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ELEMENTAL ANALYZERS

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QUALITY CONTROL OF COAL WITH ELEMENTAL ANALYZERS

AN OVERVIEW OF RELEVANT STANDARDS AND SUITABLE ANALYTICAL EQUIPMENT

Introduction

Coal is one of the most important fossil fuels. In 2018, the global stone coal output was about 7 billion metric tons[1]. A huge amount of the worldwide traded stone coal is mined in China, USA, Russia and India. Compared to the very 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. Correct sampling and sample preparation is a must for any subsequent measurement.

The correct 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 describes the chemical background of proximate and ultimate coal analysis and their correct determination with ELTRA's combustion and thermogravimetric analyzers.

The most common types of coal are lignite, bituminous and anthracite coal which can be distinguished by their chemical and physical properties. General (physical) parameters of coal are gross calorific value as well as moisture, volatile and ash content. Chemical analysis for coal samples usually means the determination of the elements carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O).
Apart from coal analysis, the characterization of coal combustion products, like ash, is also considered in this article. Ashes can be analyzed for their sulfur content, ash fusion temperature and loss on ignition value. Due to the large number of international standards

1 www.kohlenstatistik.de

for the analysis of coal and their ashes, this article summarizes all relevant standards and gives recommendations regarding the suitable analytical equipment.

Gross calorific value

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.

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

Type	Calorific value kj/kg	Volatile content
Lignite	6,700- 25,000	45 – 60 %
Bituminous coal	25,000 – 35,000	14- 45 %
Anthracite coal	≥35,000	< 14 %

The gross calorific value can be determined with standard bomb calorimeters and is described in the ISO 1928 and ASTM D5865 standard. Calorimeters for coal analysis can be divided into isoperibolic and adiabatic. In both types 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.

Proximate coal analysis

Beside the calorific value of a coal sample, its moisture, ash and volatile content is of relevance. According to ISO 17246 and ASTM D 3172 these coal parameters are named proximate coal analysis. Both standards (ASTM and ISO) define proximate coal and coke analysis, but they refer to different standards like ISO 562, ASTM D 3175 or ASTM D 7582 which describes the determination of one analysis parameter (e. g. volatiles) in more detail. Standard-compliant proximate coal analysis can be performed by utilizing furnaces and balances (ISO 562) or, according to ASTM D 7582, by using automated thermogravimetric analyzers like ELTRA's TGA Thermostep (Fig 1) or TGA Thermostep ML (Fig2).
The reliable and standard-compliant determination of moisture, ash and volatiles requires the application of different temperatures, atmospheres and measuring conditions like measuring time or stability of weight. Adjusting the different settings is time-consuming when single furnaces and balances are used because the sample always has to cool down in a desiccator before the final weight can be measured.

Fig. 1: TGA Thermostep

Fig. 2: TGA Thermostep ML

Automated thermogravimetric analyzers like the ELTRA TGA Thermostep series consist of a programmable furnace with integrated balance, a carousel with 19 sample positions and can measure all requested proximate coal parameters in a single run. Users just need to activate the application in the software, fill a suitable sample weight of approx. one gram into the ceramic crucibles and start the measurement. During analysis the carousel rotates and subsequently places every single crucible on a weighing pedestal to measure the current weight.

During the whole measuring process different temperatures and atmospheres are applied depending on the analysis step. For reliable determination of the thermogravimetric parameters an additional empty crucible at position 20 of the carousel is measured to compensate the thermal buoyancy. This procedure reduces the analysis time for proximate coal analysis significantly because the samples don't need to cool down in a desiccator to ensure correct measurement. The settings for an automated measurement of moisture, volatile and ash are defined in the ASTM D 7582 standard (table 2).

Table 2: Proximate coal analysis parameter according ASTM D 7582

Step No.	Parameter	Temperature °C	Atmosphere	Additional lid on crucible	Stop criteria
1	Moisture	107	Nitrogen	No	Constant mass
2	Volatile	950	Nitrogen	Yes	7 minutes at 950 °C
3	"Cooling down"	600	Nitrogen	Yes	Temperature
4	Ash	750	Oxygen	No	Constant mass

One special setting in a thermogravimetric analyzer is the placing of lids on the crucibles for a correct measurement of volatiles. The ELTRA TGA Thermostep analyzer utilizes an additional lid carrousel which automatically applies the lids during measurement. The TGA Thermostep ML configurations require manual application and removing of lids. A complete proximate coal analysis cycle with the ELTRA TGA Thermostep takes approx. four hours. Typical results of a simultaneous measurement of 19 samples are shown in Table 3 and figure 3. One special setting in a thermogravimetric analyzer is the placing of lids on the crucibles

Table 3: Typical results of the TGA Thermostep series analyzer: Dry base means that the given value takes the released amount of water into account. In comparison to a sample which is measured as received, the measured ash and volatile content is respectively higher (ISO 17247)

