APPLICATION NOTE

Thermal Analysis

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Proximate Analysis of Coal and Coke using the STA 8000 Simultaneous Thermal Analyzer

Abstract

The STA8000 Simultaneous Thermal Analyzer (STA) is able to analyze coal and coke to obtain Proximate Analysis data – volatiles, fixed carbon and ash – using 10 to 100 milligram samples. This paper demonstrates this utility using standard coal and coke samples.

Introduction

Proximate analysis has long been used to determine the rank of coals by separating volatile components, fixed carbon and inert components. Because of the wide ranging quality of coal products and the commercial value of ranking these products the need for good methods is obvious. To meet these needs there are ASTM® tests to perform these separations separately using specialized industrial equipment.[1] When using the ASTM® methods, these tests are carried out with gram sized samples to reduce the effort required to get a representative, smaller sample. Round robin testing using homogenized sample materials and multiple laboratories identified and documented many of the considerations for performing this coal-ranking separation reliably. Because of the wide range of volatile and pyrolytic components this is an empirical separation with an arbitrary aspect to it. Therefore, standard samples are used to allow testers to fine-tune their conditions to get the standardized analysis.[2] These standard samples are available in a -60 mesh (250 micron

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diameter particles) which is sufficiently fine to allow testing of samples in the 10 to 100 milligram size range without introducing significant statistical sampling error.[3,4] PerkinElmer was an early developer of methodology for proximate testing by TGA of coal and coke[5,6,7,8] and there is now more than 30 years experience in this technique applied to a wide range of carbonaceous products.[9] Figure 1 shows a typical TGA protocol Proximate Analysis of coal using the STA 8000.

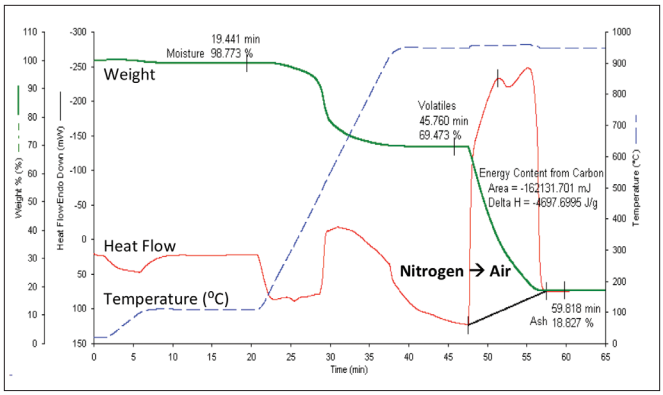

Figure 1. TGA Proximate analysis of coal using the STA 8000.

Instrument Requirements

The analytical requirements for proximate testing by TGA are modest: the ability to accurately record the weight of a sample as it is heated over a temperature range and held isothermally at designated temperatures, then change the sample's environmental atmosphere from inert to oxidizing. The PerkinElmer STA 8000 easily meets these requirements, including accurate temperature and gas control, a balance with microgram sensitivity, and software to facilitate and automate the analysis. Moreover, the top loading balance offers particular advantages for this analysis.[10]

The purpose of this study is to demonstrate the proximate analysis of two standard samples using the STA and show that the performance is easily able to allow this moderate cost, small profile and sturdy instrument to be used for this type of routine analysis.

The STA 8000

PerkinElmer offers several analyzers capable of performing this analysis. Two of them, the Pyris 1 TGA and the TGA 4000 offer autosampler accessories which have advantages for handling substantial sample throughput. However, the STA 8000 analyzer (Figure 2) also has a number of features beneficial for this application.

