Rapid thermogravimetric analysis of coal

Introduction
The quantitative determination of moisture, volatile compounds, chemically bound carbon, and ash content has long been used to determine the quality and economic value of different types of coal. High ash content is undesirable for the operation of thermal power stations because inert material increases transport and waste disposal costs, and also means that the heat exchangers have to be cleaned more frequently. To make sure that assays can be properly compared, the analysis procedures have been standardized and described in many standard methods [1-10].

Quite early on, measurement routines were developed for thermogravimetric instruments that enabled faster and more automated analyses to be performed. These techniques have been compared with the standard manual methods [11-14].

TGA (thermogravimetric analysis) is, however, also very useful for coal research, e.g. to compare combustion profiles or to determine the nature of volatile components with TGA-MS. Even the lime deposits (fur) formed in hot water systems have been investigated with TGA [15].

The determination of moisture, volatile content, soot, ash or fillers is also required for other applications. Analogous to the analysis of coal, a standardized thermogravimetric procedure is nowadays used to determine the content of elastomers, thermoplastics and thermosets, as well as lubricants [16, 17]. Conversely, procedures developed for the determination of carbon black in rubber [17] are used for the analysis of brown coal, lignite and other renewable fossil fuels [e.g. 18].

Speeding up the TGA procedure
As already indicated, the standard methods for coal analysis are laborious and often time-consuming.

To determine the moisture content exactly, the measurement is usually started at room temperature, or slightly above. This leads to long cooling times before the next sample can be measured, which in turn limits the throughput of samples. The METTLER TOLEDO STAR® system allows the analysis time to be reduced by half compared to the ASTM E1131 standard method. In this case, the measurement is started directly at 110 °C (or even higher), which means the otherwise long cooling time down to 30 °C is avoided. The moisture is, however, still accurately measured - the weight loss up to the start is automatically measured by determining the starting weight on reaching 110 °C.

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which is in fact normal in the manual procedure [1 -10]. Buoyancy effects are compensated in the TGA measurement by subtraction of a blank curve. Besides this, oxygen is used instead of air, resulting in much shorter combustion times. One must of course make sure that coal particles are not blown out of the crucible by the rapid generation of gas. This can manifest itself for example in widely differing measurement values for the ash content. As with all analytical methods, it is essential that the coal samples are homogeneous and representative if one, for example, wants to characterize one hundred tons of coal. Vaporization, degassing and combustion proceed more rapidly when shallow, open crucibles are used and small sample weights are analyzed.

**Experimental details**

A METTLER TOLEDO TGA/SDTA851® with the small furnace (up to 1100 °C) was used for the measurements. The system was automated with a TSO800R0 sample robot and a TSO800GC1 gas controller for gas switching.

The balance was purged with 40 ml/min of nitrogen as protective gas. During the measurement, first 80 ml/min of nitrogen, and afterward 80 ml/min of oxygen were used as reactive gas. The following samples were used as examples for coal analysis:

1. Coal A with a particle size of 65 µm to 90 µm,
2. Coal B with a particle size up to 1 mm,
3. Coke, finely powered, manufactured from petroleum oil.

Unless otherwise specified, alumina crucibles (30 µl) were filled with about 20 mg of coal powder. During weighing-in, the crucible weight and the sample weight were noted and entered in the software program.

Immediately after weighing-in, the special aluminum lid was placed on the crucible to prevent contamination of the sample and any large change in moisture content during the waiting time. The lid is removed by the sample robot during measurement.

At the end of the measurement, the measuring cell automatically cools down to the starting temperature. The blank curve is automatically subtracted and the evaluation macro-program calculates the weight loss immediately after the measurement is finished.

**Results**

**Fast method**

Figure 1 shows the TGA curves of the coal analyses performed with the fast method described above. The measurement conditions were chosen as follows:

- Under nitrogen: 110 °C for 0.5 min, then heating at 100 K/min to 900 °C and held at this temperature for 2.5 minutes.
- The system was then purged with oxygen for the following 4 minutes (furnace atmosphere is made up of 80 ml/min O₂ and 40 ml/min N₂).

The blank curve was measured in the same way before the measurement series with an empty crucible.

For all measurements (including the blank curve), the weight of the crucible is also entered in the software in addition to the sample weight, i.e. the total weight is determined directly after weighing-in. After insertion of the sample by the sample robot and the equilibration of the temperature at 110 °C (automatic “settling”), the total weight is determined at this instant with the first measurement point. The difference between this and the sample weight before the measurement yields the dry content (or the amount of moisture evolved). The starting weight is given by the Signal Value (Fig. 1) at the beginning of the normalized TGA curve. This means that drying or moisture uptake during the waiting time up to the actual measurement has no influence on the original moisture content. However, especially with very moist coal samples, the use of an aluminum lid is recommended as described in the experimental section.

