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Comparison of Methods for Determination of Volatile Matter and Ash in Coal

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COMPARISON OF METHODS FOR DETERMINATION OF VOLATILE MATTER AND ASH IN COAL

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ABSTRACT

This study was undertaken as part of the effort to standardize national and international methods of testing coal. Methods for the determination of volatile matter and ash in coal are empirical in nature, and details of the methods used vary considerably in different countries.

This report presents (1) determinations for volatile matter obtained by four methods, two American and two European, and (2) determinations for ash at two different final temperatures as well as at certain different rates of heating.

For volatile matter the results indicate that the slower the rate of heating, the lower will be the results obtained. Ash values obtained at the two final temperatures tried compare favorably, but too rapid a rate of heating for coals containing appreciable amounts of calcite and pyrite gives ash values which are too high.

INTRODUCTION

For many years the Illinois State Geological Survey has cooperated actively in the work of Committee D-5, Coal and Coke, of the American Society for testing Materials, whose goal is establishment of national standard methods for the analysis of coal and coke. More recently, we have also shared in the participation of Committee D-5 with the International Organization for Standardization, Technical Committee 27 (Solid Mineral Fuels), which is attempting to establish international standard methods for analyzing coal and coke. This latter activity has brought to our attention a large amount of information regarding methods used in other countries and proposals which are being advanced for International Standards.

As might be expected, methods and proposals from other countries often differ considerably from those accepted as standard in the United States. The differences frequently are not so much in fundamental design as in details of procedure. However, coal analysis methods are largely empirical in nature so that details are of prime importance. In this connection, therefore, it becomes necessary to compare methods which differ in detail in order to learn how much the differences influence results and whether or not the methods are applicable to a wide range of coals.

Methods have been found to differ considerably for the determinations of volatile matter and ash of coal. Methods in use in various countries for the determination of volatile matter vary in specified temperature of heating from 875 °C to 1040°C. and in time of heating from seven minutes to 20 minutes. Methods for determining ash specify temperatures from 700° to more than 850°C. A temperature of 815°C. is under consideration as an international standard. This is higher than the American standard specification of 700-750°C. Furthermore, there is difference of opinion as to the proper rate of heating for the determination of ash in coals high in calcite and pyrite.

For the volatile matter determination, we have compared four methods; for the ash, we have compared two final temperatures of determination. Furthermore, we have studied the effect of rate of heating on the ash determination. This report covers results of these studies.

VOLATILE MATTER

Volatile matter in coal and coke is defined by the American Society for Testing Materials (ASTM D 120-30, 1954) as "those products, exclusive of moisture, given off by a material as gas or vapor, determined by definite prescribed methods which may vary according to the nature of the material." It is one of the important determinations in the proximate analysis for use in certain classification systems and for evaluating coals as to combustion and coking characteristics.

The determination of volatile matter in coal is empirical, requiring rigidly specified conditions. Differences in temperature and in time or rate of heating are known to influence results beyond permissible tolerances. To meet the need for definite specifications, the American Society for Testing Materials in the United States sponsors two standard methods (ASTM D 271-48, 1954). The first, commonly referred to as the standard method, consists of heating the coal at a rapid rate in a vertical tube furnace maintained at 950°C.±20°C. The other method, commonly referred to as the modified method, consists of heating the coal in the same furnace at a considerably slower rate. Two methods are necessary because certain solid fuels (such as subbituminous coal, lignite, peat, certain cokes, chars, anthracites, and semianthracites) spark appreciably when heated at the rapid rate, causing high values through mechanical loss. By the slower rate of heating used in the modified method, sparking is reduced to a minimum.

Unfortunately, the two ASTM standard methods may not give the same results. The modified method frequently gives results as much as three percentage units lower than the rapid heating procedure. Because of this, it is not satisfactory to compare coals, some of which are analyzed by the standard method and some by the modified method.

At the present time, Technical Committee 27, Solid Mineral Fuels, of the International Organization for Standardization is attempting to establish international standard methods for the determination of volatile matter. The Illinois State Geological Survey is interested in the problem from the standpoint of establishing national and international standards, in addition to its own research program. Hence, we have compared the American, British, and Franco-Belgian methods, the last two of which have been proposed as international standards.

Equipment

The equipment used in this comparison was that specified by the American Society for Testing Materials for the American methods (ASTM D 271-48, 1954); by the British Standards Institution for the British method (BSI 1016-1942, 1942); and by the Association Francaise de Normalization for the Franco-Belgian method (AFN NF-M-03-004, 1950). Briefly, equipment used for the three methods is described as follows:

(1) For the American methods: Platinum crucibles of 15 ml. capacity with tightly fitting capsule lids were used for both the standard and modified methods. Heating was done in a vertical tube or volatile-matter furnace, commonly known as the Fieldner furnace.

