



Quality Control of Coal with Elemental Analyzers

Using Combustion and Thermogravimetric Analyzers from ELTRA

Coal is one of the most important fossil fuels. In 2012, the global stone coal output was about 6.6 billion metric tons [1]. A huge amount of the worldwide traded stone coal is mined in China, USA, Russia and India. Compared to the large amount of mined coal the required sample volume for the characterization of coal, varying from a few mg up to 1 gram, seems unbelievably small. The characterization of coal is important for its quality assessment and further use. Depending on the product quality, coal is suitable for coking, steel production or electrical power generation. This article takes a look at the chemical background of proximate and ultimate coal analysis and how these parameters are measured with ELTRA’s combustion and thermogravimetric analyzers.

The most common types of coal (lignite, bituminous and anthracite) can be distinguished by their different chemical and physical properties. The elements carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) are the most frequently measured elements. Additionally, the mineral content of the ash (esp. silica, alumina, ferric oxide etc.) is determined. Coal is characterized by more or less physically determined parameters such as moisture, volatile and ash content, and also calorific value and ash fusion temperature.

1. Proximate coal analysis (physical testing)

Given the variety of parameters which influence the quality of coal, it seems rather ambitious to name one parameter which best describes the coal quality. Due to the fact that coal is mostly used as fuel the calorific value is suitable to give a first impression of the product quality.

For a first (“proximate”) analysis of coal the calorific value, the moisture, ash, and volatile content are measured. From these data the so called fixed carbon content is calculated.

Table Nr. 1 shows the main types of coal with their calorific value and the content of volatiles.

Table 1: Main types of coal [1]

Type of coal	Calorific value Kj/Kg	Volatile Content
Lignite	6,700- 25,000	45 – 60 %
Bituminous	25,000 – 35,000	14- 45
Anthracite	35,000 and more	< 14

The calorific value can be determined with standard bomb calorimeters available in the market.

1) Reference: www.kohlenstatistik.de

2) Reference: ISO 17247: 2013

Calorimeters for coal analysis can be divided into isoperibolic and adiabatic. In both types of calorimeter a previously dried coal sample is introduced in a calorimetric bomb, oxygen is added and the coal is combusted. The combustion heat is measured and gives the gross calorific value.

Very important for documentation is the “base” on which all further values are calculated. The ISO Standard 17247:2013 defines the listed reporting basis (table 2).

Table 2: Reporting units [2]

Base	Acronym	Description
As received	ar, m	Including hydrogen and oxygen from moisture
As received	ar	Excluding hydrogen and oxygen from moisture
Air dried	ad	Dried at air; and excluding hydrogen and oxygen from moisture
Dry	d	Dried until steady mass and analyzed
As Analyzed	--	Including hydrogen and oxygen from moisture

AR (as received) is the most widely used basis for coal analysis. For a correct proximate analysis it is essential to know the moisture content of the coal as this value influences all other parameters. Moisture can be separated into surface, hygroscopic, decomposition and mineral moisture and can be determined by the use of a furnace and an external balance or with a thermogravimetric analyzer (TGA). The standard ASTM D7582-10 describes the proximate coal analysis by using macro thermogravimetric analyzers. These analyzers, such as ELTRA’s TGA Thermostep, fig. 1, combine the heating and the



Fig. 1: ELTRA’s Thermostep

- 1) Reference: www.kohlenstatistik.de
- 2) Reference: ISO 17247: 2013



weighing process for a convenient analysis of moisture, volatiles and ash content in one analysis cycle. Micro thermogravimetric analyzers are not suitable for coal analysis due to the limited sample weight of less than 10 mg. Macro TGA analyzers accept a sample weight of up to 1 gram which is weighed into ceramic crucibles. These crucibles are placed on a carousel providing 19 positions for different samples. The carousel is located in a heating chamber which can be purged with oxidizing atmosphere (oxygen or air) or an inert gas (nitrogen). This chamber can be heated from room temperature to 1,000 °C and is connected to an integrated weighing cell by a ceramic pedestal.

The moisture content of the coal is now determined by filling 1 g sample into the ceramic crucible and heat the TGA analyzer up to 107 °C, holding the temperature until a constant mass is detected. In contrast to the moisture content of coal, the volatile content does not consist of one species (water) but of a mixture of aliphatic and aromatic hydrocarbons. For a correct determination of the volatiles a TGA analyzer has to increase the temperature within 30 minutes to 950°C, holding this temperature for 7 minutes. During this heating process the crucibles are covered with lids and the heating chamber is purged with nitrogen. For the subsequent determination of the ash content the TGA analyzer cools down from 900 °C to 600 °C, changes to an oxygen atmosphere and heats up to 750 °C, holding this temperature for one hour.

