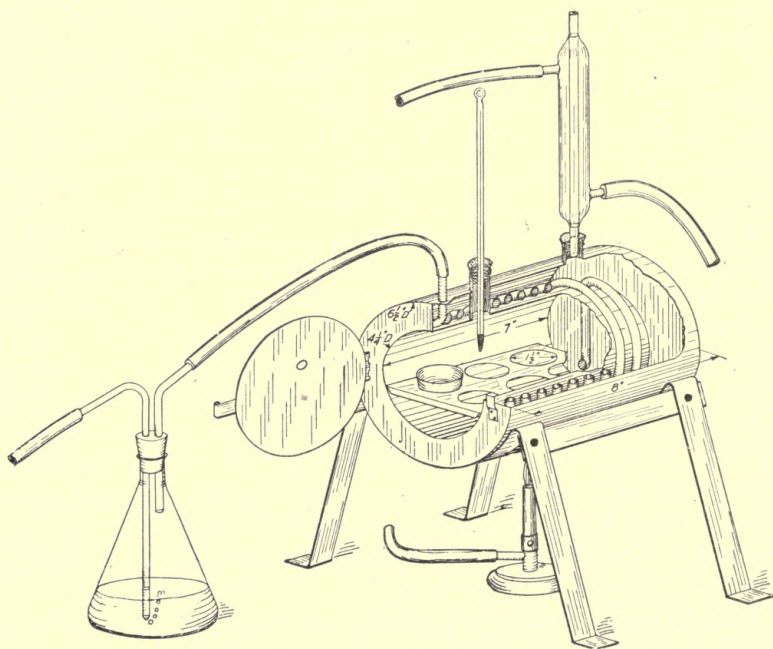


FIG. 5.—Moisture Oven.

walled copper cylinder, see Fig. 5; the space between the outer and inner walls being filled with a solution of glycerine in water, the proportions being so adjusted that the boiling solution maintains a temperature of 105° C. in the inner chamber of the oven. The inner cylinder is $4\frac{1}{4}$ inches in diameter by 7 inches long. A removable perforated shelf fits into this inner cylinder, the perforations holding six capsules. The outer cylinder is $6\frac{1}{2}$ inches in diameter by 8 inches long. Concentration of the solution is

prevented by means of a condenser fitted on to the top of the the outer cylinder. Air is admitted into the inner chamber of the oven through a coil of block tin or copper tubing, which passes around the inner cylinder and is surrounded by the glycerine solution. The inner end of this tubing is soldered into the rear wall of the inner chamber; the outer end is connected to a flask containing concentrated sulphuric acid. During a determination a current of air dried by passing through the sulphuric acid is passed through the copper or tin tube into the inner chamber of the oven. Passing over the samples it takes up the moisture and escapes through a small opening in the top of the door of the oven. The air is passed through at such a rate that a volume equal to the capacity of the oven passes through every six or eight minutes. Operating a moisture oven in this way insures a uniform condition in the oven irrespective of laboratory humidity and temperature conditions and results run at different times are strictly comparable, which is not the case in an ordinary moisture oven.

The use of sulphuric acid in the desiccator in which the moisture sample is cooled gives more concordant results than where calcium chloride is used. Experiments show that if the dry sample is allowed to remain over calcium chloride for any considerable period of time it increases in weight and the results for moisture are accordingly low. To avoid the danger of sulphuric acid, in the desiccator, splashing up on the bottom of the capsule when the desiccator is carried around the laboratory, a thin sheet of asbestos paper should be placed below the capsule, care being taken to have it fit loosely enough in the desiccator to allow free circulation of air.

The cut shows 9 turns of tubing, however, 4 or 5 turns are probably just as efficient and are less expensive.

Ash. The ash is determined on the residue of coal from the moisture determination. The capsule containing the coal is placed in a muffle furnace and slowly heated until the volatile matter is given off. This slow heating avoids coking the sample and renders it easier to burn to ash. After the volatile matter is expelled the temperature of the muffle is raised to redness and the heating is continued until all black carbon is burned out. The capsule is then removed from the muffle furnace, cooled in a desiccator and weighed. It is then replaced in the muffle

for thirty minutes, again cooled and re-weighed. If the change in weight is less than 0.0005 gram the ash is considered burned to constant weight. If the variation is greater than this the ash is again ignited for 30 minutes and again cooled and re-weighed the process being continued until the difference in weight between two successive ignitions is less than 0.0005 gram. In the case of coals high in iron, ignition to constant weight is sometimes difficult on account of small variations in weight due to oxidation and reduction of the compounds of iron. The amount of ash as determined represents the ignited mineral matter in the coal.

In regular routine work the cooling in desiccators may be dispensed with and the capsules cooled on clay triangles in the open air. A set of six triangles mounted on a wood base is very convenient for carrying the capsules from the furnace to the balance and from the balance back to the furnace. This arrangement is lighter and easier to handle than desiccators and the time required for cooling is much less.

The capsules cooled in air weigh about 0.0005 gram more than if cooled in desiccators, hence the ash results run a trifle high, but for most samples the difference is of very minor importance and the saving in time and labor considerable. If results of highest accuracy are required the cooling should be done in desiccators.

Volatile matter. A one-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished 30-gram platinum crucible with a close fitting cover. The crucible and contents are heated upon a platinum or nichrome triangle for 7 minutes over a Bunsen flame.

The crucible and residue are cooled and weighed, the loss in weight minus the weight of the moisture in the sample determined at 105° C. times 100 equals the percentage of volatile matter.

With artificial gas the height of the flame should be 18 to 20 cm. With natural gas the height of the flame should be about 30 cm. In using artificial gas the bottom of the crucible should be about 7 cm. above the top of the burner. With natural gas the bottom of the crucible should be about 12 cm. above the burner. To protect the crucible from air currents it is desirable to enclose the flame in a chimney. A cylindrical chimney 15 cm. long by 7 cm. in diameter, notched at the top so that the platinum triangle is about 3 cm. below the top of the chimney, makes a satisfactory working arrangement. This chimney is preferably

of sheet-iron lined with asbestos but a fairly satisfactory chimney can be made by moistening a thick sheet of asbestos and rolling it into a cylinder. This, if well wrapped with wire makes a fairly serviceable chimney. For lignites and coals containing a high percentage of moisture the method should be modified by giving the sample a preliminary heating at a low temperature for several minutes to drive out the moisture in order to avoid mechanical losses which will occur if such a sample is heated over the full flame of the burner from the beginning. This preliminary heating for three to four minutes should be followed by the regular 7-minute application of the full flame, after which the sample is cooled and weighed as in the regular determination.

The higher the temperature at which the volatile matter is expelled the greater is the percentage of volatile matter obtained. The latest data on this subject (Sept., 1912) is by Fieldner and Hall¹. As a result of their experiments they recommend 1000° C. as the most desirable temperature at which to make this determination. Their results using a No. 4 Meker burner with natural gas compare very favorably with their results obtained by heating the sample in an electric furnace.

Fixed Carbon. The fixed carbon is the difference between 100 and the sum of the moisture, ash and volatile matter.

Sulphur. Sulphur is determined by either of two methods:

- (a) The Eschka method.
- (b) The determination of the sulphur in the washings from the calorimeter.

The two methods give closely agreeing results on most samples. As a rule the determination on the washings from the calorimeter run a trifle lower than by the Eschka method and where the exactness of the sulphur determination is of more than ordinary importance the Eschka method should be used. The details of the methods are as follows:

Eschka Method. One gram of the sample is thoroughly mixed in a 30 c.c. platinum crucible with about one and one-half grams of the Eschka mixture (two parts light calcined magnesium oxide plus one part anhydrous sodium carbonate); about one-half gram of the mixture is then spread on top as a cover.

The burning is done over grain or wood alcohol, gasoline gas or natural gas, experiments having shown that the sulphur con-

¹ Eighth International Congress of Applied Chemistry, Vol. X, p. 139.

tained in gasoline gas and natural gas is so small that little or none of it is taken up by the Eschka mixture. Ordinary artificial gas is so high in sulphur that its use is not permissible, as blanks are likely to be large and variable and consequently the correction to be applied is uncertain. At the beginning the flame is kept low until the volatile matter is burned out. This requires from 15 to 30 minutes. The heat is then increased and the mixture stirred occasionally with a platinum wire, the heating being continued till all traces of unburned carbon have disappeared.

The mixture in the crucible is then transferred to a 200 c.c. beaker and digested with 75 c.c. of water for at least 30 minutes. The solution is then filtered and the residue washed twice with hot water by decantation and then washed on the filter, small portions of water being used for each of the washings until the filtrate amounts to 200 c.c. Bromine water in excess is then added, and the solution made slightly acid with hydrochloric acid. The amounts of these reagents usually added are 4 c.c. of water saturated with bromine and 3 c.c. of concentrated hydrochloric acid.

The solution is heated nearly to boiling and the sulphur precipitated with 20 c.c. of a hot 5 per cent solution of barium chloride, slowly added from a pipette during constant stirring. The solution and precipitate are allowed to stand at a temperature a little below boiling for two hours or longer before filtering. The filtrate from the barium sulphate is tested for acidity, with litmus paper, and for excess of barium chloride by adding a few drops of dilute sulphuric acid to a few c.c. of the filtrate in a test tube. The preliminary washing of the precipitate is done with hot water containing 1 c.c. of hydrochloric acid per liter. The final washings are made with hot water alone and the washing is continued until the washings no longer react for chlorine when tested with silver nitrate.

The precipitate is ignited in a porcelain crucible. The filter and precipitate are placed in the crucible, precipitate uppermost, and the filter folded only enough to prevent loss by spattering. A low heat is used until the paper is entirely "smoked off." The heat is then raised sufficiently to bring the precipitate to dull redness and the heating continued for a few minutes, or until the carbon is burned out. The crucible and precipitate are then cooled and weighed. The weight of barium sulphate less the blank

from the reagents, times 0.137, times 100, equals the percentage of sulphur in the sample.

Sulphur in the calorimeter washings. The determination of the sulphur in the washings from the calorimeter is as follows: The washings are slightly acidulated with hydrochloric acid and filtered from the residue of ash, the filtrate is heated to boiling and the sulphur precipitated as in the Eschka method.

ULTIMATE ANALYSIS

The ultimate analysis is best made in a 25-burner combustion furnace. The details of the train and description of the method of work are as follows:

The purifying train through which the air and oxygen are passed before they enter the combustion tube is arranged in duplicate, one part for air, the other for oxygen. The purifying reagents, arranged in the order named, are sulphuric acid, potassium hydroxide, soda-lime and granular calcium chloride. The combustion tube is about 40 inches long and about $\frac{5}{8}$ inch internal diameter. The tube extends beyond each end of the furnace about four inches, the ends of the tube being protected from the heat of the furnace by closely fitting circular shields of asbestos. The rear end of the tube (the end next to the purifying train) is closed with a rubber stopper. This end of the tube being kept cool by the protection of the circular shield and by the passage of cool air and oxygen, there is very little danger of volatile products being given off by the rubber. The other end of the tube is closed by a well-rolled cork of specially selected quality, the danger from over-heating at this end of the tube being too great to permit of the use of the more convenient rubber stopper. This end of the tube may if desired be drawn out so that the absorption train may be connected to it direct and thereby avoid the danger of leakage from the use of a cork. In selecting a tube for use care should be taken to avoid the heavy walled tubes as the thin tubes are much less liable to breakage.

The rear end of the tube for 10 inches inside the furnace is left empty; the next 14 inches is filled with a loose layer of wire copper oxide, with a plug of acid-washed and ignited asbestos at either end to hold the oxide in place. The copper oxide is followed by a layer, about 4 inches long, of coarse fused lead chro-

mate to stop sulphur products, this being held in place by a final plug of asbestos.

The absorption train is as follows: The water is absorbed in a six-inch U-tube, filled with granular calcium chloride; the carbon dioxide is absorbed by potassium hydroxide in an ordinary Liebig bulb, to which is attached a three-inch U-tube containing soda-lime and calcium chloride, the bulb and U-tube being weighed together. This is followed by a final guard tube filled with calcium chloride and soda-lime. The gases formed during combustion are drawn through the train by suction, a Mariott bottle being used to secure a constant suction head.

The oxygen used is kept over water and is supplied under small pressure. The supply of oxygen and the aspiration during a combustion are so regulated as to keep the difference in pressure between the inside and outside of the tube very small, the pressure inward being slightly greater. This reduces the danger of leaks to a minimum, and, if by chance any slight leakage does occur, it is inward rather than outward and the effect upon the determination is small.

Carbon and hydrogen. Before beginning the determination, the apparatus is tested for leaks by starting the aspirator and shutting off the supply of air. With the aspirator on full, if not more than four or five bubbles of air per minute pass through the potash bulb, the connections are sufficiently tight to proceed with the determination. Air is then admitted to the purifying apparatus, the tube heated to redness throughout and 1000 c.c. or more of air aspirated. The potash bulb and drying tube are then detached and weighed. They are again connected and 500 c.c. of oxygen followed by 1000 c.c. of air aspirated through the train.

On commencing the second aspiration the burners under the rear portion of the tube are gradually turned down and finally entirely out, so that the empty portion of the tube into which the sample for analysis is to be inserted becomes nearly or quite cool, by the time the aspiration is complete. The burners under the two-thirds of the copper oxide next to the lead chromate are kept lighted and this portion of the oxide kept at a red heat. After aspiration of the 1000 c.c. of air, the potash bulb and drying tube are detached and again reweighed. If the gain or loss in weight is less than five-tenths milligram the apparatus is ready for use.

The absorption apparatus is then again connected and 0.2 gram of the well-mixed sample weighed into a platinum boat and the boat and sample pushed into place in the combustion tube as quickly as possible and slow aspiration of the train started at the rate of one or two bubbles a second through the potash bulbs and a mixture, in the proportion of about two bubbles of oxygen to one of air, admitted into the train through the purifying apparatus. The burners under the remaining copper oxide and behind the boat are lighted and the moisture and volatile matter gradually driven off.

This part of the operation requires very careful watching and manipulation to secure correct results. The copper oxide must be at a good red heat or the combustion of the hydrocarbons is liable to be incomplete. If the evolution of the hydrocarbons is too rapid incomplete combustion or absorption also results. Also if the evolution is too rapid back pressure is developed in the train and losses are almost sure to occur, either from moisture getting back into the tube of the purifying apparatus or from slight leaks in the train. When the volatile matter is expelled that portion of the tube containing the boat is heated to redness, more oxygen is admitted into the train and the fixed carbon gradually burned off, using care not to allow the combustion to take place too rapidly or fusion of the ash and incomplete combustion may result.

Oxygen is admitted for about 2 minutes after the fixed carbon is burned out, which may be seen by the sudden disappearance of the glow. The oxygen is then turned off and air aspirated through the train, the burners under the rear portions of the tube being gradually turned down and out. After 1000 c.c. have been aspirated the absorption apparatus is detached and weighed. One-ninth the increase in the weight of the drying tube equals the weight of the hydrogen and three-elevenths of the increase in the weight of the potash bulb equals the weight of the carbon from the sample.

The weight of the hydrogen and of the carbon in grams times 5 times 100 equal the percentage of each in the sample. After the completion of a determination the platinum boat is removed from the rear of the combustion tube and the ash examined for unburned carbon. If desired the ash may be weighed as a check upon the amount determined by the regular method. With a high per-

centage of iron in the ash the ultimate ash usually runs a little higher than the results obtained by burning out a gram sample in the muffle furnace owing probably to the more complete oxidation of the iron in the sample burned in the combustion train. To make another determination, the absorption apparatus is again connected to the train and another sample weighed into the platinum boat and inserted into the rear of the combustion tube.

In weighing the sample, the work should be done as rapidly as possible and as soon as weighed the boat and sample should be placed in a glass weighing tube which should be securely stoppered to prevent moisture losses. The sample is carried from the balance room to the combustion train in the closed weighing tube. The transfer from the weighing tube to the combustion tube should be made quickly and the connections of the combustion tube fitted up without undue loss of time.

Aspiration to constant weight is unnecessary between determinations which follow one another immediately, but cannot safely be neglected if the train is allowed to stand for several hours. At the beginning of a series of determinations aspiration to constant weight is always necessary. Also aspiration to constant weight is necessary after the re-filling of the potash bulbs or if a new bulb is substituted. The potash bulbs hold sufficient potash for four or five determinations, after which the solution should be replaced by fresh reagent. The potash solution should have a specific gravity of about 1.27, which corresponds to about a 30 per cent solution. The stock solution should be treated with a few drops of permanganate solution to oxidize any ferrous iron or other oxidizable compounds present, which if not oxidized, interfere with the aspiration of the bulb to constant weight.

NITROGEN

One gram of the finely pulverized coal is digested with 30 c.c. of concentrated sulphuric acid and 0.6 gram of metallic mercury until the carbon is completely oxidized and the liquid is nearly colorless. The digestion should be continued for at least an hour after the solution has reached the straw color stage. Crystals of potassium permanganate are then added, a few at a time, until a permanent green color remains. After cooling, the solution is

diluted to about 300 c.c. with cold water. It is then transferred to a 750 c.c. distillation flask. The excess of mercury is precipitated by adding 25 c.c. of potassium sulphide (K_2S) solution (40 grams of K_2S per liter). About one gram of granular zinc is added to prevent bumping. Enough saturated sodium hydroxide ($NaOH$) solution (usually about 80 c.c.) is added to make the solution distinctly alkaline, the soda being added carefully so as to run down the side of the flask and not mix with the acid solution. The flask is then connected to a condenser, the contents mixed by shaking and then heated over a Bunsen burner until about 200 c.c. of distillate have been obtained. The distillate is collected in a receiving flask containing 10 c.c. of standard sulphuric acid solution (1 c.c.=0.005 gram of nitrogen) to which cochineal indicator in amount sufficient for titration has been added. The end of the tube carrying the distillate should dip beneath the surface of the acid at all times. The distillate is then titrated with standard ammonia solution (20 c.c. of ammonia solution=10 c.c. of sulphuric acid solution=0.05 gram of nitrogen). If trouble is experienced from frothing during distillation it may be prevented by the addition of a small piece of paraffin to the solution before distillation.

A convenient method of adding the 0.6 gram of mercury is to measure it rather than to weigh it. This can readily be done by partially filling up the opening in a glass stop-cock so that when the cock is turned it carries and delivers a drop of mercury. Such an apparatus correctly calibrated will deliver practically the same amount each time, and the addition of the mercury can be made in one-tenth the time required to weigh out the desired amount.

For further details of the Kjeldahl process, see *Bulletin* 107 (Revised) U. S. Department of Agriculture, Bureau of Chemistry.

PHOSPHORUS

In the determination of phosphorus 5 to 10 grams of sample are burned to ash in the muffle furnace. The ash is mixed in a platinum crucible with four to six times its weight of sodium carbonate and about 0.2 gram of sodium nitrate and is fused over the blast lamp. The fused mass is dissolved in water, acidified and evaporated to dryness. The residue is taken up in

hydrochloric acid and the phosphorus determined in the usual way either by weighing the yellow precipitate or titrating it with permanganate or standard alkali. For details of phosphorus determinations see Lord's "Notes on Metallurgy" or other texts on metallurgical analysis.

OXYGEN

No reliable method is known for the direct determination of the oxygen in coal and it is, therefore, determined by difference. The sum of the percentages of hydrogen, carbon, nitrogen, sulphur and ash is subtracted from 100 and the remainder is called oxygen. This result is always inaccurate in that it does not represent the true amount of oxygen in the coal. The amount of the inaccuracy increases with the percentage of the ash and sulphur. The effects of ash and sulphur upon the value obtained for oxygen have been discussed elsewhere and do not need repetition at this point.

CHAPTER V

DETERMINING THE CALORIFIC VALUE

THE establishment and use of specifications for the purchase and sale of coal based upon the heating value require the actual determination of the heating value of the sample or samples which are used as the basis of settlement, and in analyzing such samples the chemist is expected and required to make this determination along with the determination of moisture, ash and sulphur. At present some form of pressure calorimeter, in which the sample is burned in a steel bomb under 15 to 25 atmospheres pressure of oxygen, is generally regarded as the standard type of calorimeter, and specifications for the purchase of coal frequently specify that the heating value shall be determined in a bomb calorimeter. Some of the commoner types of this form of calorimeter are: the Mahler, the Atwater, the Emerson, the Williams, and the Kroecker.

The details of the method of making a determination and the calculation of the results are as follows: This description is based primarily upon the use of a Mahler calorimeter but is applicable with minor modifications to any of the other calorimeters mentioned. About 2 grams of the 60-mesh sample are pressed into a small briquet by means of a small screw press and mold. The press used by the writer is the iron frame of a 2-quart tincture press manufactured by the Enterprise Manufacturing Company of Philadelphia, Pa. After removal from the mold the briquet is broken into smaller portions and about 1 gram accurately weighed and placed in the platinum combustion tray which is covered with a thin disc of asbestos paper that has been washed with hydrochloric acid and ignited in a muffle furnace. The tray is then attached to one of the platinum terminals fitted to the lid and the terminals are connected by a piece of iron wire (platinum wire should be used when the bomb is platinum lined) about 10 centimeters long and formed into a spiral. The ends of the wire

are attached to the clean platinum terminals, by wrapping the wire tightly around them. The spiral is bent down so that it touches the coal sample in the tray. The lid is placed on the bomb and screwed down tightly against the lead gasket. Oxygen under pressure is admitted gradually into the bomb through the valve stem until the manometer recording the pressure reads 18 to 20 atmospheres. The needle valve is then closed. Very little force should be used in closing it and extra pressure should be avoided.

The bomb filled with oxygen is placed in the brass bucket containing from 2400 to 2500 grams of distilled water, the bucket having been previously placed in the insulated jacket. The stirring apparatus is then adjusted so that it touches neither the bucket nor bomb and works freely. The thermometer for recording the temperature rise is clamped into position and so adjusted that the lower end of the mercury bulb is about 5 centimeters above the bottom of the bucket. The outside terminals of the bomb are connected with wires leading to the switch. The stirrer is then set in motion and the readings of the thermometer taken by means of a telescope attached to a cathetometer. The thermometer is graduated to $\frac{1}{50}$ th degree Centigrade and the readings can be interpolated to thousandths of a degree. The stirring should be continued at a uniform rate throughout the determination and should be sufficiently rapid to insure thorough mixing. Preliminary readings are taken at intervals of one minute each for about five minutes or until the rate of change per minute is nearly uniform and a definite rate is established. The switch is then closed and the current turned on for about one-half second. The ignition of the sample is followed by a very rapid increase in temperature and the first two readings after combustion are taken one-half minute apart. Other readings are then taken at minute intervals. The temperature usually reaches a maximum in three or four minutes but the series of readings is continued until a uniform final rate has been established. Not less than five and sometimes as many as seven or eight readings are required to determine the final rate.

The calculations involved and corrections applied are shown by a typical determination on p. 93.

The readings from 7-50 to 7-54 are the readings of the preliminary period. The increase in temperature during this time

FORM FOR CALORIMETER DETERMINATIONS

DEPARTMENT OF METALLURGY,
OHIO STATE UNIVERSITY.

SAMPLE No. 5160

Date—5-24-1912.

Wet and dry bulbs = 14-22° C.