(2) For the British single-crucible method: Fused-silica cylindrical crucibles with capsule-type lids were obtained from England for this method. Heating was done in an electric muffle furnace. A refractory stand or "gas mantle" was used to hold the crucible in the furnace. Two discs of asbestos, each one mm. thick were placed between the bottom of the crucible and the inside projections of the three legs of the stand. Mounting the crucible in this way removes it about 6 mm. from the floor of the furnace.

(3) For the Franco-Belgian double-crucible method: A double-crucible (one inside the other) arrangement is specified and was used for this method. The smaller, or inner, crucible with lid was of glazed porcelain, and the larger, or outer crucible with cover was quartz. The two crucibles were separated by a layer of crushed wood charcoal. All crucibles and covers were obtained from France. Heating was done in an electric muffle furnace.

In all methods, temperatures were measured by means of thermocouples and pyrometers.

Samples

Five samples of Illinois coals representing the three ranks, high-volatile bituminous A, B, and C were used in this comparison. Because of the Survey's interest in char and because the determination of volatile matter in char is troublesome, four char samples were included in this study.

Procedure

Details of procedure as specified in the various standards were followed in this work. The more important details of the four methods are shown in Table 1.

Table 1. - Details of Methods

	ASTM Standard	ASTM Modified	British Single crucible	French Double crucible
Top temp. of heating	950°±20°C.	950°±20°C.	925°C.	960°±10°C.
Total time of heating - min.	7	15	7	20
Time subjected to top temp. - min.	7	6	7	20
Comparative rate of sample heating	Rapid	Slow	Intermediate	Slow
Crucibles	Platinum	Platinum	Fused silica	Porcelain and quartz

In all methods, 1-gram samples of minus 60-mesh coal or char were used, and all determinations were made in duplicate. In the American standard method, the sample, in a platinum crucible, was introduced directly into the hottest zone of the furnace (950°C.) for exactly 7 minutes, thus obtaining a rapid rate of heating. In the American modified procedure, the sample, in a platinum crucible, was suspended in the Fieldner furnace (950°C.) such that the top of the crucible lid was even with the top of the furnace. After 5 minutes, it was lowered one-

Table 2. - Comparison of Volatile Matter Determination
By the American, British, and Franco-Belgin Methods
(Moisture-Free Basis)

Laboratory No. and Description	C-8851 Illinois HVBB #6 Seam	C-8805 Illinois HVBB #5 Seam	UI-289 Illinois HVCB #6 Seam	DPS-2164 Illinois HVCB #2 Seam	C-8504 Illinois HVAB #5 Seam	CHAR #189	CHAR #190	CHAR #191	CHAR #192
ASTM (Reg.)	36.4 36.4 36.4	36.6 36.5 36.4	42.3 42.1 41.8	39.6 40.2 39.9 40.0	33.6 33.7 33.7				
ASTM (Mod.)	34.8 34.8 34.8	35.0 34.9 34.8	39.9 39.7 39.5	37.8 37.7 37.6	32.0 32.1 32.1	19.2 19.2 19.2	20.2 20.3 20.3	16.6 16.5 16.4	23.0 23.3 23.5
BRITISH (Single crucible)	35.6 35.8 35.9	35.6 35.5 35.3	40.7 40.6 40.5	38.3 38.3 38.2	32.4 32.4 32.4	18.8 18.8 18.8	19.5 19.5 19.5	15.9 16.0 16.0	22.8 22.9 23.0
FRANCO-BELGIAN (Double crucible)	34.8 34.8 34.7	35.0 35.0 35.0	40.0 39.9 39.7	37.5 37.5 37.5	32.5 32.5 32.4	18.6 18.6 18.5	19.7 19.8 19.8	15.7 15.9 16.1	22.8 22.8 22.7

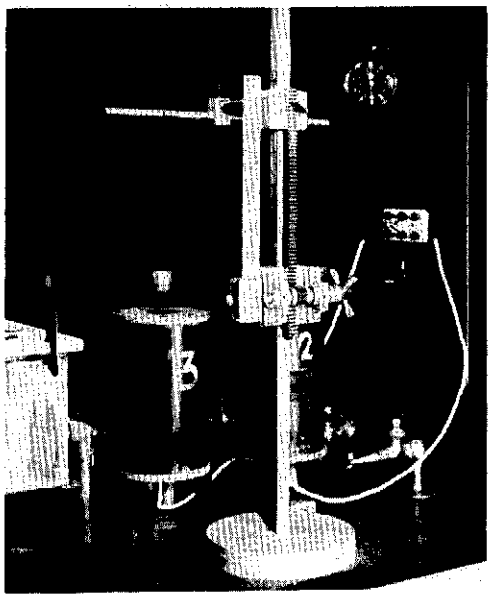

Fig. 1. - Mechanical device for positioning crucibles in furnace.

quarter inch for 2 minutes, then one-half inch further for 2 minutes, after which it was lowered to the hottest zone of the furnace and heated 6 minutes. By this means, a slower rate of heating was obtained. A mechanical device (fig. 1) was employed for lowering the samples into the furnace in order to duplicate the position for all samples. Heating rates for both American methods are shown in figure 2.