The whole analysis cycle is done automatically. Table (3) shows typical results of a stone coal sample analyzed with ELTRA's Thermostep.

Table 3: Analysis of the coal standard AR-1721

Value	Content in (%)
Moisture	1.5 +- 0.1
Volatiles	42.96 +-0.3 (dry base)
Ash	7.33 +- 0.02 (dry base)

The fixed carbon content is used as an estimate of the amount of coke that will be yielded from a coal sample. It can be calculated by subtracting the measured amount of the volatile content from the sample mass which was introduced into the ceramic crucible. The calculated fixed carbon is lower than the total carbon content as some volatile hydrocarbons are removed during the analysis process.

- 1) Reference: www.kohlenstatistik.de
- 2) Reference: ISO 17247: 2013

2. Ultimate coal analysis (chemical analysis)

In addition to proximate coal analysis ultimate coal analysis also requires the determination of the carbon (C), hydrogen (H), nitrogen (N), sulfur (S), ash and oxygen (O) content by difference. According to the ISO standard 17247 the oxygen content of a coal sample is not measured directly. This content is calculated by adding all other values. The remaining difference to 100 % is defined to be the amount of oxygen.

For determination of the elements C, H, N, S elemental analyzers are available. A typical elemental analyzer combusts the coal sample and measures the combustion gas with infrared cells, a thermal conductivity cell or a combination of both. Available analyzers differ with regards to required sample weight, combustion temperature and measured elements.

Micro elemental analyzers offer the possibility to determine C, H, N, S in one analysis cycle, but only accept a very small sample weight of max. 10 mg. This makes the sample preparation for these analyzers error-prone. The requirements for the determination of the elements C, H, N are regulated in the standard ISO 29541. Common macro elemental analyzers which fulfill these requirements use a quartz or steel combustion tube and analyze sample weights of typically 60 - 80 mg. When using these types of combustion tubes the applied temperature is limited to approximately 1,000 °C.

The correct determination of sulfur requires higher temperatures, because the sulfur, which is bonded as sulfate, will not be released in the gas phase at lower temperatures. As a consequence, common sulfur analyzers (which are described in the standard ISO 19579) use ceramic combustion tubes which can sustain higher temperatures. Alternatively, the applied temperature can be increased by adding tin to the coal sample. Due to the additional combustion energy of the tin, the local temperature of the sample is higher than the temperature in the furnace. Tin is not needed when using ELTRA's CHS 580 analyzer (fig. 2). This analyzer also determines the carbon and hydrogen content and uses a furnace with ceramic combustion tube which can apply temperatures up to 1500 °C.

For determination of the sulfur content approx. 150 mg of sample is weighed into a sample carrier (e. g. a ceramic boat). The sample carrier is introduced into the hot furnace and the released combustion gases (CO₂, SO₂, H₂O) are measured with infrared cells.



Fig. 2: In the CHS-580 analyzer, the sample is weighed into ceramic boats for subsequent combustion

- 1) Reference: www.kohlenstatistik.de
- 2) Reference: ISO 17247: 2013

3. Characterization of ash

The combustion residue of the coal (ash) can also be of analytical interest. Like for coal, the ash parameters can be separated into physical or chemical properties.

For steam power generation, for example, the physical ash behaviour at different temperatures (ash fusion test) is very important. When coal is combusted in a furnace of an electrical power plant a powder-shaped residue or a glassy slag (clinker), which has to be removed as molten liquid, are unwanted by-products. Not every electrical power plant is able to handle clinker-forming coal because of the cost-intensive furnace cleaning that is required.

When using an ash fusion analyzer (such as CAF Digital from Carbolite) the ash is formed in the shape of a cone, pyramid or a cube and is introduced into a furnace with a special window. Through this window a camera can observe the sample's behavior during heating. Typically, temperatures up to 1,600 °C are applied. During the heating process parameters such as deformation, softening, hemisphere and flow temperature are recorded. The flow temperature is crucial for deciding on the further use of the coal, for example in steam power generation.

For chemical analysis of ash, a spectrometer can be used. The element concentration of sodium, magnesium, aluminum etc. is important for the evaluation of the environmental impact. A non-destructive analysis method is X-ray fluorescence. Dissolution of the ash is needed when other techniques like ICP-OES or AAS are chosen.

Conclusion

Coal and coal ash analysis requires a variety of instrumentation. Elemental and thermogravimetric analyzers are important tools for quality control which offer fast and precise results and are easy to operate. ELTRA offers a wide range of combustion analyzers for the determination of C, H, N, O, S in solids as well as thermogravimetric analyzers.

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1) Reference: www.kohlenstatistik.de

2) Reference: ISO 17247: 2013