Sample (Coal CRM)	% Moisture	% Volatile dry base	% Ash dry base	% Fixed carbon calculated
92570-3020 (745418)	0.16 +-0.04	5.42+-0.14	0.08+-0.04	94.34+-0.13
92550-3020 (776121)	1.12+-0.02	15.79+-0.16	20.98+-0.06	62.49+-0.20
92550-3060 (782118)	1.82+-0.04	30.63+-0.11	23.42+-0.08	45.08+-0.13
92550-3060 (782118): 600 °C			23.47+-0.06	

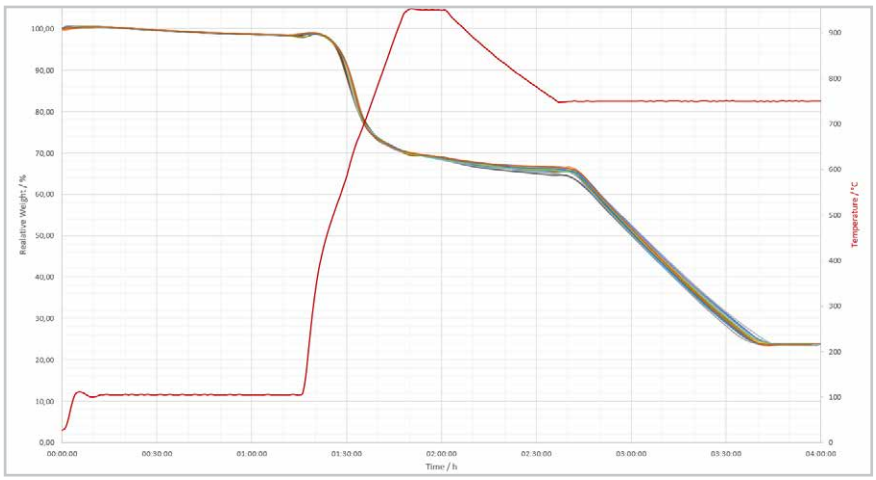

Figure 3: Typical measuring graph of ELTRA TGA Thermostep series analyzer

- y-axis (left): relative weight of the sample
- y-axis (right): temperature
- red curve: temperature
- graph 1-19: weight loss of applied coal samples

The analysis of the first three samples in table 3 have been processed with a cool down temperature of 750 °C. With this setting the TGA Thermostep can analyze the proximate coal parameter in a fast analysis time of approx. 4 hours. Of course, the standard-compliant lower cool down temperature of 600 °C can be applied in the software also. With application of the lower temperature the repeatability of the ash measurement is slightly improved, but the measuring time is prolongued by approximately one hour. Moisture and ash measurement are not affected by these alternative settings.

The fixed carbon content of a proximate coal analysis is a calculated value and 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.

Ultimate coal analysis (chemical analysis)

In addition to proximate coal analysis ultimate coal analysis requires the determination of further parameters like carbon (C), hydrogen (H) , nitrogen (N) , sulfur (S) and oxygen (O) content. The oxygen content is usually not measured directly but given by the difference between 100 % and the sum of all other measured values. For standard compliant determination of the elements C, H, N, S different types of elemental analyzers are available in the market. A typical elemental (combustion) analyzer combusts the coal sample and measures the released 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 measure 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, however, the standard does not prohibit the usage of this kind of analyzers.

The determination of the elements C, H, N is regulated in the ISO 29541 and ASTM D 5373 standards. A standard-compliant common macro elemental analyzer usually employs a quartz or steel combustion tube and processes coal sample weights of typically 60 - 80 mg. When using these types of combustion tubes the applied temperature is limited to approximately 1,000-1050 °C. The requested combustion temperature of 1150 °C for coke analysis can be provided by the application of tin foils or capsules.

Fig. 4: ELEMENTRAC CHS-r with optional monitor holder and touchscreen

Beside a simultaneous measurement of carbon, hydrogen and nitrogen also a standard-compliant single carbon analysis is defined. According to ASTM D 5372 (method B), a single carbon analysis requires combustion analyzers like ELTRA's ELEMENTRAC CS-r or CHS-r (Figure 4) which provide a minimum combustion temperature of 1350 °C. The resistance heated ceramic furnace of the CS-r or CHS-r allows the application of a maximum temperature of up to 1550 ° C which assures a complete combustion of a coal or coke sample without adding fluxes like tin. Beside carbon also sulfur and hydrogen can be measured simultaneously in up to two infrared cells with the ELEMENTRAC CS-r/CHS-r. Due to the high combustion temperature, the sulfur analysis is precise, reliable and compliant to the ISO 19579 and ASTM D 4239 standards. The application of high sample weights of 200-350 mg in ceramic boats provides excellent repeatability (table 4, Figure 5).