For the British single-crucible method, the sample was introduced into the hottest zone of the muffle furnace (925°C.) and heated for exactly 7 minutes. A rather rapid rate of heating was obtained, but not as rapid as in the American standard procedure.

For the Franco-Belgian double-crucible method, the smaller porcelain crucible, containing the coal sample, was placed inside the larger quartz crucible with a layer of wood charcoal surrounding it and separating it from the inside of the larger crucible. It was then inserted into the hot zone of the muffle furnace (960°C.) and heated for exactly 20 minutes. By this procedure, a slow rate of heating was obtained.

Results and Discussion

Volatile matter values obtained by the four methods under study for all samples are shown in table 2.

In only one case did duplicates fail to check within ASTM tolerance (0.5 percent); duplicate values by the ASTM regular method for sample DPS-2164 were slightly outside tolerance. A third value was obtained and the three averaged. For the coals, results obtained by the British method lie between those obtained by the American standard and modified methods. Results obtained by the Franco-Belgian method check closely those obtained by the American modified method. However, they are definitely lower than those obtained by the American standard method. For the chars the American modified method gave highest results. With all three methods applied to chars no objectionable sparking was evident.

The magnitude of determined values decreases with slower heating rates. In addition, experience indicates that slower heating rates are necessary for the determination of volatile matter in sparking coals. If we assume that the higher results obtained by the American standard method are more nearly correct, it would appear that, of the three methods involving slower heating rates, the British method would approach most closely the requirements for a single method equally applicable to all samples.

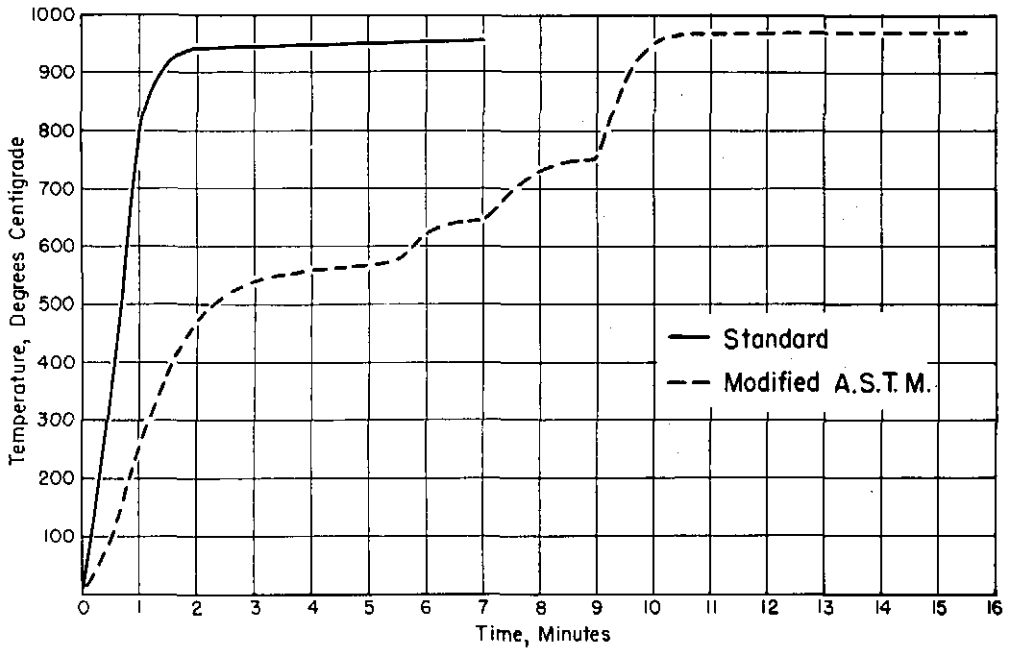

Fig. 2. - Heating rate curves.