Coal = 1.0018 gms.

Jacket water = 21° C.

Room temperature = 22° C.

Time.	Readings ° C.		Observed final temperature	21.744	
			“ initial “	19.348	
7-50	19.318	} = +0.0075	“ temperature rise	2.396	
51	19.326				
52	19.334				
53	19.340				
54	19.348	+0.0075	Radiation correction	= +0.0094	
			Calibration correction	= -0.006	
			Stem correction ...	= +0.0014	
		+0.0026			
½	20.2	+0.0030	Corrected temperature dif.	= 2.4008	
		+0.0001	Water equivalent 1°	= 2875	
55	21.40	-0.0028			
		-0.0035		5750.0	
56	21.700	-0.0043		1150.0	
		-0.0043		00.0	
57	21.746	-0.0043		00.0	
		-0.0043		2.3	
		-0.0043			
58	21.744		Calories of heat developed	= 6902.3	
59	21.740	-0.0094	Corrections	= 101.6	
60	21.736				
1	21.734	} = -0.0043	Heat from sample	= 6800.7	
2	21.728		Correction for excess sample		
3	21.722		over 1 gram	= 12.2	
4	21.718				
			Calorific value of coal	= 6788.5	

Wire fuse = 10 cm.

“ “ unburned = 2 cm.

“ “ burned = 8 cm. (1 cm. = 2.4 cal.) = 19.2 cal.

Titer, 23.8 to 31.6 = 7.8 cc. (1 cc. = 5 cal.) = 39.0 “

Sulphur in coal 3.34 per cent (.01 gm. = 13 cal.) = 43.4 “

Total correction = 101.6 “

Thermometer used, No. 5764

Position 5 c.m.

Scale reading 18.3.

Stem temperature 22° C

Atmospheres oxygen used = 18

Valve—tight.

At 19° add 4.5 c.c. of water to obtain 2400 gms.

(Signed) C.H.Y.———

Checked E.S.D.———

is 19.318 to 19.348 = 0.030 or 0.0075 degree per minute. The switch was closed and the combustion started at 7-54, the maximum observed temperature being at 7-57. From 7-58 to 7-64

the rate of loss is quite regular. Inspection shows this loss to be about 0.004 degree per minute. The temperature at 7-58 is taken as the end of the combustion period since it is the first reading that falls in line with this rate of loss. The loss during the six minutes following the combustion period is $21.744 - 21.718 = 0.026$ or 0.0043 degree per minute. The observed temperature increase is the difference between the temperature at the beginning and end of the combustion period or $21.744 - 19.348 = 2.396^\circ$. The total change in the rate of gain or loss in the system corresponding to 2.39° increase of temperature is from a rate of $+0.0075$ to a rate of -0.0043 , a total change of 0.0118° . A change of rate of 0.0118 with a change of temperature of 2.4° (counting to the nearest 0.1°) is equivalent to a change of rate of approximately 0.0005° for each 0.1° temperature change, from which the rate of gain or loss at the different readings can be obtained. The rate of gain or loss at the 58th minute is the final rate -0.0043 . The temperatures at the 57th and 56th minutes are within 0.1° of the temperature at the 58th minute and the rate of loss is the same as that at the 58th minute. The temperature at the 55th minute is approximately 0.3° lower and the rate of loss is accordingly less by $0.3 \times 0.0005^\circ = 0.0015$ or the rate of change at the 55th minute is $-0.0043 + 0.0015 = -0.0028^\circ$. At $54\frac{1}{2}$ minutes the temperature to the nearest 0.1° is 0.9° higher than at the 54th minute. The rate of change corresponding to 0.9° is $9 \times 0.0005 = 0.0045$. Subtracting this change from the rate of change at the 54th minute $= +0.0030$. The actual temperature gain or loss for each of the different intervals is found by adding the rates at the beginning and end of the interval and dividing by 2 if a minute interval or by 4 if a half-minute interval. The sum of the rates at the beginning and end of the interval from 54 to $54\frac{1}{2}$ is $+0.0075 + (+0.0030) = +0.0105$. This divided by 4 and carrying the result to the nearest fourth decimal $= +0.0026^\circ$, the temperature gain during the interval. For the interval $54\frac{1}{2}$ to 55, $+0.0030 + (-0.0028) = 0.0002$. This divided by 4 gives 0.00005 or to the nearest fourth decimal $= +0.0001^\circ$. For the minute interval 55 to 56, $-0.0028 + (-0.0043) = -0.0071$. This divided by 2 $= -0.0035^\circ$. The losses in the other intervals are obtained in a like manner. Adding together the different gains and losses the total loss is found to be 0.0094, from which the radiation correction $= +0.0094^\circ$. The

calibration correction for the thermometer used = -0.0060° . The stem correction = $+0.0014^{\circ}$. The corrected temperature difference = 2.4008° . The water equivalent of the calorimeter system is 2875 calories. Multiplying the corrected temperature change by this water equivalent (i.e., by the number of calories necessary to cause a rise of 1° of temperature), the total heat developed during combustion is $2.4008 \times 2875 = 6902.3$.

Corrections. The heat from the burning of the wire fuse is found by multiplying the weight of wire taken by its calorific value (1600 calories per gram = 2.4 calories for 1 cm.). $8.0 \text{ cm.} \times 2.4 = 19.2$ calories. The acidity of the bomb liquor after combustion is found by titrating it with a standard ammonia of such strength (0.0059 grams of ammonia per c.c., see acidity corrections) that one c.c. corresponds to a heat correction of five calories, assuming the acidity to be entirely due to nitric acid, from which 7.8 times 5 equals 39 calories, the correction due to the formation of nitric acid.

A large part of the acidity in high sulphur coal is, however due to sulphuric acid, and the heat correction for acid formed, considering it all as nitric acid, is therefore incomplete, a further correction of 13 calories for each 0.01 gram of sulphur present being required. (See acidity corrections.) 3.34 per cent sulphur in the sample is 0.0334 gram sulphur on a one gram sample taken. Therefore, the correction is $3.34 \times 13 = 43.4$ calories.

The total of these corrections is 101.6 calories. 6902.3 , the total heat developed, less this correction of 101.6 gives 6800.7 calories of heat from the combustion of the coal. These 6800.7 calories are developed by 1.0018 grams of sample. The value per gram is therefore 6800.7 divided by 1.0018. The amount of sample taken is so near one gram that this correction can be approximated as .68 of a calorie for 0.0001 gram of coal. For 0.0018 the correction is accordingly $18 \times 0.68 = 12.2$. Making this correction gives 6788.5 as the calorific value of the coal.

The foregoing description of the calculations makes them appear more difficult and troublesome than they really are, as practically all the corrections can be made mentally, and the radiation corrections can be determined very readily if the calculator is familiar with the routine of the determination. The use of printed blank forms saves time and insures regularity and completeness in the records.

SPECIAL NOTES ON CALORIFIC DETERMINATION

Complete combustion of the sample. To insure complete combustion from three to five times the theoretical amount of oxygen required should be used which for a one-gram sample of coal is equivalent to approximately from 9 to 15 grams of oxygen. In a bomb of the Mahler type with a capacity of 600 c.c., the author has found it unsafe to use less than 15 atmospheres pressure of oxygen which corresponds to about 11 grams of oxygen and in ordinary work 18 to 20 atmospheres corresponding to about 15 grams of oxygen are preferable. The complete ignition of the briquetted sample is more certain if the briquet is not made too hard and is broken up into a number of pieces. The fine sample can be weighed direct and the combustion made upon the coal in this condition if care is used in admitting the oxygen to the calorimeter not to blow any of the fine coal out of the tray. On account of this danger of blowing out fine coal the author prefers briquetting most samples. Anthracite coal and coke will not briquet readily and require to be run in powdered form. The use of a disc of ignited asbestos on the tray to lessen the rate of conduction of heat during combustion is a decided advantage in securing complete combustion of coals and anthracites which are much more difficult to burn than the ordinary bituminous coals.

Preventing leakage of valve. By use, the valve through which the oxygen is admitted into the calorimeter soon becomes corroded from the action of the acid fumes and rusted through the action of moisture and air. In this condition it is extremely difficult to prevent considerable leakage of oxygen. This leakage may be prevented and the valve made to fit tight by cutting a thin washer of lead about one-thirty-second inch in thickness and fitting into the valve, using care in its insertion not to get it in crosswise and thereby close the opening into the bomb. A very efficient way to insert it is as follows: Hold the valve stem, valve-end up and slip the washer over the tip of the needle. Then with the stem in this vertical position screw the lid on to the stem carefully till the washer is pressed into place. Very slight pressure is required to close the valve when fitted in this way and extra pressure is to be avoided as tending to force lead into the needle opening, which may be entirely closed and will in

this event require drilling out before the bomb can be used again.

Leakage around the lid. As a rule little trouble is experienced from leakage around the lid if the lead gasket is kept smooth. Moistening the gasket with a drop of water before putting on the lid considerably lessens the danger of leakage. The film of water between the gasket and the lid of the bomb appears to be of considerable advantage in securing a gas-tight joint.

Water surrounding the bomb. In the regular routine determinations the amount of water used is more conveniently measured than weighed. For this purpose the author uses a Florence flask holding about 2400 c.c. of water when filled to the middle of the neck. The number of grams of water that it delivers is determined by filling it to a fixed mark and weighing at a definite observed temperature. The flask is then emptied and allowed to drain 15 seconds and again re-weighed, an allowance of 2.4 grams being made for the effect of the buoyancy of the air displaced by this amount of water. The difference in weight is the number of grams of water the flask delivers at this temperature. A table is then prepared giving for different temperatures the number of c.c. of water which must be added to the water inside of the flask to obtain 2400 grams.

The diameter of the necks of the flasks used is from $1\frac{1}{4}$ to $1\frac{3}{8}$ inches. With this size of neck and a uniform time of 15 seconds for drainage, the amount of water can easily be measured to an accuracy of 1 c.c. and the maximum errors of measurement do not affect the calorific value obtained over two or three calories. The time required for measuring is less than that required for weighing and does not involve the continued use of an expensive balance and set of weights.

An example of the method of calibration is as follows:

Weight of flask filled with water to a definite mark	= 2842.5 grams
Weight of empty flask after draining 15 seconds	= 450.5 “
	Difference = 2392.0 “
Corrections to weights	= + .6 “
Corrections for buoyancy of air	= + 2.4 “
Total weight of water delivered	= 2395.0 “

Temperature of water = 20° C. For small corrections 1 c.c.

of water may be taken as equal to one gram and at the temperature of 20° C. the amount of water to be added to the flask in order that it may deliver 2400 grams is 5 c.c. The amounts for other temperatures based on the specific gravity of water at the different temperatures are obtained as follows:

The volume of the flask in cubic centimeters = 2395, divided by the specific gravity of water at 20° C. is $\frac{2395}{0.99823} = 2399.2$.

The density of water for the range covered by ordinary calorimetric work are as follows:

Degrees C.	Density.	Degrees C.	Density.
8°	= 0.99988	20°	= 0.99823
10°	= 0.99973	22°	= 0.99780
12°	= 0.99953	24°	= 0.99732
14°	= 0.99928	26°	= 0.99680
16°	= 0.99898	28°	= 0.99626
18°	= 0.99863	30°	= 0.99567

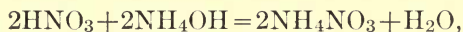
The weight of the water which the flask will deliver when filled to the mark at any temperature (t) = the volume of the flask, (2399.2) times the density of the water at temperature (t). The amount of water to be added at any given temperature when the flask is filled to the mark is 2400 minus what the flask holds at that temperature. At 10 degrees this particular flask holds $2399.2 \times 0.99973 = 2398.6$. Hence the correction to be added = $2400 - 2398.6 = 1.4$ grams or 1.4 c.c. Such a table of corrections once prepared is pasted on the side of the flask and the proper amount to add for any particular determination readily determined.

Temperature conditions. More satisfactory rates of gain or loss during a determination are secured if the temperature differences between the air of the laboratory and that of the water inside the inner bucket and in the outer insulating jacket are kept small. The author's practice is to keep the temperature of the water in the outer jacket within a few degrees of room temperature. The water to be used in the inner bucket is cooled till its temperature is about two to three degrees lower than that of the water in the outer jacket, care being taken that this temperature is not too near the dew-point. In warm, damp weather to avoid this danger, the water in the outer jacket is kept several degrees above room temperature.

With these temperature relations, the greater rate of change during a determination is before the combustion, and the rate of change after the combustion period is small. The larger the rate of change the larger is the possible error. The effects of the larger rate before the combustion period are, after the first minute, practically eliminated. By the end of the first minute most of the total temperature rise has occurred and the rate of change during the other minutes of the combustion period approximates in value the final rate. With the final rate small the total corrections are correspondingly small and errors from this source are reduced to a minimum.

CORRECTIONS TO BE APPLIED

Correction for nitric acid. The data and calculation of the correction are as follows: In burning the sample in the bomb calorimeter, under pressure, a portion of the nitrogen in the fuel and perhaps is burned of the nitrogen in the small amount of air in the bomb a portion to N_2O_5 *aqua* while in combustion of fuel under a boiler the nitrogen either escapes as free nitrogen or burns to gaseous N_2O_5 and passes off in the flue gases. The heat of formation of N_2O_5 *aqua* is approximately 1020 calories per gram of nitrogen. The heat of liberation of the nitrogen, as free nitrogen, from the coal is not definitely known but is presumably not far from 0. The heat of the formation of gaseous N_2O_5 from nitrogen and oxygen is approximately -36 calories per gram of nitrogen. In either case the heat change per gram of nitrogen is small and in correcting for the amount of nitric acid in the bomb, the heat of formation of N_2O_5 *aqua* is usually taken as the nitric acid correction. The reaction for neutralization of nitric acid by an alkali is as follows:



from which it follows that 14 parts by weight of nitrogen as nitric acid equal in neutralizing value 17 parts by weight of ammonia (NH_3). A convenient strength for the titrating alkali is one cubic centimeter equivalent to 5 calories of heat. Since 1020 calories are produced by the combustion of one gram

of nitrogen then 5 calories are produced by the combustion of $\frac{5}{1020}$ gram = 0.0049 gram; 0.0049 gram of nitrogen as nitric acid requires $\frac{17}{14} \times 0.0049$ gram of ammonia for neutralization = 0.00595 gram of ammonia per cubic centimeter or 5.95 grams per liter.

Correction for sulphuric acid. Any sulphuric acid present is titrated with nitric acid and its heat of formation is partially allowed for by considering it as nitric acid. The data for determining the amount of correction necessary and the amount which is allowed for by considering it as nitric acid are as follows: The heat of formation of aqueous sulphuric acid in the calorimeter is approximately 4450 calories per gram of sulphur. In ordinary combustion in air the sulphur is burned to sulphur dioxide, the heat of formation of which is approximately 2250 calories per gram of sulphur.

The excess heat due to the formation of sulphuric acid in the bomb is therefore $4450 - 2250 = 2200$ calories per gram of sulphur. In neutralizing with ammonia the reaction for sulphuric acid is as follows: $H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + H_2O$, or in titrating $H_2SO_4 = 2HNO_3 = 2NH_4OH$. Expressed by weight 32 parts of sulphur as sulphuric acid = 28 parts of nitrogen as nitric acid = 34 parts of ammonia (NH_3). Since 32 parts of sulphur as sulphuric acid = 28 parts of nitrogen as nitric acid, one gram of sulphur = $\frac{7}{8}$ gram of nitrogen in the titration of nitric acid with ammonia. $\frac{7}{8}$ of 1020 calories = 892 calories as the correction which is applied when sulphuric acid is titrated as nitric acid; $2200 - 892 = 1308$ calories per gram of sulphur as an additional correction which should be applied. This amounts to approximately 13 calories for each 0.01 gram of sulphur or when a one-gram sample is burned in the calorimeter, 13 calories for each per cent of sulphur present in the sample. As the amount of sulphur is frequently as high as 4, 5 or 6 per cent this correction is often large and there is no valid reason for omitting it, notwithstanding the statement often seen in print that the correction for the sulphur present is never important.

Ignition of the iron wire. In igniting the wire fuse a current of 3 or 4 amperes is usually required and an electromotive force of 15 to 20 volts is desirable. Lower voltage such as a current from 4 or 5 dry cells or from a storage battery may be used but a low voltage requires special care in making the connection or fail-

ure to ignite often results. If a current of low voltage is used, better contact between the platinum terminals and the wire is secured if the rods and wire are carefully cleaned with emery paper. Moistening the connection between the terminals and the wire with a drop of dilute calcium chloride solution is also an advantage in securing certainty of ignition. The usual laboratory practice of using a high voltage current, such as the current from a 110-volt lighting circuit, is liable to result in errors by leakage of the current after ignition of the wire and it is much safer to introduce a resistance coil in parallel with the calorimeter and shunt off only a portion of the current through the igniting wire. In this way the voltage through the calorimeter can easily be cut down to 20 volts.

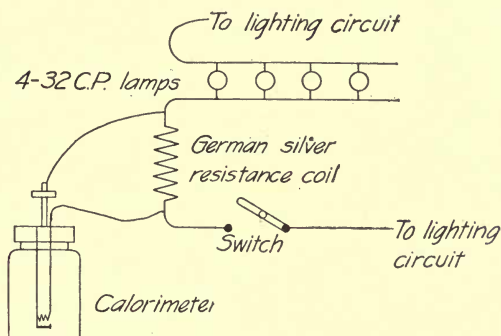


FIG. 6.—Diagram of Circuit for Igniting Wire Fuse.

A convenient resistance for furnishing the proper amount of current from a 110-volt lighting circuit is to mount four 32-candle power lamps in parallel. This will give in the neighborhood of $3\frac{1}{2}$ to 4 amperes of current which is ample for the size of wire usually used. With this arrangement a 5- or 6-ohm resistance coil of German silver or other high resistance wire, as nichrome or climax wire, used in parallel with the calorimeter is a simple way of reducing the voltage. (See Fig. 6.) Whatever be the connection the circuit should be kept closed only long enough to insure burning of the wire. This should not require at most, more than 1 or 2 seconds. If more time is required more current should be used. With leakage of current through the calorimeter and using the current direct from a 110-volt circuit, as much as 20 calories per second may be transmitted to the

calorimeter, which is an error too large to be neglected. By using the shunt and keeping the voltage below 20 the heat from 4 amperes of current cannot exceed 4 calories per second, and for the time that the circuit is usually closed it is a small error compared to the possible large one which may be introduced by using the 110-volt circuit direct.

Heat developed while the circuit is closed for ignition of the iron wire. The iron ignition wire used (about 0.12 millimeter in diameter and about 3 centimeters between the terminals) if in good contact with the platinum terminals has a resistance of less than one ohm and the amount of heat developed during the fraction of a second that the current passes through the wire before it ignites is small. The resistance of the calorimeter itself with the insulation in good condition is several millions of ohms. A test on one of the calorimeters indicated a resistance of upwards of twenty million ohms, the test being made on a 120-volt circuit. Pure water is such a poor conductor that after immersion of the calorimeter in water the resistance is still high (expressed in thousands of ohms).

In routine work the distilled water used to surround the calorimeter bomb is used over and over again. The resistance of this water, owing to traces of impurities, is not so great as that of the original distilled water, but its resistance is still high. Tests with water which had previously been used in making 40 or 50 calorimeter determinations showed with a 120-volt circuit about 1500 ohms resistance. Tests with distilled water taken directly from the laboratory supply showed a resistance of about 5000 ohms. With the resistance in excess of 1000 ohms, the heating effect due to leakage of current is quite small and the danger from excessive leakage is either from defective insulation of the bomb itself or from the use of water containing more than traces of impurities. The possible heating effects under these conditions are discussed in the next paragraph.

The heat developed in a conductor of which the resistance is R ohms by current of I amperes in a time of t seconds is $0.2387RI^2 t$ calories.

Using the current from a 110-volt circuit with 4 thirty-two candle power lamps in parallel, the greatest current is approximately four amperes. With the resistance coil (5 ohms resistance) in the circuit, the possible heat developed by passage of

current through the calorimeter is small. Before the ignition of the iron wire with a low resistance in the calorimeter circuit (a fraction of an ohm) practically all the current passes through the calorimeter, but since I cannot exceed 4, I^2 cannot exceed 16, and with the resistance less than one ohm, the product of $0.2387RI^2$ is less than 4 calories per second.

After the ignition of the iron wire under normal conditions the resistance of the calorimeter circuit is expressed in thousands of ohms and practically all the current passes through the coil having only 5 ohms resistance. With a resistance of 1500 ohms such a small portion of the current flows through the calorimeter that its heating effect is less than one-tenth calorie per second. With defective insulation in the calorimeter, or with very impure water, the resistance may be very much less and the possible effects under these conditions should be considered.

Take as special cases, resistances of 10 ohms and 100 ohms in the calorimeter. With the circuit closed the total current flowing through the resistance coil and the calorimeter is approximately 4 amperes. This varies slightly on account of small changes in the total resistance of the circuit due to the variations in the calorimeter resistance, but this variation in current is so small that it may be neglected in discussing the heat effect in the calorimeter. With the calorimeter and coil connected in parallel, the portion of the total current passing through each is inversely as its resistance is to the sum of the two resistances. With 10 ohms resistance in the calorimeter and 5 ohms resistance in the coil the portion of current passing through the calorimeter is

$$\frac{5}{10+5} = \frac{1}{3}; \frac{1}{3} \times 4 = 1.3 \text{ amperes.}$$

With 100 ohms resistance in the calorimeter the portion of current passing through it is:

$$\frac{5}{100+5} = \frac{1}{21}; \frac{1}{21} \times 4 = 0.2 \text{ ampere.}$$

Applying the formula for heat production with 10 ohms resistance $0.2387 \times 10 \times (1.3)^2 = 4$ calories per second. With 100 ohms resistance $0.2387 \times 100 \times (0.2)^2 = 1$ calorie per second.

With resistances between 1 and 10 ohms, the heating effects are very close to 4 calories. With resistances of over 10 ohms the heating effects are less than 4 calories per second, from which it appears that using the resistance coil in circuit under no condition can the leakage of current per second be large enough to very appreciably affect the results obtained on the calorific value of the materials tested.

Resistance coil left out of the circuit. Before the burning of the iron wire with little resistance in the calorimeter (less than 1 ohm) approximately 4 amperes of current will pass through the calorimeter and the heating effect is small (less than 4 calories per second). After the burning of the iron wire, under normal conditions, with the resistance expressed in thousands of ohms, the heating effect due to current passing through the calorimeter is also small. In the special test upon the calorimeter showing 1500 ohms resistance, the heating effect of the current flowing through the circuit is between two and three calories per second.

With the lower resistances, which may occur, due to defects in the insulation or the use of very impure water, the effect may be of considerable magnitude and the possible effects with resistances between 1 and 1500 ohms should be considered. Small increases in the resistance in the calorimeter diminish the amount of current flowing only slightly and the amount of heat produced increases very nearly in proportion to the increase in resistance.

