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METHODS OF PROXIMATE ANALYSIS BY THERMOGRAVIMETRY

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ABSTRACT

Two completely automated proximate analysis methods are developed for coals, cokes and other solid fossil fuel materials. The first is a dynamic–isothermal method and calculates the results on wet basis according to national standards. The second consists of two separate dynamic–isothermal methods and calculates the results of volatiles, fixed carbon, and ash content of the fuel on dry basis. Both methods were developed for a Mettler TA 3000 system but could be applicable for routine quality assurance analysis on other systems.

BACKGROUND

Several recent papers [1–4] reviewed the thermogravimetric behavior of coal proximate analysis with different instruments. Techniques of thermogravimetry (TG) and derivative thermogravimetry (DTG) were applied to a range of coal samples using Stanton-Redcroft 780 and modified 761 thermal analysers [1,2]. Francis and Harris [3] showed a bias in the results obtained on two different commercial TG analyzers which appear to be associated with coal rank and TG instrumentation. Sommerauer described the use of the new Mettler TA 3000 system for the content analysis of coal by TG [5].

Cumming and McLaughlin discussed the procedural details of the individual tests which go to make up the proximate analysis [1]. These vary somewhat in their specifications which are in common use in the West, as the American Standards, and their counterpart, the British Standards (BS). These investigators, and others [4], stated that because of instrumental and other constraints, an exact replica of the standard's requirements cannot and need not be achieved by TG. All procedures using TG produced great time savings when compared with the standard methods. Analysis time was reduced from several hours to a range of 8 to 45 min.

INTRODUCTION

This study is an evaluation of three methods used to determine the proximate analysis of solid fossil fuels using the Mettler TA 3000 System.

Proximate analysis standard specifications to rank coals are found either in the ASTM D3172-75 (1973) Part 26 or BS 1016 (1973) Part 3 methods. The standard methods calculate the results as percentages on moisture reference base (wet basis). Most workers in the field prefer to exclude the moisture from the original weight of the sample and present results on a dry basis. Amended ASTM standard classifications of coals by rank D388-77 uses either moist or dry bases in addition to a mineral-matter free basis.

Methods of proximate analysis are either dynamic or combination dynamic–isothermal. Sommerauer [5] introduced a dynamic method to heat the coal sample up to 700 °C in an inert atmosphere of nitrogen at 40 ml min^{-1}, automatically changing to oxygen at the same flow rate, with heating continuing to 900 °C at the same heating rate. Average analysis time stated was 45 min. Anthracite coal samples and certain hard western coals showed low volatile results and higher fixed carbon and ash contents. For the purpose of this investigation methods 1 and 3 were developed employing one and two dynamic–isothermal linkages, respectively. Method 2 was used previously [4] on a set of bituminous coals analyzed by ASTM methods, and the data generated were found to meet the precision tolerance criteria of the standard methods for reproducibility between different laboratories.

EXPERIMENTAL

The thermo-system used in this investigation was the Mettler M3 microbalance connected to a TG 50 thermogravimetric furnace attached to a TC 10 controller processor equipped with TA 3000 version 2 software, and a Swiss Matrix RO-80 printer plotter.

Identifiable geological samples of coal and shale were acquired from Southwest Mineral Supply Co., Santa Fe, New Mexico. Samples of North Carolina peat were provided by the Geology Department at the University of North Carolina, Chapel Hill. Other shale samples were obtained from a drill core of the black shale deposits of Tennessee known as Chattanooga shale.

About 200 g of the fuel material were crushed to pass a standard 10 mesh screen using a Quaker City Mill model 4-E. The coarse-crushed samples were kept under a nitrogen atmosphere in a freezer. Small portions of the mixed, representative sample were ground in a long agate vial with pestle of Wig-L-Bug to pass a 200 mesh screen, then divided into three portions and kept under nitrogen in a freezer at a temperature of −10 °C.

The set methods, stored and detailed as programs in Table 1, were keyed by the stored file number followed by the sample identification number. After the sample was equilibrated to ambient temperature, 5–10 mg were placed in a platinum crucible with a perforated platinum lid (or a fine mesh platinum screen) and inserted into the furnace. The system was purged with