In the first 30 seconds, the TG curves are practically horizontal with a loss of less than 3 µg (this corresponds to 0.01%), proving that drying is complete at the beginning of the measurement. The curves are also horizontal at the end of the isothermal phase at 900 °C because degassing and combustion have finished. The measured values are summarized in Table 1. The reproducibility is shown by the standard deviation and how well the measurement curves coincide. The slight differences in combustion rates are caused by small differences in the sample weights, e.g. with Coal B 19.801 mg as opposed to 21.547 mg (see Fig. 1).

In routine operation, the analysis including evaluation takes approximately 36 minutes; of this, about 15 minutes is for the actual measurement. The assay according to ASTM E1131 takes about 60 minutes because somewhat longer isothermal times are necessary and because an additional cooling time of 10 minutes is needed to reach 30 °C.

As Table 1 shows, the corresponding mean values for both methods are very close. The differences are less than the reproducibility of >0.3% given in the manual methods [5 - 7]. It is noticeable that there is a tendency for the fast method to yield higher moisture values and lower volatile contents. This can be explained by a loss due to drying of about 0.4% with the ASTM method [16] before the actual measurement. This can only be prevented if the weighed-in sample is immediately measured.

The comparatively high standard deviations with Coal B are also worth noting. This is also apparent in the manually weighed residues. Measurements in crucibles with alumina lids (with a hole) and in taller crucibles (70 µl) showed that the differences cannot however be explained through too rapid combustion with “firework-like” ejection of material (“sparkling coal”). Better grinding and homogenization of the sample however reduced the standard deviations by a factor three. The reason is the inhomogeneity of this coal sample. This underlines the necessity of good sample preparation. The comparison of the two coal types A and B show this very clearly.

**Conclusions**

The assay of moisture, volatile content, carbon and ash in coal and coke using TGA is a standardized routine method.
The time required for the method can be shortened by up to 50% without affecting the accuracy by using the METTLER TOLEDO STAR system and adapting the temperature program. In automated operation, this allows at least 35 analyses to be performed per day.

The TGA curves show whether degassing and combustion are complete. This is necessary in order to optimize the method and for the control of routine measurements. Thermogravimetry, in addition, allows drying and combustion behavior to be investigated and different coal types to be characterized.

Inhomogeneous samples must be well ground to achieve a high degree of reproducibility. If necessary, larger amounts of sample can be measured thermogravimetrically in 900 µl crucibles.

**Literature**

1. DIN 51718 Analysis of solid fuels - determination of water content and analysis moisture (in German).
2. DIN 51719 Analysis of solid fuels - determination of ash content. (In German)
3. DIN 51720 Analysis of solid fuels - determination of the content of volatile components. (In German)
8. ISO 11722 as well as BS 1016-104.1 Methods for analysis and testing of coal and coke. Proximate analysis. Determination of moisture content of the general analysis test sample.
10. ISO 1171 as well as BS 1016-104.4 Methods for analysis and testing of coal and coke. Proximate analysis. Determination of ash content.
17. ISO 9924 Rubber and rubber products. Determination of the composition of vulcanizates and uncured compounds by thermogravimetry.

**Table 1. Comparison of the contents measured using the fast method with the values according to the ASTM E1131 standard. In each case, the mean values (M) and the corresponding standard deviations (SD) are calculated from three measurements. The residue is determined by manually reweighing when the measurement is completed as specified in the standards [2 and 6]. All the values refer to the initial sample weight.**

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Method</th>
<th>Moisture</th>
<th>Volatile content</th>
<th>Coal</th>
<th>Ash</th>
<th>Residue</th>
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<tbody>
<tr>
<td>Coal A</td>
<td>Fast (M)</td>
<td>2.80</td>
<td>31.36</td>
<td>62.45</td>
<td>3.38</td>
<td>3.48</td>
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<td></td>
<td>(SD)</td>
<td>0.01</td>
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<td>0.03</td>
<td>0.06</td>
<td>0.02</td>
</tr>
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<td>ASTM</td>
<td>2.53</td>
<td>31.59</td>
<td>62.46</td>
<td>3.21</td>
<td></td>
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<tr>
<td>Coal B</td>
<td>Fast (M)</td>
<td>4.69</td>
<td>28.45</td>
<td>47.80</td>
<td>19.02</td>
<td>19.11</td>
</tr>
<tr>
<td></td>
<td>(SD)</td>
<td>0.05</td>
<td>0.33</td>
<td>0.66</td>
<td>1.00</td>
<td>1.02</td>
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<td></td>
<td>ASTM</td>
<td>4.27</td>
<td>28.66</td>
<td>47.62</td>
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<td>Coke</td>
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<td>99.38</td>
<td>0.13</td>
<td>0.10</td>
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<tr>
<td></td>
<td>(SD)</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
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</tr>
<tr>
<td></td>
<td>ASTM</td>
<td>0.01</td>
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<td>99.38</td>
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</table>

**Publishing Note:**

This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 14. See www.mt.com/ta-usercoms