With 1, 2 and 3 ohms resistance in the calorimeter, the heat produced is approximately 4, 8 and 12 calories per second. With larger increases in resistance the change in current due to the change in the total resistance of the circuit should be considered. The total resistance of the circuit is the resistance of the lamps $\frac{1}{4}$ (110 ohms), plus the resistance in the calorimeter, plus the resistance in the remainder of the circuit. The resistance of the rest of the circuit is small and the total resistance outside the calorimeter is therefore approximately that of the lamps. [$\frac{1}{4}$ (110 ohms)]. The total resistance of the circuit is approximately 27 ohms plus the resistance of the calorimeter.

Ohm's law for current flowing through a conductor is $I = \frac{E}{R}$.

Considering as special cases the effect of 10, 100 and 1000 ohms resistance in the calorimeter:

(a) With 10 ohms resistance the current is $\frac{110}{27+10}=3$ amperes.

(b) With 100 ohms resistance the current is $\frac{110}{27+100}=0.9$ ampere.

(c) With 1000 ohms resistance the current is $\frac{110}{27+1000}=0.1$ ampere.

Applying the formula for heat developed in the calorimeter:

(a) $0.2387 \times 10 \times (3)^2 = 21$ calories per second.

(b) $0.2387 \times 100 \times (0.9)^2 = 19$ calories per second.

(c) $0.2387 \times 1000 \times (0.1)^2 = 3$ calories per second.

With normal conditions, good insulation in the calorimeter and water practically free from impurities, the effects of leakage of current are unimportant, but with defective insulation or water high in impurities, the values obtained under conditions (a) and (b) show that the possible effects during the time that the switch is closed for ignition of the iron wire (about 2 or 3 seconds) may be of such magnitude (40 to 60 calories) as to change appreciably the calorific value obtained for the materials tested. The use of the resistance coil in the circuit is a safeguard against such possible errors.

Water equivalent of the calorimeter. The accuracy of the calorimetric values obtained is to an important degree dependent upon the accuracy with which the water equivalent of the apparatus has been determined. This may be determined by several methods:

(1) From the weights of the different parts by multiplying each by its respective specific heat. The water equivalent is equal to the sum of the specific heats of the different parts.

(2) By adding definite weights of warmer or colder water to the system and noting the corresponding increase or decrease in temperature.

(3) By combustion of the same weight of material but varying the amount of water used.

(4) By electric methods.

(5) By combustion of a substance of known calorific value, as naphthalene, benzoic acid or cane sugar.

The author's experience with the first three of these methods has not been very satisfactory. The fourth method requires instruments and equipment beyond the reach of most commercial and technical laboratories and practically the only available method which is satisfactory is that of the determination by combustion of a substance of known calorific value. At present the materials available are naphthalene, benzoic acid and cane sugar, samples of which together with certificates of their heating values can be obtained from the U. S. Bureau of Standards.

The calorific values of these materials as given by different authorities are as follows:

Naphthalene:

Berthelot.....	9692
Atwater.....	9628
Fischer and Wrede.....	9640
U. S. Bureau of Standards (standard sample).	9610

Benzoic acid:

Berthelot.....	6322
Stohmann.....	6322
Fischer and Wrede.....	6333
U. S. Bureau of Standards (standard sample).	6320

Cane Sugar: (sucrose)

Stohmann.....	3955
Berthelot.....	3961
Fischer and Wrede.....	3957

The equation for determination of the water equivalent(X) of the bomb, bucket, stirrer, etc., is as follows:

(Grams of water + X) \times temperature rise = the amount of sample \times the calorific value + the heat due to the ignition of the fuse + the heat due to the formation of nitric acid.

Carefully determined water equivalents based upon a number of determinations upon two or more of the standard materials ought to have not only relatively high accuracy but enable differ-

ent laboratories to work upon a common basis and make their results comparable.

Errors in the graduation of the thermometer used. These errors if not corrected for may be of considerable magnitude and every calorimeter operator should take some means of insuring the elimination of a greater part of the errors or at least assuring himself that the errors are not large enough to materially affect the accuracy of results. Three methods of checking up graduation errors are available:

(a) *Calibration of the thermometer by divided threads.* To calibrate accurately by this method requires skill and attention to details, and to cover the working range several threads of different lengths should be used and many readings taken. With thermometers in which the mercury threads break easily and regularly, the method, while it requires considerable time, presents no serious difficulties aside from care and attention to details but with some thermometers the author has found it exceedingly difficult to secure threads of the desired length.

As an example of the method, a thermometer graduated from 15 to 25° and graduated to hundredths of a degree was checked at each whole degree by the use of threads approximately 2° and 5° in length. By the measurement with the 5° thread a direct determination was obtained for 20°. By the 2° thread direct determinations were made for 17 and 23° and as secondary determinations 19 and 21°; 16° was obtained by the 5° thread from 21°, 24° by the 5° thread from 19°; 18° and 22° by the 2° thread from 20°. A number of readings should be taken for each of the thread lengths at a slightly different position and the mean of these readings taken as the length for that position. By gently tapping the thermometer the thread of mercury may be easily slipped a few thousandths of a degree or sufficiently to give a new set of readings. For example, the readings on the 5° thread measurements from 15 to 20° = 5.028, 5.027, 5.028, 5.027, 5.026, 5.027, 5.026, 5.027 = average 5.027°.

20 to 25° = 5.017, 5.019, 5.019, 5.018, 5.018, 5.017, 5.017, 5.019, 5.018 = average 5.018°. The sum of the two threads = 5.027 + 5.018 = 10.045°. According to the Reichsanstalt certificate for this thermometer the true temperature interval of 15 to 25° is 10.02, hence the true length of the measured distance, 10.045, is 10.065 and the true length of the 5° thread is

one-half of this value = 5.0325, from which the correction at 20° is $5.0325 - 5.0270 = +0.0055$. The measurement of the 2° thread and the establishment of other points by the measurements with this thread is done in the same manner.

By the use of a $2\frac{1}{2}^\circ$ thread in connection with the 2° and 5° threads as many values for $\frac{1}{2}^\circ$ readings were determined as desired. The determination of the correction for intermediate points was determined graphically by plotting the curve for the determined points.

In measuring the mercury thread the operator should work in a room at a uniform temperature or make corrections for variations in the observed lengths of thread at different temperatures. For example, a thread of mercury 5° long for a two degrees difference in temperature varies 0.0016 degree in length so that temperature differences of more than a fraction of a degree cannot be neglected if high accuracy is desired. The readings should be made by means of a telescope mounted on a fixed support movable in a horizontal direction. A cathetometer laid on its side is very satisfactory. In reading the thread the thermometer should be turned so that the ends of the short divisions touch the lower edge of the mercury column but do not cross it. This position of the ends of the divisions with reference to the ends of the mercury thread permits sharper readings.

The method of divided threads gives only the relative lengths of the degrees and in itself shows nothing as to their absolute values and unless the highest and lowest readings have been checked the numerical difference is assumed as the true value. This, of course, may make all the degrees too large or too small but does not affect their relative values to each other, and in calorimeter work usually what is desired is the relative value and hence a failure to know the absolute value is not necessarily of any serious consequence. In the calibration described it is assumed that the errors in the graduation of the few hundredths of a degree, that the threads are longer or shorter than 5, $2\frac{1}{2}$ and 2° , cannot materially affect the results. If threads are used of lengths considerably different from these values, this assumption of no material error does not necessarily hold true. For fuller details of calibration see *Physical Measurements* by Kohlraush or text-books on Physics.

(b) *Comparison with another standard thermometer.* Another method of determining the graduation errors is to compare the thermometer with another thermometer which has already been standardized. Making comparison readings to thousandths of a degree requires special equipment and special precautions to insure thorough mixing of the liquid surrounding the bulbs and to prevent rapid temperature changes in this liquid.

A simple and inexpensive equipment which the author has recently made use of in this work is a 500 c.c. Dewar vacuum flask. The two thermometers to be compared are inserted through a two-hole cork and the two bulbs brought close together but not quite touching one another. A thin strip of cork inserted between the stems just above the bulbs and a rubber band wrapped moderately tight around both stems is very efficient for holding them in their proper positions. The upper ends of the stems should be secured in a similar manner. In making temperature comparisons the flask is filled about three-fourths full of water at any desired temperature, the cork and thermometers inserted into position and the water around the bulbs well mixed by inverting the flask. The readings are taken through a telescope, the stems being tapped previous to taking a reading. A number of pairs of readings should be taken, the flask being inverted between each pair of readings. The average of the readings of each thermometer are taken as the reading at that temperature. The true reading for each thermometer is obtained by adding to the observed reading the stem correction for the thread of mercury exposed (see page 110). This method of comparison has the advantage that owing to the slow radiation changes in a vacuum flask as many readings as desired may be taken at practically the same temperature. To make a comparison at another temperature it is only necessary to warm or cool the contents of the flask to approximately the temperature desired and take a series of readings at the new temperature. One slight objection to the method is the possibility of the vacuum flask going to pieces and destroying the thermometers. This danger is, however, very slight if care be used in handling the flask. The author recommends, however, that flasks covered with metal or canvas be used so that in case of possible breakage there will be no danger to the eyes from particles of flying glass.

If the precautions regarding care in handling the flask are observed the danger of breakage is very small and the author's experience with the method has been entirely satisfactory.

The Bureau of Standards at Washington is equipped to do comparison work at a nominal charge and in many cases it may be preferable for the calorimeter operator to send thermometers there to be checked, as they will probably do it better than he can do it himself and the Government comparison will certainly carry more weight in a court of law than a comparison by a private individual. One objection to having the Government calibrate thermometers is that several weeks necessarily elapse before they are returned to the laboratory and in a busy laboratory this may be a very serious objection.

(c) *Comparison of the readings obtained at different temperatures on the same standard material.* The errors in graduation may be checked by running a number of check determinations on a material of constant composition at temperatures covering the working range of the thermometer. For example, if sets of duplicate determinations on naphthalene made at a number of different temperatures covering the range of the thermometer agree closely, evidently the graduation errors of the thermometer are not liable to be serious. Checking a thermometer by this method may not be regarded as an actual calibration but it does serve to guard against any serious graduation errors.

Stem temperature corrections. (Corrections should be made to the observed temperature readings on account of differences between the temperature of the emergent stem and the temperature of the liquid surrounding the bulb.) Most thermometers are graduated and calibrated for total immersion of the stem and bulb. As ordinarily used in calorimetric work a portion of the stem containing the mercury column always projects above the water and is usually either colder or warmer than the temperature of the water surrounding the bulb. Hence to secure readings for total immersion a correction must be applied. As ordinarily expressed this correction is $N(T-t) \times 0.00016$, where N = degrees of thread above the liquid, t = the temperature of the stem as observed by an auxiliary thermometer, T = the temperature of the bulb and the factor 0.00016 = the difference between the expansion of glass and mercury for one degree Centigrade. With $N = 5^\circ$, $t = 15^\circ$,

$T=20^{\circ}$, $N(T-t)\times 0.00016=0.004^{\circ}$, the amount that the mercury reads too low. Hence this correction must be added. With $T=15$, $t=20$, the value is this amount too high and hence has to be subtracted from the observed readings. To secure the true temperature difference in a calorimetric determination corrections of both the initial and final readings must be made. This correction may be done at one operation by combining the two corrections into the form of $Kd(T'+T''-S-t)$ in which $K=0.00016$, T' =the initial temperature at the beginning of a determination, T'' =the final temperature at the end of the combustion period, d =the observed temperature rise during a determination or $T''-T'$, S =the scale reading to which the thermometer is immersed, t =the temperature of the emergent stem measured by an auxiliary thermometer. Corrections with a plus sign are to be added to the observed temperature difference. Corrections with a minus sign are to be subtracted from the observed temperature difference.¹

Tabulation of stem corrections. A convenient method for applying the corrections is to solve the correction equations for the differences usually found in calorimetric work and arrange the results in tabular form for use as needed. The temperature rise for a given calorimeter on coal work ranges from 2.4° to 2.8° with an average for most coals of between 2.5 and 2.7° . The initial temperature should be 2° to 3° below the room temperature. For example, a table of corrections to observed temperature differences computed from the values for $N(T-t)\times 0.00016$ for the temperature at the beginning and end of the combustion period to cover the above mentioned conditions is as follows: The values given are for observed temperature rises of 2.5° and 2.7° Centigrade, where N =length of the emergent thread at the beginning of the combustion, T =the observed temperature in the calorimeter at the beginning of the combustion, t =the observed temperature of the emergent stem measured by an auxiliary thermometer. The corrections for observed rises of temperature of 2.5 and 2.7 degrees and for different values for N and $(T-t)$ are as follows:

¹ Testing of Thermometer, Bureau of Standard Circular No. 8.

STEM TEMPERATURE CORRECTION TABLE.¹

Initial Length of Emergent Thread. N.	Observed Rise in Temperature = 2.5°.								
	$T - t =$								
	-4°	-3.5°	-3°	-2.5°	-2°	-1.5°	-1°	-0.5°	-0°
.1°	-.0002	.0000	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014
1.5°	.0000	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016
2°	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018
2.5°	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020
3°	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022
3.5°	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024
4°	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026
4.5°	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028
5°	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030
5.5°	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032
6°	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034
6.5°	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036
7°	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038
7.5°	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038	+.0040
8°	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038	+.0040	+.0042

Observed Rise in Temperature = 2.7°.

N.	$T - t =$								
	-4°	-3.5°	-3°	-2.5°	-2°	-1.5°	-1°	-0.5°	-0°
1°	-.0001	+.0001	+.0003	+.0005	+.0007	+.0009	+.0012	+.0014	+.0016
1.5°	+.0001	+.0003	+.0005	+.0007	+.0009	+.0011	+.0014	+.0016	+.0018
2°	+.0003	+.0005	+.0007	+.0009	+.0012	+.0014	+.0016	+.0018	+.0020
2.5°	+.0005	+.0007	+.0009	+.0011	+.0014	+.0016	+.0018	+.0020	+.0022
3°	+.0007	+.0009	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025
3.5°	+.0009	+.0011	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0027
4°	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029
4.5°	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031
5°	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031	+.0033
5.5°	+.0018	+.0020	+.0022	+.0024	+.0027	+.0029	+.0031	+.0033	+.0035
6°	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031	+.0033	+.0035	+.0038
6.5°	+.0022	+.0024	+.0027	+.0029	+.0031	+.0033	+.0035	+.0037	+.0040
7°	+.0025	+.0027	+.0029	+.0031	+.0033	+.0035	+.0038	+.0040	+.0042
7.5°	+.0027	+.0029	+.0031	+.0033	+.0035	+.0037	+.0040	+.0042	+.0044
8°	+.0029	+.0031	+.0033	+.0035	+.0038	+.0040	+.0042	+.0044	+.0046

¹ T = the initial observed temperature in calorimeter.

t = the observed temperature of emergent stem measured by auxiliary thermometer.

From these values the corrections for all conditions usually found can be approximated readily to about 0.001°. To secure this degree of accuracy N and $T - t$ need be read to only the nearest 0.5° and the observed temperature rise need not be closer than 0.1° to the amount of rise on which the values are calculated. For example, corrections for rises between 2.4 and 2.6 can be taken from the correction based on 2.5° and corrections for rises between 2.6 and 2.8 taken from the values based on

a rise of 2.7° without any appreciable error. As an illustration, suppose the initial temperature of the calorimeter $T=16.5^{\circ}$, the temperature of the emergent stem $t=19^{\circ}$, the scale reading of the emergent stem $=12^{\circ}$ and the observed temperature difference during the determination $=2.8^{\circ}$. Then $N=16.5-12=4.5$. $T-t=16.5-19=-2.5$. From the table the correction corresponding to initial thread length N of 4.5 and $T-t=-2.5$ and an observed rise of 2.7 degrees is found to be $+0.002^{\circ}$. Inspection of the table furthermore shows that in a difference in rise of 2.5 to 2.7 the correction change is only about 0.0002° , hence the additional correction corresponding to the rise of 2.8° instead of 2.7° is approximately 0.0001° and can be entirely neglected, which makes the observed correction approximately $+0.002$.

As may be observed from the table, the amount of the correction varies from practically nothing up to 0.005° . With a water equivalent for the calorimeter of 3000 calories this latter amount is equivalent to a correction of 15 calories, a possible correction too large to be omitted if a high standard of accuracy is desired.

For similar working conditions where the correction was omitted in standardizing the calorimeter with naphthalene, benzoic acid or cane sugar, its omission on determinations made on coal introduces little or no error as one correction practically balances the other. Unfortunately similar working conditions day after day cannot be maintained and the stem corrections at different times may vary from less than 0.001° to over 0.004° . The carrying out of the values of other corrections, such as titre and burning of wire fuse, to fractions of a calorie and then omitting this correction entirely is to say the least not very consistent practice, and the author believes that the use of a table similar to the one given, whereby the errors can be eliminated regularly instead of hit or miss is well worth the little extra trouble which its use involves.

Correction for variations in the specific heat of water. Since the specific heat of water is different for different temperatures exact calorimeter determinations require corrections for determinations made at temperatures other than that at which the water equivalent of the calorimeter was determined. In making this correction the use of a thermal capacity table for water is a

great convenience. Such a table based on Barnes' values for specific heats of water is given by Loeb¹ as follows:

SPECIFIC HEAT AND THERMAL CAPACITY OF WATER FROM 0° TO 50° C.

Temp. °C.	Specific Heat.	Thermal Capacity.	Difference.	Temp. °C.	Specific Heat.	Thermal Capacity.	Difference.
0	1.00940	0.00000		25	.99806	25.05131	
1	1.00855	1.00898	1.00898	26	.99795	26.04932	.99801
2	1.00770	2.01710	1.00812	27	.99784	27.04720	.99788
3	1.00690	3.02440	1.00730	28	.99774	28.04499	.99779
4	1.00610	4.03090	1.00650	29	.99766	29.04269	.99770
5	1.00530	5.03660	1.00570	30	.99759	30.04031	.99762
6	1.00450	6.04150	1.00490	31	.99752	31.03786	.99755
7	1.00390	7.04570	1.00420	32	.99747	32.03536	.99750
8	1.00330	8.04930	1.00360	33	.99742	33.03280	.99744
9	1.00276	9.05233	1.00303	34	.99738	34.03020	.99740
10	1.00230	10.05486	1.00253	35	.99735	35.02757	.99737
11	1.00185	11.05694	1.00208	36	.99733	36.02491	.99734
12	1.00143	12.05858	1.00164	37	.99732	37.02224	.99733
13	1.00100	13.05980	1.00122	38	.99732	38.01956	.99732
14	1.00064	14.06062	1.00082	39	.99733	39.01689	.99733
15	1.00030	15.06109	1.00047	40	.99735	40.01422	.99733
16	1.00000	16.06124	1.00015	41	.99738	41.01159	.99737
17	.99970	17.06109	.99985	42	.99743	42.00899	.99740
18	.99941	18.06064	.99955	43	.99748	43.00644	.99745
19	.99918	19.05994	.99930	44	.99753	44.00395	.99751
20	.99895	20.05900	.99906	45	.99760	45.00152	.99757
21	.99872	21.05783	.99883	46	.99767	45.99916	.99764
22	.99853	22.05645	.99862	47	.99774	46.99686	.99770
23	.99836	23.05490	.99845	48	.99781	47.99464	.99778
24	.99820	24.05318	.99828	49	.99790	48.99250	.99786
25	.99806	25.05131	.99813	50	.99800	49.99045	.99795

From this table the differences in the thermal capacity of water throughout the temperature range at which calorimeter work is usually done may easily be calculated. For example, with a Mahler calorimeter having a water equivalent of approximately 500 calories and using 2400 grams of water in the calorimeter, the water equivalent of the system equals approximately 2900 calories and a rise of 3° corresponds approximately to 8700 calories of heat. As this is several hundred calories higher than the heating value of the best coal, 3° may be taken as representing the maximum rise of the thermometer during a determination where one gram of coal is used. The thermal capacity of 2400

¹ Jr. Ind. and Eng. Chem., 1911, p. 175.

grams of water for the different 3° intervals from 14 to 30° C. is as follows:

Temperature.	Thermal Capacity.	Difference.	Temperature.	Thermal Capacity.	Difference.
14 to 17°	7201.13		21 to 24°	7188.84	1.32
15 to 18°	7198.92	2.21	22 to 25°	7187.66	1.18
16 to 19°	7196.88	2.04	23 to 26°	7186.61	1.05
17 to 20°	7194.98	1.90	24 to 27°	7185.65	0.96
18 to 21°	7193.26	1.72	25 to 28°	7184.83	0.82
19 to 22°	7191.62	1.64	26 to 29°	7184.09	0.74
20 to 23°	7190.16	1.46	27 to 30°	7183.46	0.63

From which the corrections corresponding to a water equivalent determination made at any particular temperature may readily be tabulated. For example that the water equivalent of the calorimeter is determined at the temperature range 18 to 21°. Then for determinations made upon coal for this range no correction is necessary but for determinations made at temperatures above or below corrections should be used. Calculating from the differences in the thermal capacity at different temperatures, the correction for each thousand calories of heat developed by the coal is as follows:

Temperature.	Correction Calories.	Temperature.	Correction Calories.
14 to 17°	+0.90	21 to 24°	-0.51
15 to 18°	+0.65	22 to 25°	-0.64
16 to 19°	+0.42	23 to 26°	-0.76
17 to 20°	+0.20	24 to 27°	-0.87
18 to 21°	no correction	25 to 28°	-0.97
19 to 22°	-0.19	26 to 29°	-1.05
20 to 23°	-0.35	27 to 30°	-1.13

From which it may be seen that in a coal having a calorific value of 7000 calories the corrections to be applied range from the extremes of +6 calories to -8 calories. If the water equivalent determination of the calorimeter instead of being made at an intermediate temperature as 18 to 21° is made at a higher or lower range, as 25 to 28° or 15 to 18°, the maximum correction for a determination would be greater than the 8 calories in the case assumed.

With a water equivalent made at intermediate temperatures the correction to be applied is usually not large and can be neglected in routine work, but for work of the highest accuracy, this correction must be used along with other corrections of similar magnitude, which have been already discussed.

Effect of hydrogen in the sample upon observed calorific value. Any hydrogen in the sample not already combined with oxygen during combustion unites with oxygen to form water which condenses and the remaining gas expands as a result of the disappearance of this oxygen. This expansion absorbs heat, the amount absorbed being proportional to the amount of oxygen which disappears. Approximately 1.36 calories are absorbed for each 0.01 gram of hydrogen which unites with oxygen. For coals containing 4 per cent of available hydrogen the correction amounts to about $5\frac{1}{2}$ calories.

The calculation of this effect in brief is as follows: The mechanical equivalent of heat has been determined as 42,350 gram-centimeters=1 calorie. In consideration of gas volumes $\frac{pV}{T}$ is known to be a constant where V is the volume in gram-molecules. Let $p=1$ atmosphere pressure = 1033 grams per square centimeter. Let $V=1$ gram molecular volume of gas = 22.4 liters = 22400 cubic centimeters. Let $T=273^\circ$ absolute = 0° C. Substituting these values for $\frac{pV}{T} = \frac{1033 \times 22,400}{273} = 84,750$ gram-centimeters, which expressed in calories = $84,750 \div 42,350 = 2$ calories. $\frac{pV}{T} = 2$ calories or $pV = 2T$ which = 546 calories. Two grams of hydrogen at 0° C. and 760 mm. pressure = 22.4 liters. 0.01 gram of hydrogen = 0.112 liter. The equivalent volume of oxygen uniting with 0.01 gram of hydrogen = 0.056 liter. With $pV = 546$ calories, 22.4 liters = 546 calories, from which 0.056 liter = 1.36 calories as the amount of heat absorbed as a result of the contraction of the oxygen equivalent to 0.01 gram of hydrogen. Naphthalene ($C_{10}H_8$) contains about $6\frac{1}{4}$ per cent hydrogen, hence if the heat as burned under conditions of constant pressure is desired, the observed calorific value obtained in the bomb calorimeter should be increased by $6\frac{1}{4} \times 1.36 =$ about 8.5 calories.