TABLE 1

Programs for different proximate analysis methods

	Method 1		Method 2				Method 3			
Number of step analysis linkages	2		4				4			
Condition of linkages	Continuous		Continuous				Separate, after moisture			
Step analysis	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Date and time	✓		✓				✓			
Scan parameters										
Method No.	1	2	3	4	5	6	7	8	9	10
Link No.	2	0	4	5	6	0	8	0	10	0
Start temp. (°C)	35	0	35	0	135	0	35	0	135	0
Rate (K min^{-1})	100	0	100	0	100	0	100	0	100	0
End temp. (°C)	1000	0	135	0	1000	0	135	0	1000	0
Time iso. (min)	3	0	2	0	3	0	2	0	3	0
Plot (cm)	10		5		10		5		10	
Range full scale (mg)	10		10		10		10		10	
Offset (%)	98		98		90		98		90	
Valve T/t (1/2)	2		0		2		0		2	
Valve value	0.01				0.01				0.01	
Step analysis										
Dyn./iso. (1/2)	1	2	1	2	1	2	1	2	1	2
Auto limit (0/1)	0	10	0	10	0	10	0	10	0	10
Start (°C min^{-1})	35	0	35	0	135	0	35	0	135	0
End (°C min^{-1})	1000	3	135	2	1000	3	135	2	1000	3
Baseline type	1	1	1	1	1	1	1	1	1	1

A value of 0 should be used for parameters without listed numerical values.

high purity dry nitrogen using a flow rate of 200 ml min^{-1} before and during the analysis.

In method 1, the sample was heated continuously from ambient temperature to 1000 °C in dry nitrogen then oxidized in an oxygen atmosphere. In methods 2 and 3, the samples were heated from ambient temperature to 135 °C and held isothermally at that temperature for 2 min followed by pyrolysis to 1000 °C. In method 3, during the printing of the moisture value, the new method number is keyed in followed by the sample identification number. The instrument will print the weight of the sample free of moisture. The continuation of the analysis will yield the volatiles, fixed carbon and ash calculated directly on dry basis. In each procedure, switching to dry oxygen, previously adjusted to 200 ml min^{-1} flow rate, is accomplished automatically and the temperature at which switching occurs is marked by the instrument. This temperature is held for 3 min, where all the fixed carbon is combusted.

The total loss in weight at 1000 °C is due to all volatile components. The value obtained includes any decomposed inorganic salts. Some coals and other solid fossil fuel materials contain a sizable percentage of carbonates, sulfides, and chlorides, which will decompose. The remaining mass printed in method 1 represents the ASTM value of percent ash on wet basis. In method 2 the printed value represents the sum of ash plus moisture. In method 3 the remaining mass represents the percent ash on dry basis. Typical curves for each method are presented in Figs. 1 and 2. The total

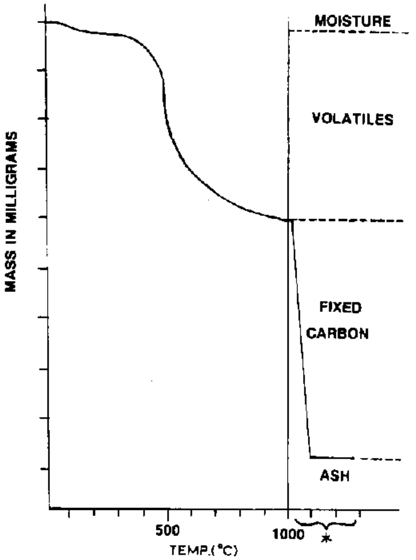

Fig. 1. Thermo curve of method 1. (*) Holding time (min) at 1000 °C.

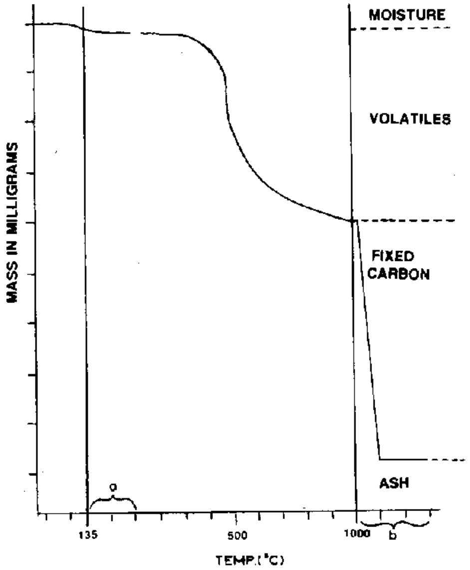

Fig. 2. Thermo curve of methods 2 and 3. (a) Holding time (min) at 135 °C, (b) holding time (min) at 1000 °C.

analysis time by method 1 is 13 min, methods 2 and 3 require 15 min each, and about 17 min are required to cool the furnace. However, using any of the given methods, it is possible to complete two tests per hour.