Table4: Typical results for coal and coke (N=10) with ELEMENTRAC CS-r & CHS-r.

Analyzer	Sample	Weight	% Carbon	% Sulfur	% Hydrogen
ELEMENTRAC CHS-r	ELTRA 92550-3040 (Lot 781411)	200 mg	67.68+-0.12	1.91+-0.02	3.97+-0.02
ELEMENTRAC CS-r	Pet coke AR 745 (Lot 745416)	350 mg	96.03+-0.25	0.9+-0.002	Not possible

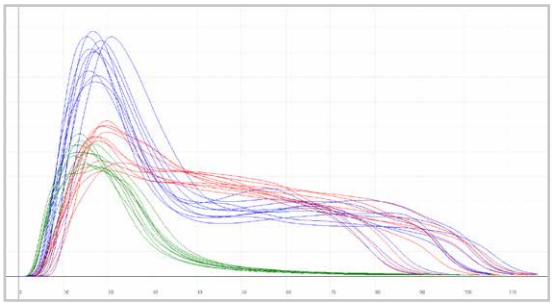

Figure 5: Measuring curve of a CHS-measurement of coal: 92550-3040(Lot 781411)

- y-axis: analysis time (sec)
- y-axis: intensity (V)
- red peak: carbon
- green peak: hydrogen
- blue peak: sulfur

Characterization of ash

Apart from the analysis of coal, the characterization of its combustion products, coal and coke ash, can be of analytical interest. Like for coal, the analysis of ash can be divided into physical or chemical analysis.
For steam power generation, for example, the physical ash behaviour at different temperatures (ash fusion test) is very important (ASTM D 1857). When coal is combusted in a furnace of an electrical power plant a powder-shaped residue or a glassy slag (clinker) 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 the CAF Digital from Carbolite Gero, the ash is formed in the shape of a cone, pyramid or 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.

Another physical parameter is the loss on ignition (LOI) value of solid combustion residues (ASTM D 7348). In a standard-compliant thermogravimetric analyzer like the ELTRA Thermostep the sample is heated from room temperature up to 950 ° C in an oxidizing atmosphere. The LOI parameter indicates if moisture, carbon, sulfur or other species are present in the combustion residue. The dedicated sulfur analysis in combustion residues of coal and coke is regulated in the ASTM D 5016 standard. For correct sulfur determination, a tube furnace analyzer like the ELEMENTRAC CS-r or CHS-r are suitable as they provide the requested minimum combustion temperature of 1350 °C.

Conclusion and summary

Correct and reliable analysis of coal, coke and their combustion residues is challenging because a variety of standards have to be considered and different analytical equipment has to be used in a standard coal laboratory. ELTRA can provide economic and reliable solutions coal, coke and ash analysis and has been accepted as a reliable partner in the coal industry for more than 40 years.

The following table summarizes the currently valid standards for coal, coke and its ash analysis and gives some recommendations regarding instrumentation:

Table 5: Relevant standards for coal, coke and ash analysis

Standard	Topic	ELTRA instrumentation
Overview standards with reference to other standards		
ISO 17246:2010	Coal- Proximate analysis	
ISO 17247:2020	Coal and coke- Ultimate analysis	
ASTM D3176- 15	Ultimate analysis of coal and coke	
ASTM D3172-13 (Reapproved 2021)	Proximate analysis of coal and coke	
Analysis of coal and coke		
ASTM D5373-16	Determination of C;H;N in coal and C in coal and coke	ELEMENTRAC C(H)S-r (Method B)
ISO 29541:2010	Solid mineral fuels – Determination of C;H;N	NN
ISO 19579: 2006	Solid mineral fuels- Determination of sulfur by IR spectrometry	ELEMENTRAC C(H)S-r
ISO 20336:2017	Solid mineral fuels- Determination of sulfur by coulomb titration	NN
ASTM D4239-18	Standard test method for sulfur in the analysis sample of coal and coke	ELEMENTRAC C(H)S-r
ISO 1928:2020	Coal and coke- determination of the gross calorific value	NN
ASTM D5865-13	Standard Test Method for Gross Calorific Value of Coal and Coke	NN
ASTM D7582-15	Standard test methods for proximate analysis of coal and coke by macro thermogravimetric analysis	TGA Thermostep series
Analysis of ash and combustion residues		
ASTM D 7348-21	Combustion residues (LOI)	TGA Thermostep series
ASTM D 1857-18	Standard test method for fusibility of coal and coke ash	CARBOLITE CAF G 5
ASTM D5016-16	Standard test method for total sulfur in coal and coke combustion residues	ELEMENTRAC C(H)S-r
Analysis of carbon black		
ASTM D 1619-20	Carbon black – Sulfur content	ELEMENTRAC C(H)S-r
ASTM D 7633-13 (Reapproved 2018)	Carbon black – Carbon content	ELEMENTRAC C(H)S-r