The value given for naphthalene by the Bureau of Standards

is the observed value obtained in a bomb calorimeter and in using naphthalene as a standard for determining the water equivalent of another calorimeter the observed value is the one that should be used. If, however, the heating value of naphthalene is compared with the heating value of carbon or coal as burned under ordinary conditions the observed value should be increased by 8.5 calories.

The available hydrogen in coal runs from $2\frac{1}{2}$ to $4\frac{1}{2}$ per cent which corresponds to corrections of from $4\frac{1}{2}$ to 7 calories. Petroleum contains about 14 per cent hydrogen which corresponds to a correction of about 20 calories.

The formation of nitric and sulphuric acids during combustion likewise causes a small absorption of heat on account of the oxygen used up. The amount absorbed = 0.58 calorie for 0.01 gram of nitrogen and 0.25 calorie for 0.01 gram of sulphur, and for the amounts of nitrogen and sulphur in coal this can be neglected without any appreciable error.

For the highest grade of work the correction due to hydrogen should be taken into consideration and applied. However, its omission in commercial work cannot cause any very large error.

Use of a cover on the water jacket of the calorimeter. A cover on the water jacket is presumably an improvement over the common open top calorimeter owing to the smaller radiation changes but unless used properly a cover may introduce errors larger than the errors that are supposed to be eliminated, and in using a covered calorimeter the author strongly advises beginning the determination at a temperature several degrees below the jacket water temperature so that the temperature of the calorimeter at the end of the combustion period will still be below the temperature of the surrounding jacket water. If this precaution is not observed a high final rate is very apt to be obtained due to the surrounding jacket being below the dew point, as compared to the surface of the water in the calorimeter bucket, and a much more rapid evaporation from the surface of the calorimeter water occurs during the final period than at the beginning period when the jacket walls are warmer than the water in the calorimeter.

Impurities in oxygen. Compressed oxygen of a high degree of purity for calorimetric work is readily obtained on the market at a comparatively low cost. The author has never found hydro-

carbons present in the oxygen in sufficient amounts to seriously affect the calorimeter determination. Their presence, however, is always a possibility and a safe rule which should be strictly followed is to run blanks on naphthalene, benzoic acid, or cane sugar on every new tank of oxygen and if impurities of any consequence are found they should be corrected for or better still the tank should be rejected and a fresh supply of oxygen obtained.

CHAPTER VI

SUMMARY OF CHEMICAL DETERMINATIONS AND RECORDS

A SUMMARY of these may help to make clear just what relation the various determinations have to one another, and to the sample of coal and serve to prevent uncertainty and confusion in the meaning and use of the terms.

Chemical records. The air drying of the coarse sample and the analytical determinations on the air-dried sample necessitate the recalculating of results to obtain the analyses of the "sample as received." Some of the analytical records of a well conducted laboratory are shown by the following record of a regular laboratory sample:

Laboratory sample number	1561
	Per Cent.
Loss of moisture in air-drying of coarse sample	3.10
Analysis of air-dried sample:	
<i>Proximate:</i>	
Moisture	1.01
Volatile matter	29.53
Fixed carbon	62.67
Ash	6.79
	100.00
<i>Ultimate:</i>	
Hydrogen	5.04
Carbon	79.35
Nitrogen	1.63
Oxygen	6.39
Sulphur	0.80
Ash	6.79
	100.00

Calorific value determined, 7984 calories = 14,371 B.t.u.

Calorific value calculated from ultimate analysis, 7890 calories = 14,202 B.t.u.

The analysis of the "sample as received" is obtained from the results on the air-dried sample by multiplying each result by $\frac{100-3.10}{100}$ and adding to the moisture result so obtained the 3.10 per cent loss on the coarse sample and to the hydrogen and oxygen results so obtained this 3.10 per cent moisture loss in the proportion in which the two elements unite to form water or $\frac{1}{8}$ of the moisture loss to the hydrogen and $\frac{3}{8}$ of the loss to the oxygen.

Performing these operations, the analysis on the "sample as received" is as follows:

"Sample as received:

	Per Cent.
<i>Proximate:</i>	
Moisture	4.08
Volatile matter.....	28.61
Fixed carbon.....	60.73
Ash.....	6.58
	100.00
<i>Ultimate:</i>	
Hydrogen.....	5.23
Carbon.....	76.89
Nitrogen.....	1.58
Oxygen.....	8.95
Sulphur.....	0.77
Ash.....	6.58
	100.00

Calorific value determined, 7736 calories = 13,925 B.t.u.

Calorific value calculated from ultimate analysis, 7645 calories = 13,761 B.t.u.

Dry coal. The result on the air-dried sample must not be confounded with the "dry coal" of the mechanical engineer, which may be obtained from either of the above ultimate analyses by subtracting from the hydrogen and oxygen shown in the analysis the amount of hydrogen and oxygen present in the moisture of the proximate analysis corresponding to the ultimate, then dividing each of these remainders and each of the other percentages of the ultimate analysis by 100 minus the moisture present in the proximate analysis.

Performing these operations, the ultimate analysis for the "dry coal" on this sample is as follows:

Hydrogen.....	4.98
Carbon.....	80.15
Nitrogen.....	1.65
Oxygen.....	5.55
Sulphur.....	0.81
Ash.....	6.86
	<hr/>
	100.00

The volatile matter, fixed carbon and ash of the proximate analysis reduced to the "dry coal" are:

Volatile matter.....	29.83
Fixed carbon.....	63.31
Ash.....	6.86
	<hr/>
	100.00

Calorific value determined = 8065 calories, 14,517 B.t.u.

Calorific value calculated from ultimate analysis, 7970 calories = 14,346 B.t.u.

This seems to be a multiplication of results but all appear to be necessary. The "as received" results certainly cannot be dispensed with, as they represent the actual sample. The results on the air-dried sample are the actual results obtained in the laboratory and are of interest as showing the analysis of the coal when in an approximately air-dried condition. The chemist has no use for the "dry coal" results but it is necessary for the mechanical engineer in calculating the heat balance by the code prescribed by the American Society of Mechanical Engineers, who report results calculated to a "dry coal" basis. The "dry coal" basis is also convenient in comparing boilers burning the same or similar coals.

CHAPTER VII

IMPROVEMENT OF COAL BY WASHING

THE proximate analysis of coal may show the need of improvement by washing, but as these results show only the amounts of sulphur and ash present they furnish no information of whether or not the impurities or sulphur may be removed by treatment. Whether or not coal can be improved by washing depends upon the mode and nature of the occurrence of the ash and sulphur present.

Sulphur. If present as organic sulphur it cannot be removed by washing. If present as pyrite, finely disseminated through the coal, it cannot be removed by washing to any considerable extent. If present as pyrite in flakes or lumps of appreciable size it may be removed by washing, especially if the coal is crushed sufficiently to separate a large part of the pyrite from the surrounding coal.

Ash. The same remarks as to distribution of sulphur are applicable to ash. If the ash is disseminated uniformly through the coal, washing will effect little improvement. If on the other hand a large part of the total ash is present as slate or as bone coal, washing will result in a decided lowering of the ash content in the washed coal. Clean coal has a specific gravity of about 1.27 to 1.32. The specific gravity of bone coal, slate and pyrite ranges from about 1.4 to 5. Laboratory tests on small portions of the coal are often sufficient to show the possible improvement of the coal by washing. For illustration, if on floating the coal on a calcium chloride solution of 1.35 specific gravity a large portion sinks, evidently the amount of clean coal is low and the amount of bone coal is high. If on the other hand only a small amount of comparatively very heavy material sinks, the indications are that a considerable part of the ash and sulphur is present in a comparatively small amount of heavy residue. By taking weighed amounts of coal at different sizes and subjecting these weighed amounts to treatment on solutions of

different specific gravities ranging from 1.35 to 1.55 or 1.65, a separation into low, medium and high ash material may be effected. From the amounts and analyses of these different materials the distribution of the ash and sulphur can be determined and the possible improvement of the coal by washing estimated.

The apparatus used for making washing tests may be very simple but if much testing is to be done, equipment adapted to the work should be obtained. Some of the necessary equipment is as follows:

(1) A set of sieves, $\frac{1}{2}$ -, $\frac{3}{8}$ - and $\frac{1}{4}$ -inch, 20-mesh and 60-mesh.

(2) For the washing work ordinary laboratory beakers, funnels, etc., may be used but a better equipment is as follows:

For holding the washing solution, two or more copper cylinders about 5 inches in diameter by 8 inches deep fitted with a handle for lifting and with a lip for pouring. For filtering, two or more 7-inch copper funnels having a stem about 3 inches long by $1\frac{1}{2}$ inch in diameter and fitted with a 60-mesh brass filter gauze 2 to 3 inches in diameter. For skimming off the light coal a semi-circular gauze skimmer fitted with a handle and having the circumference of the skimmer just a trifle smaller than the circumference of the copper cylinder.

The process is as follows: The sample for testing is put through a jaw crusher and reduced till it all passes a $\frac{1}{4}$ -inch sieve. In crushing care is taken not to force the feeding of the sample through the crusher as choking of the crusher tends to make an undue amount of fine sample. After the sample is so reduced that it all passes the coarse sieve the very fine portion—60-mesh and finer—is sifted out as this fine portion slimes badly and cannot be successfully washed. The amount of this fine portion is usually between $\frac{1}{2}$ and 4 per cent of the total sample. It is weighed and analyzed for ash and sulphur if desired. In sifting out this fine portion a preliminary sifting on a 20-mesh sieve is desirable, sifting that portion which passes through the 20-mesh on to the 60-mesh and adding the over-size of the 60-mesh to the over-size of the 20-mesh. This is much more rapid and satisfactory than the attempt to sift the entire sample direct on the 60-mesh.

The copper cylinder is filled about two-thirds full of washing solution, and about one-half of the coal to be washed (assuming 3 to 4 pounds as the amount to be tested) is poured into the cyl-

inder and stirred up well to insure thorough wetting and freeing from air bubbles. The lighter portion is then skimmed off and transferred to the 7-inch funnel. The remainder of the sample is then poured into the cylinder and stirred up as before and the lighter portion skimmed off and added to the first portion in the funnel. The heavy portion is then filtered through another funnel. As soon as the light and heavy portions have drained, the washing solution filtrate is removed (to be used for other tests) and the samples washed with water. They are then air-dried, weighed, crushed and analyzed for moisture, ash and sulphur.

If $\frac{1}{2}$ -inch size samples are to be tested somewhat larger samples—6 to 8 pounds—should be used for the tests, in which case the copper cylinders and funnels should be proportionately larger. The washing solutions used are calcium chloride and zinc chloride. In separation of very clean coal a solution as low as 1.33 in specific gravity may be used. The usual solution used has a specific gravity of 1.35. In separation of coal with moderate amounts of ash, solutions of specific gravity from 1.4 to 1.45 are used and in separating bone coal, etc., solutions with a specific gravity as high as 1.6 to 1.7 may be used.

The method of calculating and the results obtained may be shown by the following tests taken from *Bulletin* No. 9 of the Ohio Geological Survey, pages 306-307.

PUBLICATION No. 11

Unwashed coal, ash 10.81, sulphur 5.04

	Portion.		Ash.	Sulphur.	Compared with Original Sample.	
					Ash.	Sulphur.
$\frac{1}{2}$ inch to $\frac{1}{80}$ inch. =	94.52					
Lighter than 1.35. =	66.7	6.48	3.68	4.32	2.45	
Heavier than 1.35. =	27.82	21.05	8.83	5.86	2.46	
$\frac{1}{80}$ inch and finer. =	4.62			0.50	0.23	
				10.68	5.14	
$\frac{1}{2}$ inch to $\frac{1}{80}$ inch. =	96.9					
Lighter than 1.45. =	87.3	7.83	4.20	6.84	3.67	
Heavier than 1.45. =	9.6	33.88	14.24	3.25	1.37	
$\frac{1}{80}$ inch and finer. =	2.2			0.24	0.11	
				10.33	5.15	

PUBLICATION No. 29

Unwashed coal, ash 8.94, sulphur 2.11

	Portion.		Ash.	Sulphur.	Compared with Original Sample.	
					Ash.	Sulphur.
$\frac{1}{2}$ inch to $\frac{1}{60}$ inch =	99.3					
Lighter than 1.35 =	85.5	6.16	1.14	5.27	0.97	
Heavier than 1.35 =	13.8	27.64	8.83	3.81	1.22	
$\frac{1}{60}$ inch and finer =	0.5			0.04	0.01	
				9.12	2.20	

COKE

	Percentage Yield.	Ash.	Sulphur.	Phos.
Coke from unwashed coal =	59.86	15.54	1.80	
Percentage of the sulphur in the coal left in the coke =			51.1	
Coke from washed coal lighter than 1.35 =	59.80	10.35	0.93	0.016
Percentage of the sulphur in the coal left in the coke =			48.8	

Coal No. 11 shows 66.7 per cent of washed coal containing 6.48 per cent ash and 87.3 per cent of washed coal with 7.83 per cent ash as against 10.81 per cent in the original coal. The washed coal in both tests shows a material reduction in the amount of sulphur present. Coal No. 29 shows 85.5 per cent of washed coal with 6.16 per cent ash and 1.14 per cent sulphur. The coke from this washed coal runs 10.35 per cent ash and 0.93 per cent sulphur, which indicates the possibility of production of high grade coke from some Ohio coals. For further details of washing tests on coal see *Bulletin* No. 9 of the Ohio Geological Survey, also *Bulletin* No. 5 of the U. S. Bureau of Mines, Department of the Interior.

CHAPTER VIII

PURCHASE OF COAL UNDER SPECIFICATIONS

Total heating value as an index of the commercial value.

As has previously been stated under the heading of "The commercial value of coal," other things being equal, the value of coals of similar composition is proportional to the total calories or British thermal units which a unit of the coal contains. The value of different coals may conveniently be compared by determining how many large calories or British thermal units are obtained for one cent or how much one million heat units cost for each of the several coals.

For example, suppose the price asked for coal (*A*) is \$2.50 per ton of 2000 pounds with a heating value of 12,200 B.t.u. and the price asked for coal (*B*) is \$2.25 per ton with 11,500 B.t.u. The cost of 1,000,000 B.t.u. for each of the coals is as follows:

$$\text{For coal (A)} = \frac{\$2.50 \times 1,000,000}{12,200 \times 2000} = \$0.1024$$

$$\text{For coal (B)} = \frac{\$2.25 \times 1,000,000}{11,500 \times 2000} = \$0.0978$$

Other factors affecting the value of coal. The style of furnace, draft, smoke producing qualities of the coal and comparative amounts of ash and sulphur are additional factors which may have to be considered in determining what is the best and cheapest coal. No definite rule can be laid down to govern some of these points. The experience of the engineer in charge of the plant or the experience of a consulting engineer who is an expert along these lines is perhaps the best guide as to what is likely to be the best fuel for the particular plant. In general, the higher the moisture, ash and sulphur the more objectionable the coal.

Actual boiler tests upon the fuel are sometimes necessary to determine what fuel is the best for a particular plant.

Advantages and disadvantages in purchasing coal under specifications. In the consideration of the purchase of coal under specifications some of the points to be noted are as follows:

(1) Where the consumer buys direct from the operator who handles coal from a certain definite locality and of a quality known by experience to be satisfactory, the advantage in purchasing under specifications based on analysis and heating value may not be worth the extra expense involved in sampling and analyzing the coal.

(2) In markets where the coal supply is varied and where it is sold under trade names which may be uncertain or misleading, large buyers should be able to buy coal to better advantage under specifications based on analysis and heating value.

(3) Some advantages in the purchase of coal under specifications are:

- (a) Guards against delivery of poor and dirty coal.
- (b) Prevents disputes arising from the condemnation of the coal based on its physical appearance.
- (c) Places bidders on a strictly competitive basis as to the price and the quality.
- (d) Broadens the field for obtaining coal by ignoring trade names and making moisture, ash, sulphur and heating value the basis of bids.
- (e) The analytical results and heating values of the samples which serve as a basis of settlement also afford a ready check upon the manner in which the coal is being burned.

(4) The purchase of coal under specifications involves considerable expense in the sampling of the coal and in the analysis of the samples. This expense adds to the price of the coal and for small consumers may increase the cost to such an extent as to make the purchase under specifications unprofitable. When large quantities of fuel are used, the expense of sampling and analysis figured per ton of coal should be so small that any decided improvement in the quality of the coal should more than offset this expense. This reduction in expense per ton is accomplished by combining the samples from a number of cars so that each laboratory sample analyzed may represent from 5 to 15 cars of

coal. The sampler and chemist must necessarily use precautions in combining the different samples into one sample for analysis. Especial care must be taken to avoid moisture losses and to see that the portion of each sample taken is proportional to the tons of coal it represents.

Specifications. In drawing up specifications for the purchase of coal some of the points to be considered are as follows:

(1) The specifications for ash, sulphur and heating value should be adapted to the grades of coal which are available and should be sufficiently wide in their range as to enable all dealers in suitable grades of coal to submit bids.

(2) The negative value of ash in coal, due to extra expense in handling the ash and greater trouble to operate the fire together with the possible lower efficiency should be taken into consideration. The United States Government counts this negative value at two cents per ton for each per cent of ash above the standard ash established for a particular specification.

For example, in comparing the bids on the following coals: *A*, bid \$2.20 a ton, heating value 12,000 B.t.u. and ash 8 per cent; *B*, bid \$2.25 a ton, heating value 12,100, ash 7 per cent. Taking the lower ash—7 per cent—as the standard, the 1 per cent excess of ash in *A* is regarded as equivalent to 2 cents more per ton on the bid price, hence the bid price for *A* is raised to \$2.22 per ton before the estimation of the cost per million B.t.u. is made. On these two coals with this change for ash the cost per million B.t.u.,

$$\text{For } A = \frac{\$2.22 \times 1,000,000}{12,000 \times 2000} = \$0.0925.$$

$$\text{For } B = \frac{\$2.25 \times 1,000,000}{12,100 \times 2000} = \$0.093.$$

(3) Payment for the coal is based upon the amount of coal weighed and the sample should be taken at the time of weighing. The precautions to prevent moisture loss in the sample have been given in detail under "Sampling."

(4) Payment for the coal is based on the coal "as received" and specifications for bids should require that B.t.u. be on the coal "as received" rather than on the "dry coal."

(5) For comparative purposes it is more convenient to have

the ash expressed on the "dry coal" basis. This involves the use of a double standard of B.t.u. on the "coal as received" and of ash on the "dry coal." The Government specifications for bituminous coals are on this double standard.

(6) Ash in the "dry coal" can be determined at any time from analysis of a given sample of the coal, but the B.t.u. of the coal as delivered or the actual amount of dry coal in a shipment can only be determined by the taking of a sample at the time of delivery, as the amount of any moisture variation in the coal after weighing cannot be determined unless comparison is made with the analysis of the sample taken at the time of weighing.

(7) Premiums or bonuses should be allowed if the coal is better than specifications and a penalty should be exacted if the coal is lower in heating value or higher in ash than specifications. Some objections to a premium or bonus are:

(a) Municipalities may in some cases be prohibited by law or charter from paying a bonus. This is hardly an objection to the principle, though it may prevent its operation in special cases.

(b) The cost of the coal may be increased by having to pay a bonus. This seems hardly a valid objection as if the purchaser gets a better grade of coal he certainly should be expected to pay for it; and on the other hand if he fails to get a good grade of coal he is entitled to pay for just what he gets and should demand a penalty of the seller. Bonuses and penalties are vital items in the purchase based on analytical results and heating value and the author believes that the test of time will prove the soundness of the principle involved and the practicability of its operation.

(8) The contract should contain provisions for insuring regular delivery of the coal and for insuring its quality to within certain prescribed allowable variations.

Reports from twenty cities purchasing coal under specifications given in the *Municipal Journal*, Vol. 32, p. 350-351, are very favorable to the system. One report indicates a saving of 25 per cent, others 10 per cent. Some call special attention to a much more satisfactory supply of coal.

Abstracts of the specifications of some of the cities are as follows:

New York City. The B.t.u. standard per pound dry coal for broken coal is 13,200 to 12,000 for buckwheat No. 3. The ash, 11 per cent in broken coal to 19 per cent in buckwheat No. 3. The volatile combustible matter is 8 per cent maximum and volatile sulphur 1.5 per cent. Moisture is 4 per cent for broken coal to 6 per cent for buckwheat No. 3. If the moisture is in excess of the limit, the gross weight of the coal is corrected by an amount directly in proportion to such excess of moisture, that is, with 2 per cent excess moisture the gross weight of the coal is reduced by 2 per cent. After this reduction the weight is reduced by 1 per cent for each per cent of ash in excess of the standard. The gross weight after correction for excess moisture is reduced by 1 per cent for each 100 B.t.u. below the standard, 5 per cent for each 1 per cent of volatile sulphur in excess of the standard, 2 per cent for each 1 per cent volatile combustible matter in excess of the standard. Payment is made on the gross weight less the deductions as described.

Cleveland. The standard calorific value for all coal is 13,005 B.t.u., and moisture is not to exceed 3 per cent, ash 13 per cent or sulphur 3.5 per cent. The price per ton of coal is increased above or reduced below the contract price according as the heating value is more or less than the standard, the increase being $1\frac{1}{2}$ cents per ton for each 100 B.t.u. up to 13,900 and 2 cents per ton between 13,900 and 15,000, remaining constant at 2.6 cents for all over 15,000. Reduction at the rate of $1\frac{1}{2}$ cents per ton down to 12,600, 2 cents per ton from 12,600 to 12,000, 3 cents per ton from 12,000 to 11,000, 4 cents per ton from 11,000 to 10,000 and the constant amount of \$1.00 where the heat units fall below 10,000.

Toronto. 13,000 B.t.u. is taken as the standard, 10 per cent ash, 2 per cent moisture and $1\frac{1}{2}$ per cent sulphur. If coal delivered shows a lower heating value than the standard, the city may reject or accept it, the amount paid in the latter case being "such a reduced price as shall make the uniform coal equal in heating value to the city to the contract grade," and there shall be deducted from the contractor's price for such coal a proportionate amount; and if the coal shall show a higher heating value than specified the contractor shall receive a proportionate allowance.

Norfolk. The standard is 14,500 B.t.u., $2\frac{1}{2}$ per cent moisture, $7\frac{1}{2}$ per cent ash, 1 per cent volatile sulphur and 22 per cent volatile

combustible matter, but a bidder may submit a proposition for coal of a different standard. If a coal delivered shows moisture, ash, sulphur and volatile combustible matter in excess of requirements the price is to be fixed by arbitration, the contractor and the city each appointing one arbitrator and these two selecting a third. The gross tonnage of the coal is reduced at the rate of 1 per cent for each 100 B.t.u. below or increased 1 per cent for each 100 B.t.u. above the standard analysis.