ASH - EFFECT OF FINAL TEMPERATURE

The American Society for Testing Materials defines ash as inorganic residue remaining after ignition of combustible substances, determined by definite prescribed methods. For this determination two temperatures, 750° and 815°C., were compared. The equipment used for both methods was identical: porcelain capsules, 7/8 inch in depth and 1 3/4 inches in diameter, and an electric muffle furnace capable of maintaining predetermined temperature. Nine coal samples were used in this comparison, eight representing the various ranks of bituminous coal and one anthracite coal.

Procedure

One-gram samples of coal were used for all determinations at 750°C. Two-gram samples were used for the determinations at 815°C.

For the 750°C. procedure, the coal was placed in the cold muffle furnace and the temperature raised to 750°C. in one hour and retained at this temperature for one hour. After cooling in a desiccator, the loss in weight was recorded. The crucible and ash were returned to the furnace (maintained at 750°C.) for half-hour intervals until constant weight was obtained.

For the 815°C. procedure, the coal was placed in the cold muffle furnace and heated to a temperature of 815°C. in one hour and allowed to remain at this temperature for one hour. The samples were removed, allowed to cool in a desiccator and loss in weight recorded. They were then brought to constant weight by returning them to the furnace (at 815°C.) for half-hour intervals. Very little variation was noticed for the additional heating periods at both temperatures.

Results and Discussion

Results for all determinations are shown in table 3. With the exception of Coal C-8504, there is very good agreement in the results obtained at the two temperatures.

ASH - EFFECT OF RATE OF HEATING

In the determination of ash, particularly in coals containing appreciable amounts of pyrite and calcite, there is danger that the ash will retain indefinite amounts of sulfur which causes erratic results. Although it is widely recognized that the rate of heating influences the sulfur retention, there is disagreement as to how fast the heating rate may be and still give reliable test results.

Recently, a proposal has been made which would permit samples of this type to be heated to 500°C. in 30 minutes and then to 815°C. in another 30 minutes. The ASTM specification D-271 states that such samples be heated to 500°C. in 60 minutes and then to 750°C. in another 60 minutes. The more rapid heating rate proposed led us to wonder if it might not be too rapid. Hence, a brief study was made.

Table 3. - Comparison of Ash Determination at Two Different Temperatures

(Moisture-Free Basis)

Sample	Rank	At 750° Ash, percent		At 815° Ash, percent	
C-9010	HVBB #5 Seam	6.98 6.99	6.99	6.99 6.93	6.96
C-9039	HVBB #6 Seam	7.74 7.74	7.74	7.69 7.79	7.74
UI-289	HVCB #6 Seam	15.06 14.94	15.00	15.15 14.96	15.06
DPS-2164	HVCB #2 Seam	11.50 11.38	11.44	11.27 11.44	11.36
C-8504	HVAB #5 Seam	9.52 9.80 9.90	9.74	10.27 10.36	10.32
C-9023	LVB	6.22 6.30	6.26	6.27 6.24	6.26
C-8994	HVAB	4.30 4.31	4.31	4.34 4.34	4.34
C-8977	HVCB	12.83 12.78	12.81	12.52 12.76	12.64
C-9006	Anthracite	37.45 37.28	37.37	37.33 37.31	37.32

Two samples (1 and 2, table 4) of coal containing pyrite and calcite were obtained for this work and a third, or composite, sample was prepared by mixing

equal portions of samples 1 and 2. Ash values were determined on the three samples. Table 4 shows pyritic sulfur and mineral carbon dioxide values, as well as ash values, obtained at different rates of heating.

Table 4. - Effect of Rate of Heating on Ash Determination
(Moisture-Free Basis)

	SAMPLE NUMBER		
	1	2	3
	%	%	%
Pyritic sulfur, dry	0.41	0.79	0.57
Mineral CO_2, dry	2.17	0.77	1.47
Ash, dry			
500° in 30 min. 750° in 60 min.	14.36	7.98	11.44
500° in 60 min. 750° in 120 min.	13.28	7.87	11.14
500° in 30 min. 815° in 60 min.	14.69	8.04	11.64
500° in 60 min. 815° in 120 min.	13.60	7.77	10.89
500° in 60 min. 850° in 120 min.	13.57	7.68	10.89

The data show that for all samples, heating from room temperature to 500° C. in 30 minutes produces ash values which are significantly higher than when the heating is done in 60 minutes. This is true regardless of the final temperature of ashing. By way of explanation, we believe that with the slower rate of heating (500°C. in 60 minutes) the sulfur is oxidized and lost before the decomposition of calcite becomes appreciable. In this way, a minimum of sulfur is retained in the ash and lower values are obtained.

On the basis of these data, we conclude that the heating rate whereby temperature is raised from room temperature to 500°C. in 30 minutes is too rapid and that this should be accomplished in 60 minutes.

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