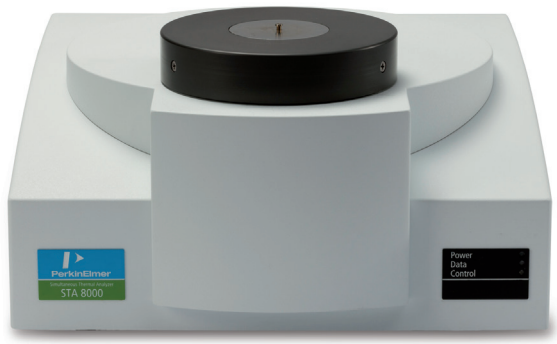

Figure 2. The STA 8000 Simultaneous Thermal Analyzer.[10]

The weighing mechanism is ideally suited for routine quality testing use. Unlike the taut-band fulcrum approach, the STA 8000 uses a top loading balance. This makes it easier to load, and when loading there is no force applied to a long balance arm or hang-down wire that could result in damage to the balance system. Furthermore, unlike the horizontal TGAs and STAs, the position of the sample has no effect on the moment arm between the sample and the fulcrum, which determines the weighing constant. So if the sample shifts on melting there is no apparent weight change. If the sample is loaded asymmetrically in the pan it won't affect the apparent weight. The STA capsules also are better able to hold in the ash than a boat-shaped sample holder or a system where the purge flows directly across the sample. The small, low mass furnace is closely coupled to the sample, and atmosphere switchover from inert to oxidizing is rapid and complete. A range of purge gas flow rates from 40 to 200 cc/minute were successfully used. Finally, having the balance positioned below the furnace and separated by a purged channel ensures that the pyrolysis products do not contaminate the balance.

Experimental

Two standard sample materials were obtained from Alpha Resources: a metallurgical coke standard, AR-733, and a bituminous coal standard, AR-1720. They were initially run using a TGA proximate analysis technique. See Figure 1. This temperature program called for sample loading and weighing at 25 ˚C, heating to 110 ˚C, holding for 10 minutes then heating to 950 ˚C where the temperature was held until constant weight was achieved in nitrogen. Then the sample atmosphere was switched to air (somewhat diluted by the balance purge). When the weight was again constant after the combustion of the fixed carbon component the analysis was ended and the apparatus cooled for the next analysis. This yielded consistent values but different from those certified. The main difference is that the certified sample tests, like the ASTM® tests, assume samples have previously been thoroughly dried to constant weight at 107 ˚C. This post-drying proximate test is exemplified in Figure 3.

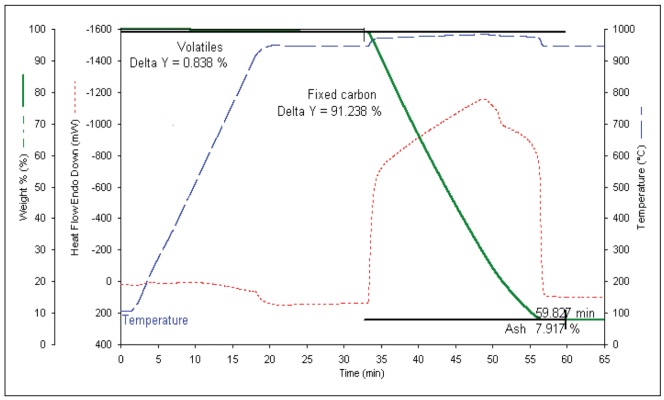

Figure 3. Proximate analysis of metallurgical coke.

Results and Discussion

Total volatiles. For determination of total volatiles the sample is heated from 107 ˚C to 950 ˚C and held isothermally to drive off all volatile components. Figure 4 shows this first part of the analysis for the metallurgical coke sample on an expanded scale. After 20 minutes the weight loss at this temperature is typically less than 2 µg/min, which demonstrates that no appreciable oxygen is getting into the STA. In other tests it was shown that a purge rate of 40 cc/min was sufficient to prevent measurable back diffusion of oxygen from air into the sample/furnace chamber. For the data below: a purge rate of 100 cc/minute was used. The switch-over to air or oxygen for the combustion step can be programmed to occur at a set time or when a rate-of-weight-loss criterion is met.