Grand Rapids. The city requires that the heating value per pound of dry coal be stated by the bidder and if calorimeter tests show the coal to fall below this standard a rebate is made from the contract price and an increase if the coal comes above the standard, the rebate or increase being made in exact proportion to the B.t.u. For instance, if the bidder guarantees 15,000 B.t.u. per pound and the coal contains only 14,000 the contractor would receive $\frac{14}{15}$ of the contract price. Any coal which shows more than 5 per cent less heat units than the fixed standard may be rejected. Standards are established for different kinds of coal varying between the limits of 15,000 to 11,000 B.t.u., a minimum of 44 to 71 per cent fixed carbon, a maximum of 15 to 6 per cent ash and a maximum of 3 to $\frac{3}{4}$ per cent sulphur.

Details of the purchase of coal by the United States Government under specifications together with the form of specifications, proposals, guarantees, contracts, bonds, etc., are given in *Bulletin* 41 of the United States Bureau of Mines.

CHAPTER IX

ANALYSIS OF FLUE GASES

Composition of flue gas. Flue gas consists of carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), small amounts of carbon monoxide (CO), and small amounts of sulphur dioxide (SO_2), and sometimes probably traces of hydrogen (H_2) and hydrocarbons. The gas also contains water vapor but in ordinary flue gas analysis the water vapor is not considered, as the analysis is made on the basis of dry gas. In technical analysis, usually only the carbon dioxide, oxygen, and carbon monoxide are determined, the remaining gas being considered as nitrogen.

Analysis of the gas. In making the analysis a measured volume of the gas is treated successively with a series of reagents that absorb the several constituents, the volume remaining being read after each absorption. The measurement of the gas is made in a graduated tube or burette which should be surrounded by a water jacket to insure constant temperature during the time of the analysis. The measurements of the gas are all done at atmospheric pressure and as the time of making analyses is short, it is assumed that the barometer remains constant during that period, while the use of the water jacket should prevent any appreciable temperature changes. However, a thermometer hung in the water jacket is a decided advantage if the apparatus is exposed to draughts of air or in a room where the temperature varies.

Sampling the gas. The tubes best adapted for sampling depend upon the particular conditions under which the sample has to be taken. In collecting samples at very high temperatures, 1500 to 1600° C. (2700 to 2900° F.) a quartz tube is perhaps the best means of obtaining a sample. Such a tube stands high temperatures and has no action on the gas. It is somewhat expensive and must be handled with care to prevent breakage bills becoming excessive. In sampling at these high temperatures

the tube is inserted and removed at the taking of each sample. If the tube is allowed to remain in the furnace, slag, etc., soon destroy it. In sampling at temperatures from 400 to 800° C. (750 to 1500° F.) water jacketed iron tubes permanently installed during the period of the test are satisfactory. Sufficient water must be used to insure proper cooling if entirely satisfactory results are desired. (See Fig. 7.)

A disadvantage of the quartz and water jacketed tubes just described is that the sample drawn is from only one portion of the furnace and does not necessarily represent the average of the gas coming off at that time. Shifting the end of the tube to

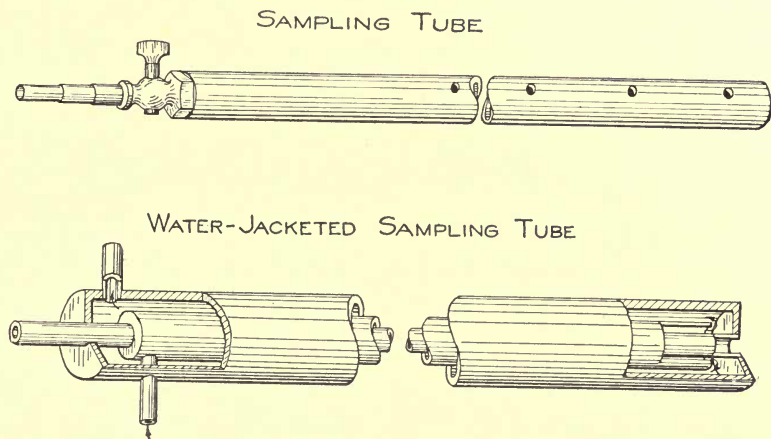


FIG. 7.—Sampling Tubes.

different portions of the furnace during a series of tests partially eliminates error, but cannot be regarded as entirely satisfactory.

Sampling gas from boiler flues. As a rule, the temperature of the gas from a boiler flue is considerably below 330° C. (625° F.) and at temperatures less than this, an ordinary iron sampling tube may be used. (See Fig. 7.) The tube should cross the flue at a right angle and extend to within 6 inches of the further wall. The end of the tube is closed with a cap and along the lower side of the tube are a number of small holes $\frac{3}{32}$ inch in diameter distributed at regular intervals of 6 inches apart. The last hole should be not less than 6 inches from the near wall of the flue. The diameter of the holes given as $\frac{3}{32}$ inch is based on the use of a pipe not less than 1 inch in diameter. If the holes are too large

in proportion to the diameter of the pipe, too much of the gas will enter through the holes which are nearest to the aspirator.

Aspiration of the gas. During a test, gas should be drawn continuously from the flue by means of a steam or water aspirator. The gas should be passed through a bottle (about 16-oz.) filled with absorbent cotton to filter out the dirt and should bubble through water in a second bottle. (See Fig. 8.) The use of the water bottle is to enable the operator to ascertain the rate and regularity of the aspiration. In connecting the sampling tube to the bottles and Orsat apparatus, rubber tubes should be avoided as much as possible. Any long length of pipe or tube should be of iron or lead with only short rubber connections at the joints. All rubber connections should be well wired and the apparatus tested for leaks by closing the stop cock on the sampling tube and noting whether the aspiration of gas continues for any length of time or whether it ceases to bubble through the water as soon as a partial vacuum is produced. If any leaks are discovered they must be stopped, otherwise air will be introduced into the gas analyzed and give incorrect results.

Apparatus for making the analysis. Some form of Orsat apparatus is very generally used in making the flue-gas determinations. A typical one is shown in Fig. 8. This differs from most of those sold by dealers in that the absorption pipettes are connected at the rear to a tube connecting to the two bottles below, which form a water seal protecting the reagents from the action of the air. The ordinary Orsat apparatus as furnished by the supply houses has small thin rubber bags for attaching to the rear of the absorption pipettes but these soon rot and leak and are generally not so satisfactory as the water bottles which are permanent and need only to have the rubber tube connections renewed occasionally.

Operation of the Orsat Apparatus. Sufficient water is poured into the levelling bottle so that when the three-way cock is opened and the bottle raised, the gas will escape and the water fill the burette to a point in the capillary tube. A few drops of sulphuric acid and a piece of litmus paper should be added to the water in the levelling bottle in order to insure against an alkaline reaction. The adjustment of the level of the reagents in the absorption pipettes to a fixed point in the capillary tube is best made as follows: The stop-cock to each of the absorption pipettes

being closed, the 3-way cock is opened to the air and the levelling bottle lowered sufficiently to draw in 25 to 30 c.c. of air. The

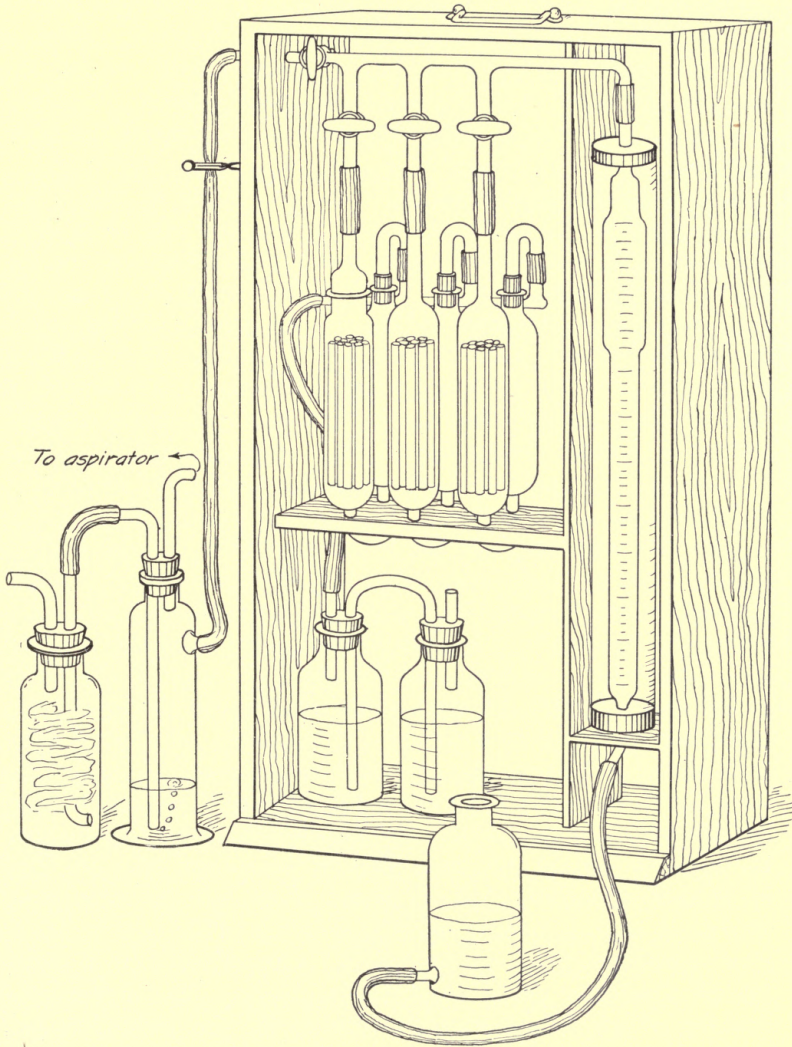


FIG. 8.—Orsat's Apparatus.

3-way cock is then closed. Now, holding the levelling bottle high enough so that the air is under some pressure, the stop-

cock to the first pipette is opened. Some air will rush over and the level of the liquid will be lowered. The levelling bottle is then gradually lowered until the liquid in the absorption pipette begins to rise. The lowering of the levelling bottle is continued gradually until the liquid in the absorption pipette reaches the mark on the capillary. The stop-cock is then closed. The levelling of the reagents in the other pipettes is done in the same manner.

This method of levelling prevents the suction of any of the reagents up into the capillary tubes. The author prefers, in using the apparatus, that the marked point on the capillary of the absorption pipette be placed considerably below the stop-cock (in the apparatus shown in Fig. 8, the marks are below the rubber connections rather than above them). This position of the mark on the capillary greatly diminishes the danger of allowing the reagent to pass up into the stop-cock and above and while a little more residual gas is left in the capillaries, in a series of analyses any individual errors so introduced are eliminated in the average of the series.

Drawing a sample into the Orsat apparatus. If the burette is not completely filled with water, it is filled by raising the levelling bottle and opening the 3-way cock to the air until the water enters the capillary. The cock is then closed and the levelling bottle lowered. If the apparatus is tight the level of the water in the capillary and the level of the reagents in the absorption pipettes should remain constant. If any leaks are present they must be stopped before trying to make an analysis. If the apparatus is tight, the 3-way stop-cock is turned so as to connect the gas burette with the gas bottles through which the gas is passing to the aspirator and the pinch cock on the rubber tube (see Fig. 8), is opened and 50 or 60 c.c. of gas drawn into the apparatus. The pinch cock is then closed, the levelling bottle raised, the 3-way cock opened to the air, and the gas is forced out of the apparatus till the water again enters the capillary. This preliminary drawing of gas is essential in order to fill the capillaries and rubber tube with gas having approximately the same composition as the sample to be analyzed.

With the levelling bottle lowered, the 3-way cock is again opened to the gas supply, the pinch cock again opened and gas drawn in until over 100 c.c. are obtained. The pinch cock and

3-way cock are then closed. The levelling bottle is raised until the gas in the burette reads zero. The rubber tube connecting the levelling bottle to the burette is then pinched with the thumb and finger and the 3-way cock opened to the air to allow the excess of gas to escape. The cock is then closed, the levelling bottle adjusted and the reading of the gas noted. It should read zero or at most 0.1 or 0.2 c.c. above zero. The actual reading is recorded, the levelling bottle raised and the gas run over into the first absorption pipette containing the potassium hydroxide solution. The cock is closed and the gas allowed to remain in the pipette for about a minute. It is then run back into the burette, the levelling bottle adjusted and a reading taken. A second absorption in the potassium hydroxide pipette is then made and a second burette reading taken. This reading should check the first one. If not, a third absorption is necessary. The difference between the initial readings and the reading after absorption in the potassium hydroxide pipette equals the percentage of carbon dioxide. The gas is next run into the pyrogallic acid pipette and run back and forward several times before a reading is made. After a reading it is again run back and forward several times and a second reading taken. The absorption and readings are continued until the last two readings agree exactly. The difference between the final reading from pyrogallic acid absorption and the absorption in the potassium hydroxide pipette equals the percentage of oxygen present. The determination of carbon monoxide is made in a similar manner by running the residual gas into the cuprous chloride pipette and allowing it to stand for some little time. The absorption is continued until two readings check. The difference between the reading from the pyrogallic acid pipette and the reading after the absorption by cuprous chloride equals the percentage of carbon monoxide present, provided that all of the oxygen had been completely absorbed, as any oxygen not taken out by the pyrogallic acid pipette is taken up by the cuprous chloride and hence counts as carbon monoxide.

In beginning a series of analyses it is necessary to draw several preliminary samples of the flue gas in order to saturate the water in the burette with the gases being analyzed. Otherwise, the first few results will be too low due to the absorption of the gas in the water.

REAGENTS USED AND THEIR PREPARATION

For absorbing carbon dioxide (CO_2) a 25 per cent solution of potassium hydroxide is used. For absorbing oxygen (O_2) an alkaline solution of pyrogallie acid is generally used. For absorbing carbon monoxide (CO) an acid or ammoniacal solution of cuprous chloride is used. The preparation of these reagents is as follows:

Potassium hydroxide (KOH) solution. Dissolve 100 grams of the best quality potassium hydroxide in 300 grams of water. Let the solution stand in a closed bottle till any oxide of iron settles and use only the clear solution. If many analyses are to be made it is best to prepare a large quantity of this solution and keep it ready for use.

Pyrogallie acid solution. The white re-sublimed acid should be used. In ordinary flue gas analysis 15 grams of pyrogallie acid are dissolved in 150 c.c. of the 25 per cent potassium hydroxide solution, the solution of the pyrogallie acid being made at the time the Orsat apparatus is filled.

Cuprous-ammonium chloride solution. This is prepared as follows: 250 grams of ammonium chloride are dissolved in 750 c.c. of water in a bottle provided with a good rubber stopper and 200 grams of cuprous chloride are added. The latter on frequent agitation dissolves, leaving a little cupric oxychloride behind, forming a brown liquid which keeps for an indefinite time, especially if a copper spiral long enough to reach from the top to the bottom of the solution is inserted into the bottle. In contact with air the solution forms a precipitate of green cupric oxychloride. In order to make it ready for use, it is mixed with one-third its volume of ammonia, specific gravity 0.910.

Acid cuprous chloride solution. To prepare 125 c.c. of solution the process is as follows: 12 grams of pulverized and recently ignited cupric oxide (CuO), are dissolved in 125 c.c. of concentrated hydrochloric acid. Next 40 grams of crystallized copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) are dissolved in about 200 c.c. of water, adding a few drops of sulphuric acid. To this solution are added 12 grams of granular or mossy zinc which is added carefully to avoid violent effervescence. This zinc may be added to the copper sulphate solution before the copper sulphate has entirely dissolved. The zinc precipitates the copper as a brown powder and the excess of zinc is dissolved in the sulphuric acid more of which is added

if necessary to complete the solution. The liquid is then decanted closely and washed by decantation till free from zinc sulphate. The precipitated copper is then transferred to a small flask (about 150 c.c. capacity) and the water used in transferring poured off as completely as possible. The solution of the cupric oxide in hydrochloric acid is then added to the flask which is stoppered loosely and shaken occasionally until the solution becomes almost or entirely clear. The rapidity of reduction may be increased by dropping into the flask several long pieces of sheet copper or copper wire which accelerate the reduction of the upper portion of the liquid. After the solution has become practically clear it is either transferred at once to the absorption pipette of the Orsat apparatus or poured into a stock bottle containing strips of metallic copper. The solution should almost fill this stock bottle which must be well stoppered.

Filling the Orsat apparatus. The old solutions in the absorption pipettes are removed by forcing air from the gas burette into the absorption bulbs and forcing the liquid into the rear bulbs. Each is then emptied by a small syphon first filled with water and inserted to the bottom of the bulb. The first rear bulb—the one nearest to the measuring burette—is then filled with a proper amount of potassium hydroxide solution. To fill the second bulb with pyro solution place a large funnel into the bulb and put into it 12 grams of pyrogallic acid. This is then washed down in to the bulb with 120 c.c. of the 25 per cent potash solution. If this amount of reagent does not properly fill the pipette more or less potash solution should be taken and the amount of pyrogallic acid increased or reduced proportionately. The filling of this pipette should be done as quickly as possible and as soon as filled it should be stoppered to protect from the action of the air. The third bulb is filled with cuprous chloride solution, the proper amount being poured into the pipette as quickly as possible and the pipette stoppered to protect the reagent from the air. The stoppers are next removed from the absorption bulbs and the stoppers on the connections to the water sealed bottles securely pushed into place, as it is essential that there be no leakage if the reagents are to be properly protected from the air.

Absorbing power of reagents. 100 c.c. of a 25 per cent potassium hydroxide solution will quickly and completely absorb 500 or 600 c.c. of carbon dioxide. Theoretically it is capable of

absorbing several thousand c.c. but practically it should never be used to any where near its theoretical limit and it is advisable to use fresh reagent in the Orsat apparatus after 50 or 60 flue gas determinations have been made as the loss of time due to the slowness of the absorption of carbon dioxide more than counterbalances the slight cost for new reagent. 100 c.c. of the alkaline pyrogallic acid solution is capable of absorbing several hundred c.c. of oxygen and if the reagent is kept properly protected from the air the Orsat solution should easily be good for 30 or 40 determinations of oxygen. However, the author prefers to begin each day's work with an Orsat apparatus with a new solution of pyrogallic acid, as any slowing up in the absorption by an old solution, which frequently occurs if a solution is used a second day, more than makes up for the trouble or expense of renewing the solution each day.

100 c.c. of cuprous chloride solution should readily absorb 50 c.c. of carbon monoxide. However, the last traces are absorbed very slowly or not at all by a solution which has previously absorbed very much carbon monoxide, and the author prefers to renew the cuprous chloride solution in the Orsat apparatus quite frequently even though the actual absorption during the tests upon which it has been used do not total up very many c.c.

Care of apparatus. In setting up the Orsat apparatus, the capillary tubes and absorption pipettes should be washed with dilute hydrochloric acid and then rinsed with pure water. The ends of the tubes fitting into the rubber tube connections should be coated with vaseline and the connections should be securely wired to prevent leaks; the stop-cocks should be well lubricated with vaseline or some similar lubricant. In cleaning out an old solution of cuprous chloride it is sometimes advisable to wash out the cuprous chloride pipette with rather strong hydrochloric acid to dissolve any precipitated cuprous chloride which cannot be removed by the use of pure water. If at any time any reagent gets into a stop-cock or capillary it should be at once flushed out with water and if necessary the apparatus disconnected and cleaned. Before putting the apparatus away all stop-cocks should be loosened slightly and given an application of vaseline if needed. If the apparatus is to be set away for any great length of time, it is advisable to remove the stop-cocks

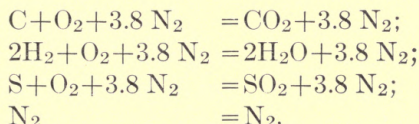
entirely and to insert a narrow strip of paper into each socket before replacing the stop-cock. These strips of paper are permanent safe-guards against the cocks sticking, as is frequently the case if the apparatus is set away without any care being given to them. The gas burette should be left filled with gas or air rather than with water so that if any leak develops there can be no possibility of drawing reagents up in the capillaries.

DISCUSSION AND INTERPRETATION OF ORSAT RESULTS

These may perhaps best be understood by discussing the reactions which take place during combustion of a coal. The average analysis of a number of samples of Ohio No. 6 coal (Hocking or Middle Kittanning coal) is as follows:

Carbon.....	69.03
Total hydrogen.....	5.43
Nitrogen.....	1.26
Oxygen.....	13.62
Sulphur.....	3.30
Ash.....	7.36
Available hydrogen.....	3.73

The available hydrogen is obtained from the total hydrogen by subtracting from the total hydrogen $\frac{1}{8}$ of the oxygen in the coal = $5.43 - (\frac{1}{8} \text{ of } 13.62) = 3.73$. The reactions for complete combustion of this coal in air (air = by volume one part of oxygen and 3.8 parts of nitrogen) are as follows.



Gas reactions are most easily handled if the gases produced are figured with a molecular volume as the unit for calculation. A molecular volume of gas is the volume which the molecular weight of the gas in grams occupies. Under standard conditions, 0° C. and 760 mm. of mercury pressure, this = 22.4 liters (0.79 cu.ft.). As an illustration, the molecular weight of carbon dioxide (CO₂) = 44. The molecular weight of carbon monoxide (CO) = 28. 44 grams of carbon dioxide (CO₂) or 28 grams of carbon monoxide

(CO) = 22.4 liters by volume, at 0° C. and at a pressure of 760 mm. of mercury.

1 molecular volume of CO₂ = 12 grams of carbon or 0.01 gram carbon = 0.000833 molecular volume of CO₂.

1 molecular volume of H₂O = 2 grams of hydrogen (H₂) or 0.01 gram of hydrogen = 0.005 molecular volume H₂O.

1 molecular volume of SO₂ = 32 grams of sulphur or 0.01 gram of sulphur = 0.00031 molecular volume of SO₂.

1 molecular volume of N₂ = 28 grams of N₂ or 0.01 gram of nitrogen = 0.000357 molecular volume of N₂.

From these relations the molecular volumes of the products of complete combustion of 1 gram of coal with no excess air are as follows:

For the carbon to $C + O_2 + 3.8N_2 = CO_2 + 3.8N_2 = 69.03 \times 0.000833 = 0.0575$ molecular volume of CO₂ + (0.0575 × 3.8 = 0.2185) molecular volume N₂.

For the available hydrogen to $2H_2 + O_2 + 3.8N_2 = 2H_2O + 3.8N_2 = 3.73 \times 0.005 = 0.01865$ molecular volume H₂O +

$$(0.01865 \times \frac{3.8}{2} = 0.0354) \text{ molecular volume } N_2.$$

The hydrogen present in the coal in the form of water = $\frac{1}{8}$ the oxygen in the coal = $\frac{1}{8}$ of 0.1362 = 0.0170 gram of hydrogen. This hydrogen to $2H_2O = 1.70 \times 0.005 = 0.0085$ molecular volume H₂O.

For the sulphur to $S + O_2 + 3.8N_2 = SO_2 + 3.8N_2 = 3.30 \times 0.00031 = 0.001$ molecular volume SO₂ + (0.001 × 3.8 = 0.0038) molecular volume N₂.