RESULTS AND DISCUSSION

The record from TG dynamic methods is a weight loss vs. temperature (time) curve. A typical example for each method is shown in Figs. 1 and 2. Isothermal holding time introduced to completely remove the moisture content of coals and cokes are presented in Fig. 2. The different stages of weight loss are shown, and the component of loss which relates to each of these is listed. The position of atmosphere change is automatically marked with a vertical line on the temperature axis. After changing to oxygen, the residual carbon is burned and the remaining mass is the ash content of the sample.

The continuous dynamic method shown in Fig. 1 and Table 1 normally includes small percentages of moisture with the volatile matter. By recalculating the first part of mass loss and using DTG, an accurate value is derived for moisture and is subtracted from the total volatile matter. This problem is not encountered in methods 2 and 3 due to the isothermal heating for 2 min at 135 °C.

Duplicate experiments were carried out on the samples employed. These were two coals, two shales, and one peat sample. Table 2 lists results from the three methods evaluated. Results of methods 1 and 2 were recalculated as dry-basis values for volatiles, fixed carbon and ash content for comparison with the values of method 3. The values of each method were in accordance with the duplicate criteria of ASTM repeatability for moisture (D3173), volatiles (D3175) and ash (D3174) for the corresponding coal or fossil fuel material. Each of the methods was run on a separate portion of the original 200 mesh crushed sample.

All TG results reported in this paper were carried out using a sample of < 10 mg. No homogeneity problems were encountered with these samples which had been ground to < 212 μm, the standard size for proximate analysis. The perforated platinum lid or screen used to cover the sample crucible was found necessary in order to eliminate material loss in the case of finely divided fuel materials, such as peat, at the stage of combustion in a high oxygen flow.

Method 3, in the opinion of the authors, has a distinct advantage over the other two. This advantage is the complete removal of moisture, allowing volatiles, fixed carbon, and ash to be obtained automatically and directly on dry basis. Method 1 runs unattended from start to finish and is therefore intuitively desirable. However, this method has two shortcomings. These are: (1) if moisture is $< 2.5\%$ it is included in the computation of volatiles; and

TABLE 2

Comparison of different proximate analysis methods using a Mettler TA 3000 [a]

Sample identification (type/source)	Method No.	% Moisture	% Volatiles [b]	% Fixed carbon [b]	% Ash [b]
Anthracite coal, Madrid, NM	1	2.43	12.22	80.02	7.67
	2	2.41	12.21	80.05	7.68
	3	2.38	12.07	80.12	7.72
Bituminous coal, Gallup, NM	1	2.32	41.98	50.91	5.75
	2	2.22	42.02	51.39	5.47
	3	2.18	42.00	51.13	5.67
Western shale, Green River	1	0.59	36.49	0.00	63.50
	2	0.68	36.69	0.00	63.38
	3	0.60	36.42	0.00	63.52
Eastern shale, Tennessee	1	1.33	14.16	4.49	81.35
	2	1.37	13.86	4.68	81.46
	3	1.39	12.98	5.48	81.48
Peat, North Carolina	1	7.49	59.67	36.92	3.40
	2	7.58	59.37	37.04	3.59
	3	7.40	59.62	36.86	3.45

[a] All data are average of two determinations and meet the ASTM criteria for duplicate results on "Repeatability".

[b] Corrected to dry basis.

(2) all values are given on wet basis. Method 2 has the disadvantage of reporting all parameters on wet basis in addition to combining moisture with ash in the printed results.

Modification of the described method 1 may sometimes be required to achieve total separation of the weight losses. Soft coals of lignite and peat type can completely lose their volatiles at temperatures below 900 ° C. Such a temperature is recommended to extend the lifetime of the furnace.

CONCLUSIONS

Two automated proximate analysis methods were introduced for the direct determination of total moisture, volatiles, fixed carbon and ash of coals, cokes and other solid fuel materials. The first calculates the results on wet basis while the other calculates the results of volatiles, fixed carbon, and ash content of the sample on dry basis. Both methods were made on the Mettler TA 3000 system with complete programs for storage on TC 10 but could be applicable to other instruments.

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REFERENCES

1 J.W. Cumming and J. McLaughlin, Thermochim. Acta, 57 (1982) 253.
2 M. Ottaway, Fuel, 61 (1982) 713.
3 H.E. Francis and M.B. Harris, Proc. 12th NATAS Conf., 1983, p. 285.
4 F.S. Sadek and H.Y. Herrell, Am. Lab., 16 (3) (1984) 75.
5 H. Sommerauer, Proc. Coal Testing Conf., Vol. 2, Division of Standards Laboratory, Charlston, WV, 1982, p. 56.