Analysis of the sulfur content in coal and cokes with the rapid CS cube

Elementar as the expert for CHNS elemental analyzers has developed a fully automatic instrument for the determination of the total content of sulfur: the rapid CS cube. The instrument is based on quantitative high temperature oxidation and IR detection. It is able to analyze almost any kind of sample from solid to liquid, organic or inorganic, with sample weights from micro to macro. One of the major applications of the rapid CS cube is in the mining and petrochemical industry.

Introduction

For quality control of coal and cokes in the mining industry the determination of the sulfur content is of major interest. It is an important parameter for evaluating the fuel value of coal and its environmental impact, since SO_2 emissions into the atmosphere are directly related to the sulfur content of the burned coal. For this, the sulfur content has to be analyzed with high precision.

The determination of the sulfur content in coal and cokes underlies strong regulations, which are defined in the international standard ASTM D 4239 standard on "standard test method for sulfur in the analysis sample of coal and cokes using high temperature tube furnace combustion methods", and in the German DIN 51724-3 standard on "solid mineral fuels – determination of sulfur". The rapid CS cube is in full agreement with the DIN standard, however, not entirely with the ASTM standard. This standard requires a combustion furnace temperature of 1350 °C.

Although the rapid CS cube could be operated with 1350°C, the decision to operate the rapid CS cube with a combustion furnace temperature of 1150 °C has some convincing reasons. At 1350 °C the instrument has to be operated with a ceramic combustion tube, which has major disadvantages compared to the quartz combustion tube, which is used in the rapid CS cube.

- ceramic combustion tubes are more expensive
- ceramic combustion tubes are less robust, leading to a shorter lifetime
- ceramic combustion tubes produce false results at low S contents, leading to a much higher detection limit
- even at 1350 °C combustion additives are necessary to increase the actual combustion temperature beyond 1350 °C, so that also hard combustible materials such as $BaSO_4$ (melting point at 1580 °C) and $CaSO_4$ (melting point at 1460 °C) digest completely

This report shows the excellent performance of the rapid CS cube using a series of coal and coke measurements including a comparison of sulfur measurements on the rapid CS cube with an independent high temperature combustion instrument.

Procedure

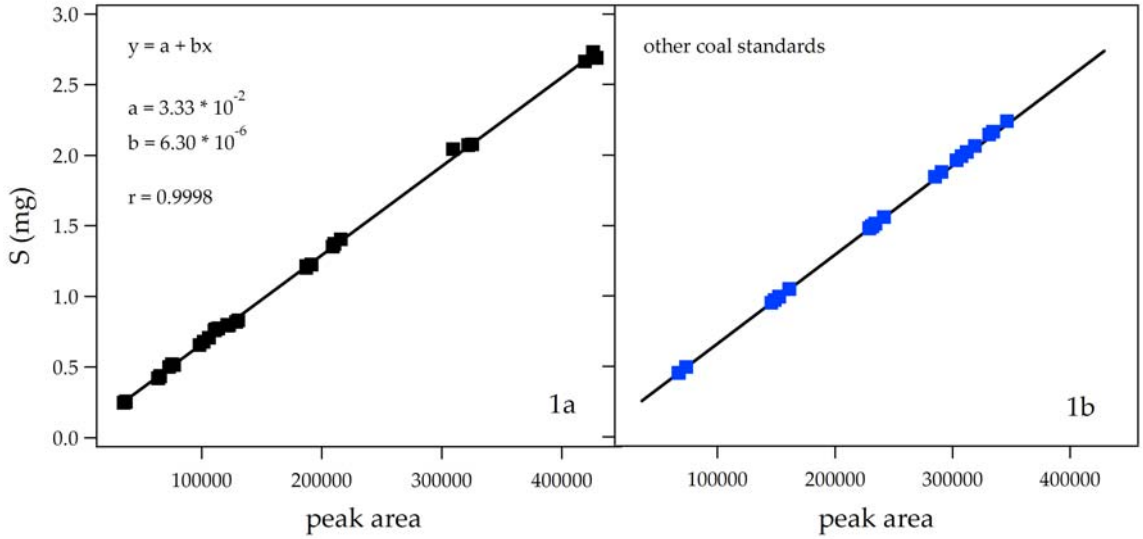
All samples have been weighed into tin foil cups or boats with a sample weight of 100 mg. For the calibration the sample weight ranged between 50 and 200 mg. WO_3 powder has been added to all samples in a ratio of at least 1:1 in order to bind alkaline earth ions.

Due to the simple configuration with oxygen as carrier as well as combustion gas, no special methods have to be developed. The instrument automatically detects the end of the analysis and then triggers the start of the next run from the integrated automatic sampler (60, 80 or 120 positions).

Calibration

Figure 1a shows the standard *Elementar* coal calibration of the rapid CS cube with coal standards ranging from 0.25 to 2.75 mg sulfur absolute (50 mg of 0.51% S standard to 200 mg 1.36% S standard). The calibration function is linear over the entire calibration range, showing that also at higher sulfur contents a complete digestion is achieved. The quality of the linear calibration function is given by the correlation coefficient r, which is 0.9998 in this case, indicating a good quality.

If necessary, the instrument can be calibrated for lower or higher sulfur values (up to 20 mg S absolute and down to the rapid CS cube detection limit of 1 ppm).



Instrument performance

Figure 1b shows the analyses of different coal standards, plotted on top of the calibration curve. These standards have not been used for the calibration itself. The graph shows that the sulfur content of the additional standards can be reproduced very well.