For the nitrogen in the coal to $N_2 = 1.26 \times 0.000357 = 0.00045$ molecular volume of N₂.

Collecting together the nitrogen from the air required for complete combustion, 0.2185 + 0.0354 + 0.0038 = 0.2577 molecular volume of nitrogen.

If 100 per cent excess air be assumed the nitrogen in this 100 per cent excess air = therefore 0.2577 molecular volume and the oxygen in this 100 per cent excess air = $\frac{0.2577}{3.8} = 0.0678$ molecular volume.

Collecting these values for the products of combustion, allowing the 100 per cent excess of air, the molecular volumes of

gas from the complete combustion of one gram of coal are as follows:

CO ₂	=	0.0575	molecular volume
O ₂	=	0.0678	“
H ₂ O (vapor)	=	0.0271	“
SO ₂	=	0.0010	“
N ₂	=	0.5158	“

Total molecular volumes = 0.6692 = 15.0 liters at 0° C. and 760 mm. pressure.

The Orsat analysis of the gas determines only the carbon dioxide, the carbon monoxide, and the oxygen present. With complete combustion it is assumed that no carbon monoxide is produced and the analysis has only to do with carbon dioxide and oxygen, the difference being nitrogen. The sulphur dioxide formed during combustion amounts by volume to about $\frac{1}{50}$ of the volume of carbon dioxide and a small portion of this sulphur dioxide may be absorbed by the potassium hydroxide solution and hence count as carbon dioxide. However, it is altogether probable that the greater part is absorbed in the water in the Orsat apparatus or elsewhere before the actual carbon dioxide determination is made and for all practical purposes the volume of the sulphur dioxide in the Orsat determination may be neglected. The excess of water vapor in the gas condenses and the Orsat gases are saturated with water vapor at the temperature at which they are analyzed. With no change in temperature, the proportion of water vapor present during an analysis remains unchanged and the absorption of the gas by the potash or pyrogallie acid or cuprous chloride pipette represents the percentage of carbon dioxide, oxygen, and carbon monoxide present in the gas, as the effect of the presence of water vapor merely diminishes the pressure of the residual gas analyzed, but it has no effect on its relative percentage composition.

Referring to the reactions given (p. 141) for the combustion of the Ohio No. 6 coal, for one gram of coal burned there are present in the flue gas, assuming theoretical combustion, 50 per cent excess air and 100 per cent excess air, gases as follows: (H₂O vapor and SO₂ are omitted from the tabulation since they do not enter into the Orsat analysis).

Gas Composition.	Theoretical Combustion.		50 Per Cent Excess Air.		100 Per Cent Excess Air.	
	Mol. Vol.	Per Cent.	Mol. Vol.	Per Cent.	Mol. Vol.	Per Cent.
CO ₂	0.0575	18.22	0.0575	12.02	0.0575	8.98
O ₂	0.0339	7.09	0.0678	10.58
N ₂	0.2581	81.78	0.3870	80.89	0.5158	80.44
	<u>0.3156</u>	<u>100.00</u>	<u>0.4784</u>	<u>100.00</u>	<u>0.6411</u>	<u>100.00</u>

The effect of the formation of carbon monoxide instead of carbon dioxide is to lower the nitrogen percentage since only one-half as much air is required to burn carbon to carbon monoxide as is required to burn it to carbon dioxide and less residual nitrogen remains after the absorption of carbon dioxide, oxygen and carbon monoxide. 0.01 gram of carbon to CO = 0.000833 molecular volume of CO = .00158 molecular volume of N₂ as against 0.00316 molecular volume of N₂ required for an equivalent amount of carbon to CO₂. With 50 per cent excess air and 0.01 gram of carbon burned to CO instead of CO₂, the products of combustion of 1 gram of coal, omitting the tabulation of H₂O and SO₂ are as follows:

	Mol. Vol.	Per Cent.
CO ₂	0.0567	11.93
O ₂	0.0337	7.09
CO.....	0.00083	0.17
N ₂	0.3841	80.81
	<u>0.4753</u>	<u>100.00</u>

The higher the sulphur and the available hydrogen the more oxygen is required for combustion and the greater the volume of nitrogen in the residual gas. 0.01 gram of available hydrogen requires air for combustion equivalent to 0.0095 molecular volume of N₂. With 50 per cent excess air this equals 0.0143 molecular volume of N₂ + 0.0013 molecular volume of O₂ = 0.0156 molecular volume increase in the residual gas. In this case, assuming the other constituents of the coal to remain the same, the products of combustion of 1 gram of this coal containing 4.73 per cent available hydrogen (omitting H₂O and SO₂ from the tabulation) are as follows:

	Mol. Vol.	Per Cent.
CO ₂	0.0575	11.64
O ₂	0.0352	7.12
N ₂	0.4013	81.24
	<hr/>	<hr/>
	0.4940	100.00

With 50 per cent excess air, 1 per cent more of available hydrogen raises the nitrogen about 0.35 per cent. The effect of sulphur is about $\frac{1}{8}$ as great as the effect of an equal weight of hydrogen or an increase of 1 per cent in sulphur increases the nitrogen by about 0.05 per cent.

With 100 per cent excess air present the effects of hydrogen and sulphur are about $\frac{2}{3}$ as great as with 50 per cent excess or approximately 0.24 for the hydrogen and 0.03 for the sulphur. The available hydrogen in the sample calculated is 3.73 per cent and an increase in available hydrogen of 1 per cent higher than this amount is more than is ever actually found. Most coals contain less than 4 per cent. On the basis of not over 4 per cent available hydrogen and with the amount of carbon corresponding to that usually found in coals high in available hydrogen and with 50 per cent excess air corresponding to approximately 12 per cent of carbon dioxide in the flue gas, the nitrogen should not run above 81 per cent. With larger excess air, as 100 per cent, corresponding to approximately 9 per cent of the carbon dioxide in the flue gas, the nitrogen should be appreciably less than 81 per cent. With smaller excess air and higher carbon dioxide and the absence of carbon monoxide, the nitrogen may possibly exceed 81 per cent.

The effects of the presence of unburned hydrogen should be considered as to its relation upon the Orsat analysis and the heat balance. If it be assumed for illustration that of the 3.73 per cent available hydrogen, one part escapes as free hydrogen and the remaining 2.73 burn to water, allowing 50 per cent excess air, the products of combustion from 1 gram of coal (omitting H₂O vapor and SO₂ from the tabulation), are as follows:

	Mol. Vol.	Per Cent.
CO ₂	0.0575	12.29
O ₂	0.0326	6.97
N ₂	0.3727	79.67
H ₂	0.0050	1.07
	<hr/>	<hr/>
Total	0.4678	100.00

Deducting the sum of the carbon dioxide and oxygen (19.26) from 100 = 80.74 as the percentage of nitrogen obtained. This is only 0.15 per cent lower than the figure obtained for complete combustion, hence as far as any visible effects in the Orsat determination are concerned, unburned hydrogen has little effect upon the totals of the carbon dioxide, oxygen, and carbon monoxide. A failure of this amount of hydrogen to burn would mean, however, a loss of 334 calories or 5 per cent of the total heat in the fuel.

In a similar way it may be shown that the presence of large amounts of methane in the gas would have little effect upon the percentage result obtained for nitrogen. With 50 per cent excess air and assuming 0.01 gram of carbon and a corresponding amount (0.0033 gram) of hydrogen remaining as methane (CH_4), the products of combustion of 1 gram of the coal (omitting H_2O and SO_2 from the tabulation), are as follows:

	Mol Vol.	Per Cent.
CO_2	0.0567	12.12
O_2	0.0327	6.99
N_2	0.3776	80.71
CH_4	0.00083	0.18
Total	0.46783	100.00

The sum of the nitrogen and methane equals 80.89 which is the same as the value for nitrogen assuming complete combustion and 50 per cent excess air.

The above calculations may serve to make clear why the nitrogen from different determinations is not a fixed quantity, and also that the value obtained for nitrogen is not necessarily all nitrogen. By applying similar calculations to any coal for any observed or assumed set of conditions, possible and probable percentages may be readily calculated and may serve to prove or disprove speculations as to the possible or probable effects of unburned hydrogen, carbon, etc. Such calculations usually make plain or certain the fact that as a rule irregular determinations cannot be satisfactorily explained in such a way and that irregular results are more probably due to errors of manipulation, leaks in the apparatus, etc.

Errors in the Orsat determination. (1) Leaks in the apparatus or connections leading to the sampling tube.

(2) Errors due to reagents getting into the apparatus, especially into the capillary connecting tube.

(3) Errors in levelling.

(4) Errors due to insufficient time of drainage of the burette before taking a reading.

(5) Use of old reagents and failure to absorb completely tend to give low results for carbon dioxide, low results for oxygen, high or low results for carbon monoxide, but a low total for the three.

(6) Errors due to temperature changes during a determination.

Nos. 1, 3, 4 and 5 need no special comment, except to call attention to possible errors from these causes.

No. 2. Any absorption of oxygen or carbon dioxide by traces of potassium hydroxide or pyrogallie acid solution in the connecting tube gives of course too low a result for oxygen or carbon dioxide and consequently too high a result for nitrogen. Many high nitrogens are probably due to carelessness in this particular.

No. 6. Errors due to temperature changes during a determination may be of considerable magnitude, which may perhaps best be shown by a particular example. Suppose the temperature of the gas at the beginning of a determination = 20° C. At the end of the carbon dioxide absorption = 20° C. At the end of the oxygen absorption = 21° C. and at the end of the carbon monoxide absorption = 22° C., what is the effect upon an analysis, the observed readings of which are as follows:

	Observed Readings.	Observed Per Cent.
Initial readings	= 0.0	
CO ₂	10.00	10.00
O ₂	19.00	9.00
CO	19.00	0.00
N ₂		81.00

Since there is no temperature change during the carbon dioxide determination the determined percentage of carbon dioxide (10 per cent) equals the true percentage present. During the determination of oxygen the temperature increases one degree or from 293 degrees absolute to 294 degrees absolute. Hence the observed volume of residual gas (81 c.c.) is $\frac{1}{293}$ larger than the volume of the gas at 20° C. $\frac{1}{293}$ of 81 = 0.27 c.c. or the corrected volume of the residual gas is 80.73, from which the corrected percentage of oxygen = 9.27 as against 9.00 observed. Likewise, for carbon

monoxide, the observed volume 81.00 at 22° is $\frac{2}{295}$ larger than the volume of the gas at 20° or the volume of the residual gas corrected to 20° C. is approximately 80.46 c.c. and the corrected percentage of carbon monoxide is 0.27 instead of zero, the determined percentage. This error appears large enough but there is still another effect to be considered. The aqueous tension of the water vapor of the gas at 20° C.=17.4 mm. of mercury, at 21° C.=18.5 mm. of mercury, at 22°=19.7 mm. of mercury. Assuming a total observed barometric pressure of 740 mm. of mercury, the actual pressure of the gas in the burette at the different temperatures is therefore,

$$\text{for } 20^{\circ} \text{ C., } 740 - 17.4 = 722.6;$$

$$\text{for } 21^{\circ} \text{ C., } 740 - 18.5 = 721.5;$$

$$\text{for } 22^{\circ} \text{ C., } 740 - 19.7 = 720.3;$$

and the corrected volume of the 81 c.c. at 21° C. allowing for this change is less by $\frac{1.1}{722.6}$ of 81 = 0.12 c.c. and the corrected volume of the 81 c.c. observed at 22° C. is less by $\frac{2.3}{720.3}$ of 81 = approximately 0.26 c.c. This error adds to the error introduced by the temperature changes.

Combining the two corrections, the true reading and percentages are as follows:

	Observed Reading.	Observed Per Cent.	Corrected to 20° C.	
			True Reading.	True Per Cent.
Initial reading	0.00			
CO ₂	10.00	10.00	10.00	10.00
O ₂	19.00	9.00	19.40	9.40
CO	19.00	0.00	19.81	.41
N ₂	81.00	80.19
		100.00		100.00

The above corrections are obtained as follows:

For oxygen, correcting from 21° to 20° C. = 100 - 19 = 81 c.c.

$81 \times \frac{293}{294} \times \frac{721.5}{722.6} = 80.60$. The correct oxygen reading is therefore $100 - 80.60 = 19.40$.

For carbon monoxide, correcting from 22° to 20° C., $100 - 19 = 81$ c.c. $81 \times \frac{293}{295} \times \frac{720.3}{722.6} = 80.19$. The correct carbon monoxide reading is therefore $100 - 80.19 = 19.81$.

With an initial temperature of 20° C., a change of 1° during the determination of any constituent introduces an error of about 0.4 per cent. If the temperature has increased the observed result is too low. If the temperature has decreased the observed result is too high. For higher temperatures the effect of aqueous tension is appreciably larger. For 30° C. (89° F.) the error for 1° change of temperature being approximately 0.06 per cent more than at 20° C.

The magnitude of these errors certainly shows the impossibility of securing accurate results with unjacketed burettes and shows the possibility of serious errors even where jacketed burettes are used, if the apparatus is exposed to draughts or rapid temperature changes. The use of a thermometer in the water jacket and the taking of temperature observations before and after the absorption serve as a check on this error and allow for corrections if temperature changes are noted.

ALTERATION OF SAMPLES ON STANDING AND EFFECTS UPON THE ORSAT RESULTS

The foregoing discussion of the Orsat analysis and results is based on the supposition that the samples are drawn directly into the Orsat apparatus and analyzed at once. When samples are collected in sample tubes or bottles, or in metal tanks, the possible and probable alteration of the samples and the effect upon the Orsat determination should be considered.

The changes to which a stored sample are liable are, (1) leakage, (2) chemical changes, (3) absorption of the gas in the water over which it is collected or over which it is allowed to stand.

(1) *Leakage*. The danger from alteration of a stored sample from leakage should not be overlooked. Samples stored in rubber containers or in containers with rubber connections of any length

are practically sure to alter if kept for any considerable time, and sample tubes closed by stop-cocks even if well lubricated and well tied are liable to possible leakage. A slight leak in a rubber connection or around a stop-cock, if the sample is analyzed promptly, may not have any measurable effect upon the sample but if the sample is stored and the leakage allowed to continue during twenty-four or forty-eight hours the sample may be so changed in composition as to render any results obtained upon it entirely worthless. Every rise or fall in the temperature of the gas from that at which it was collected subjects it to an increased or diminished pressure and hence any slight leaks are likely to be continually acting.

If samples must be collected and kept before being analyzed the author prefers to so take them that they will be under considerable pressure when sealed and any leakage be continually outward rather than alternately inward and outward. Also if collected and kept over water the exposure to water while collecting should be reduced to a minimum and the amount of water allowed to remain in contact with the sample should be relatively small in comparison to the volume of the sample. (For example preferably not over one volume of water to 10 volumes of gas.)

Leakage of sample outward may merely change the volume of the sample without altering its composition. However, as carbon dioxide diffuses through small orifices less readily than the lighter gases (oxygen, nitrogen and carbon monoxide), a considerable leakage of gas especially if through rubber may result in the residual gas being higher in carbon dioxide than the original sample. Leakage inward is certain to raise the oxygen content since the oxygen percentage of the air surrounding a sample is certain to be much higher than the oxygen content of the flue-gas sample. The effects of leakage and consequent alteration of the composition of the sample upon the value of the Orsat determination are discussed in detail later.

(2) *The chemical alteration of the sample.* The chief sources of error from chemical changes are the absorption of oxygen by reducing reagents in the water over which the sample is collected or stored, and the absorption of carbon dioxide as carbonate by salts of calcium which may be in the water, or in some cases the enrichment of the gas in carbon dioxide by its liberation from bi-carbonate salts in the water. The usual reducing agents are the

ferrous salts of iron which readily use up oxygen, and water which carries iron in solution should not be used in filling the tanks or tubes in which gas samples are to be collected. Rain-water, well water or hydrant water which has been exposed to the air for some time before using is to be preferred to water taken directly from the pump or water main. The water should, however, not be too thoroughly aerated, as if saturated with air it will give up oxygen to flue-gas samples kept over it. To avoid as much as possible errors from chemical changes, the exposure of the sample to water should be reduced to a minimum and only a small amount of water be allowed to remain in contact with the sample.

ALTERATION OF SAMPLES BY ABSORPTION IN THE WATER OVER WHICH THEY ARE COLLECTED OR STORED

Samples collected over water are certain to suffer alteration from this cause and the extent of such alteration and the effect upon the Orsat determination should be well understood by everyone who has to do with gas sampling.

The following values for solubilities are taken from Landolt and Bornstein's tables, the solubilities being given in volumes of gas absorbed by one volume of water at the temperatures given and with the gas at a pressure of 760 mm. of mercury.

	0° C. (32° F.).	15° C. (59° F.).	30° C. (86° F.).
O ₂	0.0489	0.03415	0.02608
N ₂	0.02388	0.01786	0.01380
CO.....	0.03537	0.02543	0.01998
CO ₂	1.713	1.019	0.665

The solubilities of these gases for the same temperature varies directly as the pressure of the gas and for a mixture of gases the solubility of each gas is proportional to the partial pressure of each gas independent of the other gases present. The partial pressure exerted by each gas in a gas mixture is proportional to the percentage of each gas. For example in a mixture of 20 per cent oxygen and 80 per cent nitrogen under atmospheric pressure

the partial pressure of the oxygen is 0.20 of an atmosphere and the partial pressure of the nitrogen is 0.80 of an atmosphere.

The solubility of a mixture of gases (flue gas) in water should be considered under several particular conditions:

(1) *An unlimited supply of gas and a limited supply of water.* With an unlimited supply of gas and a limited supply of water the volumes of gas which can be absorbed by the water at any given temperature and pressure may be calculated directly from the solubility values previously given.

(2) *A limited supply of gas and an unlimited supply of water.* With a limited supply of gas and an unlimited supply of water the gas will be entirely dissolved in the water.

(3) *A limited supply of gas and a limited supply of water.* With a limited supply of gas and a limited supply of water the gas will dissolve in water until a condition of equilibrium is attained. This condition of a limited supply of gas and a limited supply of water is the one that exists where gases are stored in sampling tubes or containers over water and the possible alteration of such samples should be well understood. This may perhaps best be shown by an example. For illustration, what is the solubility and the resultant volume and composition of one liter of gas stored over one liter of pure distilled water at a temperature of 15° C. (59° F.), at an atmospheric pressure of 742.7 mm. of mercury, the composition of the original gas being,

CO ₂	10.0 per cent
O ₂	9.0 “
CO	0.5 “
N ₂	80.5 “
	100.0 “

The pressure of aqueous vapor at 15° C. = 12.7 mm. of mercury or the total pressure of the gas present = 742.7 - 12.7 = 730 mm. of mercury. From the values for solubilities given for 760 mm. pressure of gas and 15° C. the solubilities of CO₂, O₂, CO, and N₂ in 1000 c.c. of water for 730 mm. are found to be,

CO ₂	= 978.8 c.c.
O ₂	= 32.79 “
CO	= 24.42 “
N ₂	= 17.17 “

Since the partial pressure of each constituent of a mixture is proportional to the percentage of each constituent present, the solubilities of the different gases in 1000 c.c. of water at 15° C. (assuming an unlimited supply of gas) are as follows:

$$\text{CO}_2 = 978.8 \times \frac{10}{100} = 97.88 \text{ c.c.}$$

$$\text{O}_2 = 32.79 \times \frac{9}{100} = 2.94 \text{ "}$$

$$\text{CO} = 24.42 \times \frac{5}{1000} = 0.12 \text{ "}$$

$$\text{N}_2 = 17.17 \times \frac{805}{1000} = 13.8 \text{ "}$$

For 1000 c.c. of the original gas the volumes of the constituents are as follows:

10	per cent	CO ₂	=	100	c.c.
9	"	O ₂	=	90	"
0.5	"	CO	=	5	"
80.5	"	N ₂	=	805	"
100.0	"			1000	"

Comparison of the amount of each gas in 1000 c.c. of the mixture with the solubility in 1000 c.c. of water based on the supposition of an unlimited supply of gas shows at a glance that the solubility of oxygen, carbon monoxide and nitrogen from the limited supply of gas (1000 c.c.) is not very far from the amount taken up from an unlimited supply, since the amount of each dissolved is small compared to the amount of each present in 1000 c.c. of the gas.

With an unlimited supply of gas the solubility of carbon dioxide is 97.88 c.c. Since the total c.c. of carbon dioxide in one liter of the gas is only 100 c.c. if this amount were absorbed, only 2.14 c.c. of carbon dioxide would be present in the residual gas. The volume of the residual gas, allowing for this absorption and allowing for the absorption of oxygen, carbon monoxide and nitrogen is 885 c.c. or the 2.14 c.c. of carbon dioxide = 2.4 per cent

of the residual gas. The solubility of carbon dioxide in 1000 c.c. of water with this per cent present in the gas over the water is $978.8 \times 0.024 =$ approximately 2.3 c.c. and the actual condition of equilibrium for solubility of the carbon dioxide in the 1000 c.c. of water is evidently somewhere between these two extremes of solubility, 2.3 c.c. and 97.88 c.c. or something over 50 c.c.

As a preliminary approximation, assume the solubility of carbon dioxide from the limited volume of gas (1000 c.c.) to be 51 c.c.; oxygen 3 c.c.; and carbon monoxide 0.12 cc. and for nitrogen 14 c.c., then the amounts and percentages of gas remaining are as follows:

$\text{CO}_2 = 100 - 51 = 49$	c.c. = 5.26 per cent
$\text{O}_2 = 90 - 3 = 87$	“ = 9.33 “
$\text{CO} = 5 - 0.12 = 4.88$	“ = 0.52 “
$\text{N}_2 = 805 - 14 = 791$	“ = 84.89 “
Total	931.88 “ 100.00 “

Multiplying the solubility of each gas at 730 mm. pressure and at 15°C . by the percentage of gas remaining, the amounts of gas dissolved in 1000 c.c. for these percentages are as follows:

$\text{CO}_2 = 978.8 \times 0.0526 = 51.48$	c.c.
$\text{O}_2 = 32.79 \times 0.093 = 3.04$	“
$\text{CO} = 24.42 \times 0.0052 = 0.127$	“
$\text{N}_2 = 17.17 \times 0.849 = 14.58$	“

From which it is seen that the first approximation for solubility does not give actual equilibrium, but a second approximation using values based on the ones already obtained will give practical equilibrium.

These values are about as follows:

CO_2 absorbed	= 51.25 c.c.
O_2	“ = 3.05 “
CO	“ = 0.13 “
N_2	“ = 14.6 “

Using these values the volumes, percentages and equilibrium conditions are as follows:

	c.c.	Per Cent.	Equilibrium Solubility.
CO ₂ =100	-51.25 = 48.75 =	5.24 =	51.28 c.c.
O ₂ = 90	- 3.05 = 86.95 =	9.34 =	3.06 "
CO = 5	- 0.13 = 4.87 =	0.52 =	0.13 "
N ₂ =805	-14.6 = 790.4 =	84.90 =	14.6 "
Total		<hr/> 930.97	<hr/> 100.00

The values obtained serve to show the possible changes that gas stored over water may undergo. The actual solubilities under working conditions will differ from these values on account of the fact that ordinary water contains dissolved in it some carbon dioxide, oxygen and nitrogen, hence the solubilities under ordinary conditions will not be as high as the calculated.