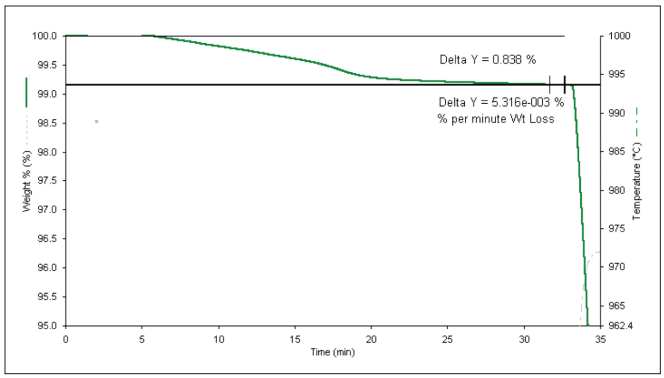

Figure 4. Proximate analysis of coke (expanded scale).

Fixed carbon. After the switch to an oxidizing atmosphere combustion at 950 ˚C is rapid and complete (Figures 3 and 5). The use of a relatively deep sample capsule instead of a shallow boat minimizes the loss of fly ash during combustion, which would add error to both the fixed carbon and the ash data. The use of oxygen instead of air for combustion shortens the test time to 30 to 50 minutes depending on sample size and type.

Ash. After combustion, the remaining residue is the ash content of the coal, which can be read directly from the weight.

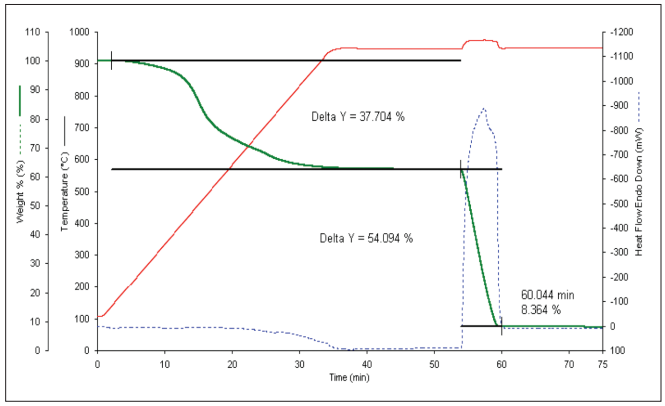

Figure 5. Proximate analysis of AR-1720 Std. Coal.

Agreement with certificate. Despite the range of sample sizes investigated, the results for the AR-733 coke sample were all within the uncertainty of the certificate values (Table 1).

For the AR-1720 Coal sample the ash results were within 0.1% of the certificate values. (Table 2) For the volatiles the percent found was low by 1.4%, and for the fixed carbon the percent found was 1.7% high. This is not too surprising since the ASTM® method calls for a sample geometry which exposes a much higher surface area for volatiles off-gassing.

Table 1. **Results for metallurgical coke standard AR-733.**

Sample Wt (mg)	Volatiles %	Carbon %	Ash %
30.82	1.03	91.01	7.81
70.25	0.84	91.24	7.92
107.8	0.46	91.05	8.03
89.96	0.81	91.02	8.12
Average	0.785	91.08	7.97
Average Deviation	0.162	0.080	0.105
Certificate value	0.85±0.36	91.11±0.36	8.04±0.42

Table 2. **Results for coal standard AR-1720.**

Sample Wt (mg)	Volatiles %	Carbon %	Ash %
25.04	37.7	54.09	8.36
22.46	37.01	54.09	8.99
61.04	37.98	54.51	7.68
86.49	37.75	54.22	7.73
Average	37.61	54.2275	8.19
Average Deviation	0.30	0.14	0.48
Certificate value	39.17±0.45	52.54	8.29±0.07

Calorific calculation

The STA 8000 simultaneous thermal analyzer is also able to make direct determinations of the energy associated with thermal events, such as the combustion of carbon. This calculation can easily be performed on the carbon oxidation step of the proximate analysis. However, as an assessment of the calorific content of the coke or coal the calculated value using the fixed carbon and coal rank is considered more accurate.[8]

Conclusion

The data in this study demonstrates that the STA 8000 is capable of giving reproducible proximate analysis of coal and coke. Since this is an empirical analysis, the dwell times and separation temperatures may have to be adjusted in order to obtain sufficiently identical results to those obtained from the commercially accepted large sample ASTM® tests. This work and several others show that the proximate analysis as performed with a TGA or STA analyzer continues to be a useful tool for rapid analysis of small quantities of coke and coal.

References

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