Chemical changes may also enter in to alter the composition of the final sample so that any calculated solubility change cannot be depended upon for great accuracy.

The values obtained in the foregoing illustration serve, however, to emphasize and make clear the following facts:

That the alteration of the sample in carbon dioxide may be very great and that the composition of the remaining sample is as a result higher in both oxygen and nitrogen.

Effect of the solution of CO₂ upon other determinations.

The excess-air ratio as determined by the ratio between oxygen and nitrogen is not however affected by the solubility of carbon dioxide and in so far as carbon dioxide is concerned the excess air may be determined almost as accurately on a stored sample as on one freshly taken, provided of course that chemical changes have not used up oxygen.

In the illustration given above, the excess air in the original sample containing 10 per cent of carbon dioxide calculated from the oxygen-nitrogen ratio, is 73.9 per cent. The excess air in the sample after it has reached equilibrium over the 1000 c.c. of water is 71.8 per cent or a change of only 2 per cent in the figured excess air with a change of nearly 5 per cent in carbon dioxide (nearly one-half of the amount originally present) and a change of over 4 per cent in nitrogen.

The calculation of heat loss due to formation of carbon monoxide rather than carbon dioxide is made inaccurate by any

absorption of carbon dioxide. In the original sample the amount of carbon burned to carbon monoxide is $\frac{5}{105}$ of the total carbon in the coal, while in the sample which has reached equilibrium over the 1000 c.c. of water, the carbon burned to carbon monoxide is $\frac{5.2}{76}$ of the total carbon present, or a ratio almost twice as large as the true ratio $\frac{5}{105}$, so that with large amounts of carbon monoxide present in the gas the absorption of carbon dioxide in the water, before the determination of the Orsat analysis, makes the heat balance inaccurate in so far as the heat loss due to carbon monoxide is concerned, but for the more important item of excess air the absorption of carbon dioxide is without effect.

EFFECT OF A WATER SEAL UPON COMPOSITION OF SAMPLES

Where samples are stored in bell jars or inverted cylinders and protected from the atmosphere by a water seal the action of this water seal should be noted. The surface of the water in contact with the gas continually tends to reach a condition of equilibrium with respect to the gas above it. Likewise the surface of the water seal which is exposed to the air is continually tending to reach a condition of equilibrium with respect to the air above it. Since the composition of the stored gas and the composition of the air on the outside are radically different, equilibrium conditions on the two sides are different and the result is a continual absorption of carbon dioxide from the sample into the water which gradually diffuses through the water seal and escapes into the open air on the other side. Likewise there is in the opposite direction a continual absorption of oxygen from the air into the water and diffusion of this oxygen through the water seal into the stored gas. The final effect, if the sample is stored long enough, will be that the composition of the sample will approximate that of the outside air, the excess carbon dioxide and carbon monoxide gradually diffusing and escaping and the oxygen content of the sample continually increasing from diffusion inward. On account of this diffusive action the author prefers in storing samples over water that there be no actual contact of the water seal with the outside air.

Details of the determination of hydrogen and hydro-carbons

in the flue gases and are given in special texts upon gas analysis. The determination of carbon monoxide as made in the Orsat apparatus is satisfactory only when small amounts of carbon monoxide are present in the gas, as is the case in a boiler flue gas. In the analysis of a gas high in carbon monoxide, as gas from an iron blast furnace or gas from a gas producer, the method and apparatus used should be such as to secure rapid and complete absorption of the large amount of carbon monoxide present. For the description of suitable methods and apparatus special texts on gas analysis should be consulted.

CHAPTER X

ANALYTICAL TABLES

COMPARATIVE COMPOSITION OF DIFFERENT FUELS

Fuel.	Moisture, Per Cent.	Remarks.
Wood.....	30 to 60	Green wood.
Peat.....	50 to 90	As dug.
Lignite.....	30 to 45	As mined.
Bituminous coal	2 to 25	As mined.
Semi-bituminous coal.....	1 to 5	As mined.
Anthracite coal.....	1 to 3	As mined.

COMPOSITION AND HEATING VALUE OF AIR-DRIED MATERIALS

	Wood.	Peat, ³ Florida No. 1.	Lig- nite, ¹ North Dakota No. 2.	Bituminous Coal.			Semi- bitu- minous Coal. ¹	Anthra- cite Coal. ¹
				Illinois, ¹ No. 6.	Ohio, Hock- ing, ⁴	Penn. No. 5. Pitts- burgh. ²		
<i>Proximate:</i>								
Moisture.....	20.0	21.00	16.70	5.13	3.00	1.00	0.76	2.08
Vol. matter.....	51.72	37.10	32.68	39.00	35.00	20.54	7.27
Fixed carbon.....	22.11	39.49	47.46	50.50	57.85	73.61	74.32
Ash.....	5.17	6.71	14.73	7.50	6.15	5.09	16.33
		100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Ultimate:</i>								
Carbon.....	40.0	46.57	55.16	60.51	70.70	78.75	82.41	75.21
Hydrogen.....	7.2	6.51	5.61	4.88	5.20	5.14	4.38	2.81
Nitrogen.....	.8	2.33	.91	1.23	1.30	1.55	1.05	.80
Oxygen.....	50.7	38.97	30.98	14.20	11.95	7.56	5.87	4.08
Sulphur.....	5.17	.63	4.45	3.35	.90	1.20	.77
Ash.....	1.3	.45	6.71	14.73	7.50	6.10	5.09	16.33
	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Determined calo- rific value =	4200	4515	5273	6199	7155	7865	8254	6929
Calculated calo- rific value ÷	4338	5071	6059	7100	7845	7942	6886

¹ U.S.G.S. *Professional Paper* No. 48.

² U.S.G.S. *Bulletin* No. 290.

³ U.S.G.S. *Bulletin* No. 332.

⁴ Ohio Geol. Survey, *Bulletin* No. 9.

COMPOSITION OF COALS OF THE UNITED STATES ARRANGED ALPHABETICALLY BY STATES

The results given in the following tables are upon car samples of the coal as received unless otherwise noted.

Authorities: 1 = U. S. Geological Survey, *Professional Paper* No. 48.

2 = " " " " " "

3 = " " " " " "

4 = Ohio Geological Survey, *Bulletin* No. 9.

5 = Bureau of Mines, *Bulletin* No. 5.

Coal.	County or Location.	Seam or Bed.	Kind of Coal.	Moisture.	Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Determined Calories.	Calculated Calories.	Determined B. T. U.	Authority.
ALABAMA																
1	Walker Co.	Horsecreek	Lump and nut	2.34	31.84	53.28	12.54	0.72	5.01	71.58	1.65	8.50	7142	7160	12856	1
2	"	Jagger	Lump, nut, and pea	3.36	32.88	51.33	12.43	1.01	4.84	68.69	1.54	11.49	6861	6745	12350	1
2 B	"	"	Run-of-mine	3.95	30.70	50.76	14.59	1.12	4.57	66.21	1.49	12.02	6547	6433	11785	3
3	Bibb Co.	Thompson	"	2.72	29.46	53.46	14.36	0.55	4.55	69.99	1.14	9.41	6923	6829	12461	3
4	"	Youngblood	"	6.43	28.56	52.09	12.92	1.18	5.23	69.07	1.18	10.52	6886	6952	12395	3
5	Blount Co.	Blackcreek	"	5.59	25.05	53.28	16.08	1.40	4.70	66.58	1.27	9.92	6616	6604	11906	3
6	Jefferson Co.	Pratt	"	3.23	26.16	63.90	6.71	0.61	4.99	78.33	1.42	7.94	7819	7690	14074	3
ARKANSAS																
1	Sebastian Co.	Huntington	Lump and nut	3.24	17.46	66.69	12.61	1.24	4.15	74.09	1.44	6.47	7294	7165	13128	1
1 B	"	"	Slack	7.49	15.16	59.38	17.97	1.06	4.34	65.54	1.36	9.73	6316	6304	11369	3
9	"	"	Slack through 1 1/2"	5.26	14.71	55.22	24.81	1.00	3.31	59.87	1.23	9.18	5800	5812	10451	3
2	"	Jenny Lind	Lump	2.23	16.02	72.55	9.20	1.87	4.24	78.83	1.38	4.48	7639	7677	13750	1
3	"	"	Lump and slack	2.19	19.47	66.71	11.63	1.58	4.17	75.31	1.53	6.08	7480	7289	13464	1
5	Johnson Co.	Denning	"	2.36	12.68	72.88	12.08	1.99	3.82	76.44	1.37	4.30	7366	7353	13259	1
7 A	Sebastian Co.	Hartshorne	Lump over 2"	5.47	16.27	66.57	11.69	2.02	4.33	72.63	1.26	8.07	7050	7058	12690	3
7 B	"	"	Slack through 2"	6.89	15.23	62.88	15.00	2.24	4.44	68.28	1.26	8.78	6700	6718	12060	3
8	Johnson Co.	?	Size 4, through 1 1/2"	5.19	10.49	70.31	14.01	2.05	3.78	72.43	0.51	7.22	6922	6891	12460	3
10	Ouachita Co.	?	Run-of-mine	39.43	26.49	24.37	9.71	0.49	6.98	36.33	0.68	45.81	3531	3377	6356	3
13	Franklin	?	Slack	2.91	12.65	66.93	17.51	3.12	3.60	70.88	1.17	3.72	6840	6876	12312	3
1	Alameda Co.	?	Run-of-mine	18.51	35.33	30.67	15.49	3.05	5.93	47.34	0.66	27.53	4726	4752	8507	2
COLORADO																
1	Boulder Co.	Simpson mine	Run-of-mine	18.68	34.88	40.45	5.99	0.55	6.07	57.46	1.15	28.78	5635	5507	10143	1
16	Las Animas Co.	Sopris	"	2.35	30.69	52.80	14.16	0.64	4.63	71.12	1.04	8.41	7104	6995	12787	5
D 17	"	Walsen	"	1.90	31.36	48.92	17.82	0.68	4.63	67.82	1.18	7.87	6703	6753	12065	5

D 18	Las Animas Co.	Primero.	Run-of-mine.	1. 24 31. 65 50. 99 16. 12 0. 54 4. 73 69. 96 1. 36 7. 29 7001 6981 12602	5
D 25	"	Cameron.	1' screenings.	3. 11 35. 22 67. 68 13. 99 0. 81 4. 86 67. 60 1. 36 11. 38 6775 6666 12195	5
D 26	Boulder Co.	Lower seam.	Run-of-mine.	19. 28 34. 61 41. 41 4. 70 0. 39 5. 99 97. 94 1. 28 29. 70 5591 5476 9064	5
D 30	Pitkin Co.	"	"	3. 75 22. 12 62. 41 11. 72 0. 40 4. 79 75. 80 1. 45 5. 84 7416 7533 13349	5
D 27	Las Animas Co.	Berwind.	"	4. 22 32. 38 50. 22 13. 18 0. 64 5. 14 70. 69 1. 20 9. 15 7045 7105 12681	5
D 28	Mesa Co.	"	4' run-of-mine.	8. 52 33. 98 45. 20 12. 30 0. 58 5. 38 64. 50 1. 31 15. 93 6288 6393 11318	5
D 29	Pitkin Co.	Upper.	Run-of-mine.	3. 07 27. 67 65. 10 9. 16 0. 63 4. 96 78. 81 1. 69 4. 75 7772 7888 13990	5
D 32	Routt Co.	Yampc.	"	7. 53 36. 36 45. 46 10. 65 1. 51 5. 29 64. 90 1. 41 16. 24 6366 6400 11459	5
1	FLORIDA	"	"	"	"
1	Orange Co.	"	Machined peat.	21. 00 51. 72 22. 11 5. 17 0. 45 6. 51 46. 57 2. 33 38. 97 4. 515 4338 8127	3
1	GEORGIA	"	"	"	"
1	Chattooga Co.	Little River.	Lump over 1 1/2"	3. 80 15. 88 65 83 14. 49 1. 27 4. 32 70. 59 1. 09 8. 24 7106 6866 12791	3
1	ILLINOIS.	"	"	"	"
1	O'Fallon, Ill.	Belville.	Lump and nut.	9. 75 37 48 39 57 13. 20 4. 10 5. 31 59. 72 1. 03 16. 64 6125 6031 11025	1
2	"	"	Slack.	12. 03 31. 86 33. 67 22. 44 4. 00 5. 04 50. 22 0. 72 17. 58 5083 5124 9149	1
4	"	"	Lump.	12. 91 31. 90 43. 55 11. 64 1. 32 5. 43 60. 74 1. 15 19. 72 6002 5959 10804	1
5	Madison Co.	"	Washed slack.	17. 02 30. 60 35. 59 16. 79 3. 29 5. 50 50. 77 1. 11 11. 51 77 9319	1
3	Williamson Co.	Carterville.	Run-of-mine.	8. 50 29. 47 50. 75 11. 28 1. 72 5. 09 65. 48 1. 39 15. 04 6542 6436 11776	1
6	Montgomery Co.	No. 5. coal.	"	14. 43 29. 48 42. 81 13. 28 4. 01 5. 49 54. 59 1. 11 21. 52 5591 5465 10064	1
14	Sangamon Co.	"	Lump over 1 1/2"	11. 93 29 99 43 90 14. 18 4. 29 5. 21 56. 94 1. 01 18. 37 5724	2
26	Logan Co.	"	Run-of-mine.	12. 77 34. 68 40. 77 11. 78 4. 16 5. 49 58. 74 1. 09 18. 74 5976	2
29 A	Madison Co.	"	Screenings through 2"	15. 08 32. 41 39. 72 12. 09 3. 51 5. 56 56. 76 1. 06 21. 02 5675 5743 10215	3
29 B	"	"	Run-of-mine.	13. 10 30. 73 40 12 16. 00 4. 17 5. 26 54. 26 0. 89 19. 42 5546	3
34 A	Saline Co.	"	Screenings over 1 1/2"	12. 36 33. 44 41 76 12. 44 4. 40 5. 41 57. 74 0. 90 19. 12 5941	3
34 B	"	"	Run-of-mine.	9. 33 30. 92 47 86 11. 89 2. 76 5. 12 62. 85 1. 29 16. 09 6429	3
7 B	Madison Co.	"	Nut over 1"	7. 81 33 54 50 27 8. 38 2. 36 5. 31 67. 40 1. 44 15 11 6899	3
7 D	"	"	Run-of-mine.	11. 46 34. 98 36 25 17. 31 4. 40 5. 05 94. 56 0. 94 17. 74 5570	3
9 C	Macapin Co.	No. 6 coal.	Slack.	10. 83 36. 24 39 38 59 13. 18 4. 53 3. 58 35. 58 0. 99 17. 37 6009	2
12	Williamson Co.	"	Run-of-mine.	15. 25 28. 47 40 83 15 35 3. 81 5. 22 63. 95 0. 82 20. 85 5439 5344 9790	3
12 B	"	"	Size 5, washed.	8. 20 32. 26 46 59 12 95 3. 48 5. 60 62. 52 1. 10 14. 86 6312	2
13	Franklin Co.	"	Egg through 6" and over 1 1/2"	15. 87 28 19 46 42 9. 52 2. 34 5. 60 59 66 1. 06 21. 82 5991 5862 10784	3
15	Marion Co.	"	Lump over 6"	8. 31 31. 65 49 56 10 48 1. 55 5. 18 65. 83 1. 48 15. 48 6315	2
20	Macapin Co.	"	Screenings.	9. 95 34. 76 42 06 13 23 3. 87 5. 25 59. 64 1. 04 16. 97 6089	3
21	Madison Co.	"	Lump over 2 1/2"	14. 08 31 32 40 32 13 68 3 88 5 41 55 2 1 00 20 82 5585 5517 10053	3
22 A	"	"	Lump over 4"	15. 54 31 26 42 27 10 93 1. 38 5 59 58 0 2 1 09 22 99 5837 5655 10507	3
22 B	"	"	Nut, pea and slack through 2"	11. 91 35 65 39 43 13 01 5 34 5 21 57 35 1 00 18 09 5897 5771 10615	3
				13. 03 32 65 39 79 14 53 4 35 5 25 55 94 0 89 19 04 5662 5607 10192	3

1 = Professional Paper 48, U.S.G.S.

2 = Bulletin No. 290, U.S.G.S.

3 = Bulletin No. 332, U.S.G.S.

4 = Bulletin No. 9, Ohio Geological Survey.

5 = Bulletin No. 5, Bureau of Mines.

ANALYTICAL TABLES

Coal.	County or Location.	Steam or Bed.	Kind of Coal.	Moisture.	Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Determined Calories.	Calculated Calories.	Determining B. T. U.	Authority.
<i>ILLINOIS—Continued</i>																
23 A	Madison Co.	No. 6 coal.	Lump over 5"	13.47	34.35	40.65	11.53	4.41	5.63	57.61	0.91	19.91	5839	5836	10510	3
24 B	"	"	Slack through 2"	15.68	31.28	37.45	15.59	3.98	5.42	89.00	0.90	21.22	5304	5317	9655	3
25 B	Clinton Co.	"	Lump over 5 1/2"	11.44	33.93	43.92	10.71	4.94	5.39	60.06	1.02	17.88	6088	6049	10958	3
27	"	"	Lump over 1 1/2"	11.35	34.62	40.63	13.40	4.76	5.11	57.36	1.05	18.02	5963	5831	10733	3
31	Sangamon Co.	"	Run-of-mine.	16.00	32.41	37.82	13.77	4.05	5.55	53.89	0.91	21.83	5522	5417	9940	3
8	St. Clair Co.	"	Screenings over 1 1/2"	13.10	32.16	41.49	13.25	3.66	5.44	57.31	1.03	19.31	5774	10363	3
9 A	Montgomery Co.	"	Nut.	13.20	34.33	39.94	12.53	4.47	5.51	57.25	1.02	19.22	5841	10514	2
9 B	Macoupin Co.	"	Run-of-mine.	13.54	35.69	40.03	10.74	4.03	5.71	58.69	0.95	19.88	6004	5946	10807	2
10	"	"	Lump.	13.72	36.24	39.72	10.32	3.96	5.74	58.95	0.98	20.05	6039	10870	2
11 A	Franklin Co.	"	Slack.	9.50	31.98	47.08	11.44	1.45	3.51	63.83	1.36	16.61	6392	11506	2
11 B	Williamson Co.	Big Muddy.	1/2 screenings 1/2 egg.	7.76	31.44	50.19	10.61	1.97	5.14	66.55	1.32	14.41	6643	11957	2
11 C	"	"	1/2 run-of-mine, 1/2 lump.	8.86	31.25	48.23	11.66	2.46	5.24	64.29	1.29	15.05	6501	11702	2
19 A	"	"	1/2 No. 5 washed, 1/2 No. 4 washed	8.61	32.40	51.33	7.66	1.65	5.38	68.14	1.34	15.83	6798	12236	2
19 B	Franklin Co.	"	3/4 coal over 3 1/2"	14.91	26.66	49.50	8.93	0.52	5.42	62.76	1.35	21.02	6088	10958	2
16	"	"	3/4 coal over 1 1/2"	10.72	29.86	50.06	9.36	0.91	5.30	66.74	1.40	16.29	6492	11686	2
28 C	Williamson Co.	No. 7 coal.	Lump and egg.	8.43	30.08	51.89	9.60	1.14	5.18	67.33	1.50	15.25	6644	11959	2
30	St. Clair Co.	"	Lump over 3"	7.78	29.85	52.39	9.98	1.32	5.06	67.45	1.21	14.98	6644	11959	3
18	La Salle Co.	No. 2 coal.	Nut through 3" and over 2"	11.69	35.70	39.42	13.19	1.38	5.46	57.15	0.94	18.88	5944	10699	3
	"	"	Lump over 6"	12.39	36.89	41.80	8.92	3.92	5.85	61.29	1.00	19.02	6333	11399	2
<i>INDIANA</i>																
1	Sullivan Co.	No. 6 coal.	Run-of-mine.	11.40	33.81	41.39	13.40	2.50	5.37	60.34	1.18	17.21	6145	6044	11061	1
10	Park Co.	"	Lump over 1 1/2"	10.72	39.29	41.42	8.57	3.83	5.86	63.48	1.16	17.10	6537	11767	2
13	Vigo Co.	"	Run-of-mine.	12.97	37.45	39.67	12.09	3.18	5.58	59.84	0.82	18.49	6055	6033	10899	3
2	Warwick Co.	No. 5 coal.	"	9.62	36.14	41.22	13.02	4.43	5.33	60.70	1.20	15.32	6179	6180	11122	1
3	"	"	Nut and slack.	13.18	31.92	39.27	15.63	4.79	5.36	54.52	1.08	18.62	5572	10030	2
7 A	"	"	Lump over 1 1/2"	8.90	38.52	43.37	9.21	3.74	5.61	65.54	1.20	14.70	6671	12908	2
7 B	"	"	Screenings through 1 1/2"	11.12	36.98	42.55	9.35	3.78	5.63	63.01	1.13	17.10	6416	11549	2
12	"	"	Run-of-mine.	10.57	35.03	42.75	11.65	3.87	5.40	61.11	1.17	16.80	6239	6161	11266	3
16	Greene Co.	"	"	10.30	36.31	41.64	11.75	4.23	5.38	61.00	1.06	16.58	6282	6164	11218	3
17	Knox Co.	"	"	12.08	32.48	44.11	10.23	3.65	5.34	60.45	0.89	18.65	6117	11011	3
18 B	Pike Co.	"	Lump over 1 1/2"	11.13	35.11	46.78	6.98	1.64	5.65	66.94	1.34	17.45	6684	12031	3
4	Sullivan Co.	"	Screenings through 1 1/2"	13.99	29.40	42.29	14.32	2.31	5.36	57.18	1.11	19.72	5732	10318	2

5	Sullivan Co.	?	Run-of-mine.	12.03 35.65 41.44 10.88 14.27 5.50 60.73 1.08 17.54 6218 6144 11192	2
6	"	?	"	10.80 36.09 40.49 12.62 4.39 5.46 60.88 1.13 15.52 6214	2
11	"	No. 4 coal.	Lump over 1½" and 3"	12.15 33.48 46.23 8.14 1.41 5.46 64.92 1.38 18.69 6534	2
15	Greene Co.	"	Run-of-mine.	13.58 32.07 46.20 8.15 0.91 5.65 63.53 1.42 20.34 6344	3
8	Vigo Co.	?	Lump over 1½"	9.55 36.19 43.65 10.61 3.72 5.69 64.08 1.08 15.02 6533	11419
9A	"	No. 7 coal.	"	12.82 34.80 42.10 3.30 3.27 5.66 61.16 1.03 18.58 6177	11119
9B	"	"	Run-of-mine.	13.53 34.80 40.91 10.78 3.15 5.78 59.64 1.06 19.61 6082 6037 10948	3
14	"	No. 3 coal.	"	7.88 36.85 41.07 14.20 5.14 5.22 59.75 0.93 14.76 6192	11146
20	Clay Co.	Brazil Block.	Screenings through 1½"	16.91 26.85 38.87 17.37 1.89 5.48 52.97 1.01 21.28 5291	6524
INDIAN TERRITORY					
1	Henrietta, I. T.		Lump and slack.	7.04 34.55 48.40 10.01 1.92 5.34 67.55 1.25 13.93 6779 6741 12202	1
2	Harishorne, I. T.		Run-of-mine.	4.45 36.15 48.40 11.00 1.52 5.17 69.49 1.67 11.15 7004 6952 12607	1
3	Choctaw, Okla.		"	4.61 37.00 47.25 11.14 3.63 4.92 67.37 1.48 11.46 6844 6729 12319	1
4	Lehigh, I. T.		Pea and slack.	8.29 30.61 36.05 95.05 3.95 4.37 50.98 1.19 14.46 5061 5000 9110	1
5	"		Lump.	6.24 37.26 43.29 13.21 3.96 4.93 62.34 1.36 14.20 6238 6212 11228	1
9	Panama.	?	Run-of-mine.	5.11 13.65 73.21 8.03 1.18 1.65 78.37 1.60 6.17 7590 7696 13662	3
IOWA					
1	Wapello Co.		Run-of-mine.	8.24 30.74 45.02 16.00 5.03 4.81 59.82 0.94 13.40 6126 6031 11027	1
2	Marion Co.		"	14.21 33.17 37.40 15.22 4.66 5.50 54.08 1.31 19.23 5566 5540 10019	1
3	Polk Co.	Big Vern.	Lump.	13.88 36.94 35.17 14.01 6.15 5.25 54.68 0.84 18.80 5691 5656 10244	1
4	Centerville, Ia.	Mystic Coal.	"	14.08 35.59 39.37 10.96 4.26 5.57 58.49 0.90 19.82 5957 5888 10723	1
5	Lucas Co.		Run-of-mine.	15.39 30.49 41.49 12.63 3.19 5.74 55.81 1.14 21.49 5690 5634 10242	1
KANSAS					
1	Crawford Co.	Lower	Run-of-mine.	4.99 32.68 49.36 12.97 4.28 4.98 67.34 1.08 9.35 6801 6850 12242	1
2	"	Weir	Lump and nut.	4.18 31.23 46.68 17.91 6.27 4.69 61.88 0.92 8.33 6468 6397 11642	1
3	Cherokee Co.	Pittsburg	Run-of-mine.	2.50 33.80 51.25 12.45 5.68 4.91 69.07 1.20 6.69 7166	12900
5	"	Weir Pittsburg.	Lump and nut.	4.10 31.65 53.71 10.54 3.77 5.10 70.25 1.06 9.28 7164 7120 12895	1
6	Linn Co.	"	Lump over 1½"	9.04 29.69 45.55 15.12 9.78 72.51 0.61 60.99 1.06 13.50 6190 6156 11142	3
4	Atchison Co.		Lump	6.95 35.70 45.16 12.19 8.04 5.25 62.74 1.04 10.74 6614 6600 11905	1
5	West Mineral, Kan.	?	Over ¾"	4.10 31.65 53.71 10.54 3.77 5.10 70.25 1.06 9.28 7164	12895
D 23	Crawford Co.	Cherokee.	Run-of-mine.	5.75 33.28 47.29 13.68 3.07 5.01 66.68 1.15 8.41 6721 6866 12098	5
KENTUCKY					
1	Bell Co.	Straight Creek.	Run-of-mine.	3.10 36.12 56.39 4.39 1.22 5.43 77.37 1.83 9.76 7860 7729 14148	1
1	"	No. 11.	"	5.21 37.47 53.10 8.22 1.12 5.28 73.08 1.67 10.63 7341	13214
2	Hopkins Co.		Run-of-mine.	7.91 37.04 45.02 9.13 3.62 5.85 81.22 14.74 6778 6655 12200	1
4	Webster Co.		"	5.27 35.07 48.14 18.44 5.34 4.71 64.65 1.24 10.68 6639 6490 11950	1

Coal.	County or Location.	Seam or Bed.	Kind of Coal.	Moisture.	Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Determined Calories.	Calculated Calories.	Determined B. T. U.	Authority.
KENTUCKY—Cont.																
3	Hopkins Co.	Bed No. 9	Run-of-mine	7.92	36.09	45.93	10.06	3.52	5.39	65.29	1.40	14.34	6679	6598	12022	1
9	Muhlenburg Co.	"	Lump over 1½"	8.47	35.24	46.81	9.48	3.60	5.24	65.77	1.28	14.63	6659	11986	2
7	Ohio Co.	"	Nut through 1½" and over ¾"	8.70	35.00	47.34	8.96	3.14	5.61	65.63	1.20	15.46	6710	12078	3
5	Big Black Mtn.	High Splint	Run-of-mine	4.36	35.02	56.92	3.70	0.67	5.16	77.44	1.57	11.46	7735	7758	13923	2
6	Johnson Co.	No. 1	"	5.12	36.49	55.63	2.76	0.57	5.47	77.20	1.45	12.55	7635	7593	13743	2
8	Union Co.	No. 1 B.	"	5.46	30.99	55.63	7.92	1.18	5.07	72.59	1.19	12.05	7355	13239	3
MARYLAND																
1	Garrett Co.	?	Run-of-mine	2.33	16.11	68.43	13.13	1.49	3.99	75.21	1.29	4.89	7364	7275	13255	2
MISSOURI																
1	Rates Co.	Run-of-mine	8.33	33.58	58.73	19.36	5.25	4.97	57.00	0.94	12.48	5881	5896	10586	1
2	Macon Co.	Bever Coal.	"	11.50	33.63	58.01	16.86	5.16	5.12	54.79	0.96	17.11	5655	5570	10179	1
10	"	"	Screenings through ¾"	15.23	26.32	57.95	20.50	3.69	5.02	49.41	0.84	20.54	5055	9099	3
3	Putnam Co.	Mendota Coal.	"	15.71	28.62	54.89	20.78	3.69	5.23	48.87	0.82	20.61	4911	4948	8840	1
4	Morgan Co.	?	Run-of-mine	12.67	41.45	41.05	4.83	5.12	6.18	66.87	0.69	16.31	6937	6946	12487	1
5	Randolph Co.	?	"	12.92	33.64	59.82	13.62	5.03	5.43	57.16	0.90	17.86	5860	5834	10548	3
6	Adair Co.	?	Lump over 6"	13.80	34.29	40.17	11.74	5.60	5.48	58.09	0.96	18.13	5998	5926	10796	3
7	"	?	No. 1 nut	16.36	29.12	35.01	19.51	3.53	5.23	49.44	0.87	21.42	5004	4953	9007	3
7	"	?	No. 2 nut	16.39	29.01	34.42	20.18	3.12	5.28	49.03	0.91	21.48	4970	4924	8946	3
MONTANA																
1	Red Lodge, Mont.	Black lignite.	Washed nut.	11.05	35.90	42.08	10.97	1.73	5.37	59.08	1.33	21.52	5855	5739	10539	1
3	Carbon Co.	?	Lignite	8.51	31.58	44.52	15.39	0.60	4.96	58.96	1.10	18.99	5821	5670	10478	3
3	"	?	"	8.56	32.36	45.69	13.39	0.54	5.06	60.39	1.06	19.56	5936	5795	10685	3
NEW MEXICO																
1	McKinley Co.	No. 3 or 3½	Lump and slack	12.29	34.58	46.14	6.99	0.63	5.82	63.31	1.03	22.22	6251	6177	11252	1
2	"	Thatcher and Otero.	Slack	10.79	33.82	36.73	18.66	1.26	5.22	55.07	0.95	18.84	5504	5468	9907	1
3	Colfax Co.	(Main Raton	Run-of-mine	3.45	32.00	47.82	16.67	0.73	4.95	66.19	1.23	10.23	6607	6629	11893	3
2	"	or	Lump over ¾"	2.75	33.19	48.54	15.52	0.64	4.84	67.70	1.18	10.12	6759	6715	12166	3
2	"	Lower	Slack through ¾"	4.36	32.21	47.31	15.32	0.83	4.79	65.96	1.18	11.32	6618	6509	11912	3
4	"	Laramie	Run-of-mine	2.78	34.31	48.34	11.37	0.61	5.06	68.51	1.51	9.74	6830	6873	12294	3

4 B	Colfax Co.	{ Main Raton or } { Lower Laramie }	Slack through 1 1/2"	3. 38 34. 63 48. 45 13. 54 10. 61 5. 13 68. 67 1. 50 10. 55 69 14. 68 75 12 45	3
5	"	"	Run-of-mine.	2. 72 31. 58 50. 86 14. 57 0. 69 4. 88 69. 96 1. 17 8. 73 69 60 69 74 12 39	3
D 31	Socorro Co.	Carthage.	"	2. 96 37. 20 45. 12 14. 72 0. 79 4. 78 67. 73 1. 26 10. 71 67 86 66 76 12 15	5
NORTH DAKOTA					
1	Stark Co.	"	Screened coal.	35. 38 29. 59 25. 68 9. 35 1. 55 6. 61 40. 23 0. 54 41. 72 38 40 37 67	1
1 B	"	"	Brown lignite.	32. 64 29. 19 26. 75 11. 42 3. 54 6. 15 39. 53 0. 49 38. 87 38 72	2
2	Williston, N. D.	"	Screened.	36. 78 28. 16 29. 97 5. 09 0. 48 6. 93 41. 87 0. 69 44. 94 40 02 38 49	2
2 B	Williams Co.	"	Run-of-mine.	36. 13 29. 28 29. 55 5. 04 0. 59 6. 60 42. 00 0. 73 45. 04 40 70 37 41	2
3	McLean Co.	"	Lump.	35. 96 31. 92 24. 37 7. 75 1. 15 6. 54 41. 43 1. 21 41. 92 39 27 38 21	2
OHIO					
1	Jackson Co.	No. 4	Run-of-mine.	7. 71 38 32. 42 02 11. 95 4. 61 5. 41 62. 49 1. 11 14. 43 63 97 63 85 11 51 5	2
9 A	Vinton Co.	"	Lump over 1 1/2"	5. 59 30. 86 49. 26 8. 29 3. 15 4. 88 69. 76 1. 18 12. 74 70 96 68 41 12 73	2
9 B	"	"	Nut and slack.	8. 10 30. 87 43. 10 11. 93 3. 35 5. 15 63. 54 1. 06 14. 97 64 24	2
0 4	(See Note 1).	"	Mine sample.	5. 34 38. 94 44. 92 10. 80 4. 33 5. 30 65. 01 1. 25 13. 31 66 37 66 05 11 94 7	4
2	Jackson Co.	No. 5	Run-of-mine.	9. 01 35. 85 43. 80 11. 34 4. 02 5. 38 62. 79 1. 20 15. 27 63 86 63 60 11 94 5	2
10	Tuscarawas Co.	"	Lump over 1 1/2"	4. 49 40. 55 47. 43 7. 53 2. 93 5. 68 69. 64 1. 29 12. 93 71 99 70 92 12 95 8	3
0 5	(See Note 2).	"	Mine sample.	6. 18 37. 15 48. 80 7. 87 3. 26 5. 44 68. 65 1. 26 13. 52 69 88 69 11 25 7 8	4
3	Perry Co.	No. 6	Run-of-mine.	9. 90 35. 66 44. 86 11. 58 1. 81 5. 28 63. 06 1. 23 17. 04 62 65 62 22 11 27 7	2
8	"	"	"	7. 55 38. 00 46. 08 8. 37 2. 84 5. 48 67. 02 1. 29 15. 00 67 38 67 23 12 18	2
0 6	(See Note 3).	"	Mine sample.	5. 56 38. 11 48. 96 7. 36 3. 30 5. 43 69. 03 1. 29 13. 62 69 80 69 35 12 50 4	4
4	Jefferson Co.	No. 8	3/4" coal over 3/4"	3. 53 37. 45 49. 90 9. 12 3. 47 5. 15 71. 66 1. 31 9. 29 72 62	2
5	"	"	3/4" coal over 1/2"	4. 34 35. 53 52. 83 7. 30 1. 72 5. 21 72. 65 1. 42 11. 70 73 21	2
6	Belmont Co.	"	Run-of-mine.	5. 31 36. 72 49. 45 8. 52 3. 35 5. 89 70. 71 1. 12 10. 93 71 55 71 74 12 84 3	2
11	"	"	Lump over 1 1/2"	3. 44 36. 04 47. 58 12. 94 4. 32 4. 81 66. 64 1. 17 10. 12 68 26	2
12	"	"	Run-of-mine.	4. 14 39. 30 47. 18 9. 38 3. 96 5. 19 69. 58 1. 20 10. 69 71 52 70 38 12 87 4	3
0 8	(See Note 4).	"	Mine sample.	4. 70 36. 35 49. 87 9. 10 3. 81 5. 20 68. 99 1. 13 11. 17 69 77 69 45 12 59 9	2
7	Guernsey Co.	No. 7	Lump over 1 1/2"	6. 65 33. 94 88. 10 55 3. 13 5. 07 67. 38 1. 20 12. 44 67 66	4
0 7	(See Note 5).	"	Mine sample.	7. 97 32. 93 49. 48 10. 31 1. 62 5. 18 65. 32 1. 28 16. 30 65 04 63 98 11 70 7	4
0 7	(See Note 6).	"	"	5. 28 39. 81 47. 13 7. 78 3. 80 5. 47 68. 38 1. 25 13. 32 69 68 69 19 12 54 2	4

Note 1 = Average of 17 samples from Lawrence, Scioto, Jackson, and Vinton counties.
 Note 2 = Average of 9 samples from Lawrence, Jackson, Perry, Muskingum, Jefferson, Tuscarawas, and Mahoning counties.
 Note 3 = Average of 65 samples from Lawrence, Gallia, Athens, Vinton, Hocking, Perry, Muskingum, Coshocton, Tuscarawas, Carroll, Holmes, Stark, and Columbiana counties.
 Note 4 = Average of 32 samples from Gallia, Athens, Morgan, Belmont, Jefferson, and Harrison counties.
 Note 5 = Average of 8 samples from Lawrence, and Gallia counties.
 Note 6 = Average of 4 samples from Muskingum and Coshocton counties.

5	Morgan Co.	Brushy Mountain	5.59.33.62.51.03	9.76.3.23.5.24.70.08.1.62.10.07.7135.7107.12841	3	
6	Cumberland Co.	Lower Sewanee	3.80.27.61.34.07.14.43.0.78.4.84.70.04.0.98	8.93.6952.6959.12514	3	
7 A	Fentress Co.	Wildor	3.03.34.91.49.21.12.85.3.26.5.03.69.26.1.27	8.33.7001.7043.12602	3	
8 A	White Co.	First above	2.63.33.51.50.44.13.42.4.38.4.89.69.32.1.15	6.84.7064.7092.12715	3	
8 B	"	Sewanee	3.12.32.91.49.85.14.12.4.74.4.68.68.20.1.23	7.03.6954.6927.12517	3	
9 A	Grundy Co.	Run-of-mine	3.92.27.23.54.76.14.00.0.94.4.81.69.97.1.29	8.90.6949.6950.12508	3	
9 B	"	Lump over 1"	5.68.25.36.50.41.18.55.0.74.5.02.64.58.1.20	9.91.6378.6537.11480	3	
9 C	"	Raw slack	4.68.28.75.57.31.9.26.0.65.5.04.73.85.1.24	9.96.7313.7288.13163	3	
11	Cumberland Co.	Slack through 1 1/2"	3.53.20.75.47.85.27.87.0.90.4.13.59.07.1.10	6.83.5702.5931.10264	3	
TEXAS						
1	Houston Co.	Screened over 1/2"	34.70.32.23.21.87.11.20.0.79.6.93.39.25.0.72.41.11.39.20.3805	7056	1	
3	Milam Co.	Lump over 1/2"	31.06.27.67.33.39	7.88.0.99.6.53.44.7.0.90.39.00.4372.4203	7870	3
4	"	Run-of-mine	33.85.27.50.31.35	7.30.0.51.6.68.43.12.0.71.41.68.4163.4002	7497	3
1	Carbon Co.	Run-of-mine	6.05.42.02.47.06	4.87.0.55.5.76.72.32.1.38.15.12.7306.7189.13151	3	
UTAH						
1	Lee Co.	Wilson	4.06.34.93.56.28	4.73.1.20.5.32.76.59.1.24.10.92.7681.7577.13826	2	
2	"	McConnell	3.35.35.13.55.94	5.58.0.92.5.19.77.02.1.42.9.87.7740.7608.13932	2	
3	Wise Co.	Upper Banner	3.05.31.65.60.82	4.48.0.67.5.17.80.35.1.59.7.74.8039.	14470	
4	Lee Co.	Darby	4.35.36.89.54.43	4.33.0.79.5.25.76.99.1.32.11.32.7744.	13639	
5 A	Montgomery Co.	Big Seam	4.80.10.12.67.05	18.03.0.63.3.91.69.27.0.66.7.50.6645.6635.11961	3	
5 B	"	Pea	7.52.10.29.65.96	16.23.0.65.4.37.69.05.0.69.9.01.6607.	11893	
6	Tazewell Co.	No. 4	5.62.23.07.61.52	9.79.1.21.4.78.73.35.1.26.9.61.7369.7188.13264	3	
WASHINGTON						
1 A	King Co.	Pea	16.04.31.39.41.04	11.53.0.61.5.57.56.51.1.16.24.62.5521.5438.9938	3	
1 B	"	Run-of-mine	14.30.33.03.41.30	11.37.0.72.5.73.57.27.1.17.23.74.5671.5595.10208	3	
2	Kittitas Co.	Lump	3.16.36.49.48.09	12.26.0.38.5.13.69.35.1.24.11.62.6992.6879.12386	3	
D 20	Pierce Co.	Run-of-mine	4.66.29.07.50.31	15.96.0.45.4.95.67.18.2.11.9.35.6740.6740.12132	5	
D 21	Kittitas Co.	Roslyn	7.82.33.06.44.94	14.18.0.45.5.48.64.67.1.41.13.81.6613.6529.11903	5	
WEST VIRGINIA						
1	Marion Co.	Pittsburgh	1.75.36.77.55.14	6.34.0.90.5.28.78.00.1.54.7.94.7837.7801.14107	1	
2	Clarksburg, W. Va.	"	1.95.39.94.50.25	7.86.3.48.5.13.74.07.1.36.8.10.7661.7479.13790	1	

* Sample from about 6 tons of coal.
 Note 7 = Average of 6 samples from Gallia and Meigs counties.
 Note 8 = Average of 19 samples from Washington, Noble, Morgan, Belmont, and Harrison counties.

ANALYTICAL TABLES

Coal.	County or Location.	Seam or Bed.	Kind of Coal.	Moisture.	Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Determined Calories.	Calculated Calories.	Determined B. T. U.	Authority.
W. VIRGINIA—Cont.																
15	Harrison Co.	Pittsburg	Run-of-mine.	2.01	37.31	52.13	8.55	2.54	5.08	75.83	1.43	6.57	7673	13811	2
16	Marion Co.	"	"	5.57	31.61	54.45	8.37	1.20	5.08	72.74	1.46	11.15	7274	13093	2
3	Morgantown, W. Va.	Upper Freeport.	Run-of-mine.	2.29	29.86	57.62	10.23	1.06	4.99	75.13	1.42	7.17	7532	7506	13558	1
4	Preston Co.	"	"	1.48	28.58	61.55	8.39	0.90	4.49	77.82	1.48	6.52	7816	7711	14069	1
4	"	Freeport.	"	3.91	26.68	59.30	10.11	1.07	4.60	74.73	1.56	7.84	7428	13370	2
5	Randolph Co.	Upper Freeport.	Screened over 1½"	1.45	28.97	59.48	10.10	0.98	4.53	75.75	1.47	6.87	7621	7510	13718	1
6	Fayette Co.	Quinnomont.	Run-of-mine.	1.53	21.54	71.88	5.05	0.65	4.76	82.87	1.68	4.99	8226	8134	14807	1
7	"	Sewell.	"	3.94	19.88	71.25	4.93	1.16	4.60	79.78	1.01	8.52	7990	7688	14382	1
8	"	"	"	2.96	22.74	69.29	5.01	0.89	4.81	81.64	1.57	6.08	8014	14425	2
8	"	Amsted.	"	4.16	31.28	57.39	7.17	0.90	5.32	76.70	1.34	8.57	7659	7679	13786	1
13	"	"	"	3.74	31.04	61.31	3.91	0.89	5.31	80.50	1.22	8.07	8020	14436	2
9	"	Powellton.	"	4.08	28.61	60.73	6.58	0.77	5.23	76.89	1.58	8.95	7736	7645	13925	1
10	Mercer Co.	No. 6 bed.	"	1.75	18.59	75.08	4.58	0.56	4.65	84.97	1.06	4.18	8346	8299	15023	1
11	McDowell Co.	No. 3 or Pocahontas.	"	4.07	16.34	68.47	11.12	0.51	4.27	76.51	1.00	6.59	7505	7379	13509	1
12	"	Tug River or No. 8.	"	1.72	17.85	73.56	6.87	0.68	4.43	82.71	1.33	3.98	8065	8054	14751	1
14	Fayette Co.	Eagle.	"	5.09	29.07	62.57	3.27	1.03	5.33	78.23	1.51	10.63	7839	7723	14110	2
17	Preston.	Bakerstown.	"	3.46	27.29	61.13	8.12	1.45	4.68	76.98	1.37	7.40	7705	13869	2
18	Mingo Co.	Local Glen Alum.	"	2.86	33.23	58.08	5.83	0.67	5.01	78.38	1.43	8.68	7836	7700	14106	2
20	Kanawha Co.	Keystone.	"	2.82	32.20	56.95	8.03	1.38	5.16	76.74	1.34	7.35	7648	13766	2
21	"	Winifrede.	"	3.57	36.38	55.27	4.85	1.32	5.33	77.49	1.49	9.52	7749	7718	13948	2
22 B	"	"	"	3.42	33.49	55.27	7.82	0.83	5.27	74.49	1.20	10.39	7492	13486	3
23 A	"	Cedar Grove.	"	2.05	34.71	55.14	8.10	1.35	5.08	75.56	1.18	8.73	7615	7510	13707	3
23 B	"	"	Slack through 1½"	3.25	34.61	54.56	7.58	1.22	5.23	75.27	1.43	9.27	7513	13523	3
25	"	Black Band.	Lump over 1½"	4.21	35.41	53.16	7.22	0.64	5.16	72.89	1.40	12.69	7453	13379	3
WYOMING																
1	Sheridan Co.	"	Lump.	22.63	35.68	37.19	4.50	0.59	6.39	54.91	1.02	32.59	5408	5247	9734	1
2 B	Camden, Wyo.	?	Run-of-mine.	8.93	36.52	33.76	20.79	4.03	4.88	53.33	0.81	16.16	5556	5585	10001	2
4	Carbon Co.	"	"	11.30	40.32	41.07	7.31	0.28	5.66	61.24	0.88	24.79	5975	5806	10755	3
5	Sweetwater Co.	Rock Springs	"	11.64	36.37	48.58	3.41	0.81	5.72	66.08	1.43	22.53	6538	6557	11768	3
6	Uinta Co.	"	"	19.00	36.64	41.24	3.12	0.49	6.41	59.38	0.98	29.62	5726	5743	10307	3
D 33	Sweetwater Co.	No. 7.	"	8.64	38.47	48.30	4.59	1.09	5.53	69.55	1.53	17.71	6764	6788	12175	5

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