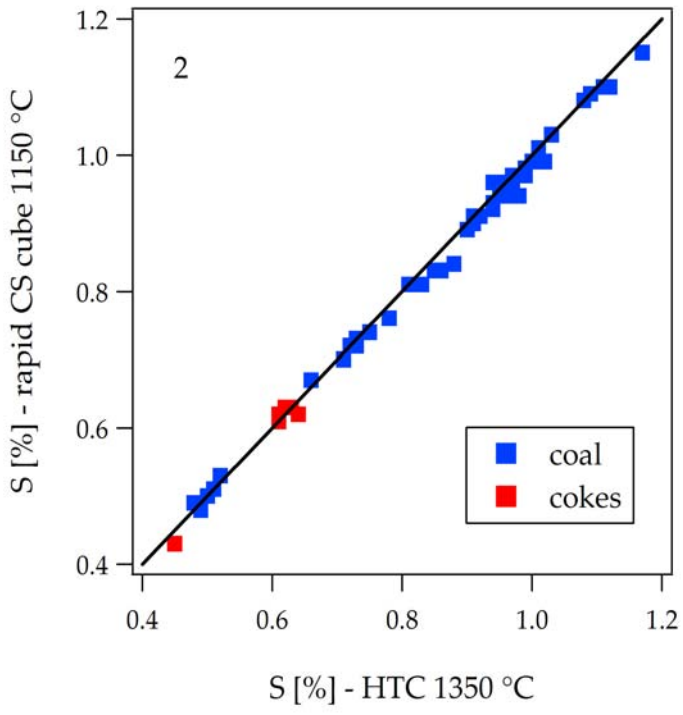
The following table shows the measured sulfur content (two analyses per standard) of four selected standards. The absolute difference of the two analyses and the maximum allowed difference ($Diff_{max}$) according to the international ASTM D 4239 standard are also given.

Standard	$S_{nominal}$ [%]	S [%]	S_{ave} [%]	Diff [%]	$Diff_{max}$ [%]
coal-1	0.21 ± 0.02	0.217 0.227	0.222	0.010	0.027
coal-2	0.49 ± 0.03	0.464 0.477	0.471	0.013	0.034
coal-3	0.99 ± 0.03	0.951 0.997	0.974	0.045	0.049
coal-4	2.20 ± 0.07	2.180 2.153	2.166	0.027	0.085

The results show that the sulfur content of different coal samples can be measured with a very high accuracy. The measured sulfur content was found to agree well with the nominal S content of the standard. The absolute difference found during paired analyses is well below the repeatability interval limit required by the ASTM standard.

Comparison of the rapid CS cube with an instrument with a combustion temperature of 1350°C

According to the international ASTM D 4239 standard, the combustion furnace temperature has to be at least 1350°C. On the other hand, the German DIN 51724-3 standard states that the combustion furnace should be between 1100 °C and 1400 °C. But that it should be guaranteed that the combustion temperature exceeds 1250 °C, so that the complete conversion of all S to SO_2 is assured. This can be achieved via the furnace temperature directly or by the application of for example tin boats, which combust with the sample exothermically and thereby increase the combustion temperature to up to 1800 °C.



The rapid CS cube works with a permanent combustion furnace temperature of 1150 °C. The samples are packed into tin boats, so that the instrument is in full agreement with the DIN 51724-3 standard. Figure 2 shows a comparison of coal and cokes measurements with the rapid CS cube and another high temperature combustion instrument (HTC) with a combustion furnace temperature of 1350°C. Both instruments give similar results, indicating that a combustion furnace temperature of 1150 °C is enough for the complete conversion of S to SO_2 when the samples are packed in tin boats. For this comparison, the samples have been analyzed once on each instrument.

The table below shows the results of the comparison for other coal and cokes samples which have been determined by multiple analyses in order to determine the precision of the measurements. The samples have been analyzed five times on the rapid CS cube, whereas on the HTC two analyses per sample were performed.

Sample	S [%] – rapid CS T = 1150 °C	S [%] – HTC T = 1350 °C	Sample	S [%] – rapid CS T = 1150 °C	S [%] – HTC T = 1350 °C
brown coal-1	2.44 ± 0.045	2.50 ± 0.10	cokes-1	0.58 ± 0.004	0.58 ± 0.005
brown coal-2	3.07 ± 0.086	2.95 ± 0.21	cokes-2	0.52 ± 0.005	0.51 ± 0.005
brown coal-3	3.97 ± 0.21	4.05 ± 0.28	cokes-3	0.47 ± 0.003	0.47 ± 0.007

The results show that the rapid CS can determine the sulfur content with a very high accuracy and precision, especially for the homogeneous cokes samples. The sulfur content determined by the rapid CS cube is in very good agreement with the sulfur content determined by the instrument with a 1350 °C combustion furnace.

The coal and cokes measurements shown in this section have been performed in cooperation with the RAG RUHRANALYTIK GmbH, Germany.

Conclusions

The rapid CS cube is very well suited for the routine analyses of the sulfur content of coals and cokes. The fast analysis and easy sample preparation enables the fully automated analyses of up to 60 samples within 5 hours with the rapid CS cube.

When coal and coke samples are packed into tin boats, the combustion furnace temperature of 1150 °C of the rapid CS cube is sufficient for the excellent analysis of the sulfur content. Major advantages of this lower combustion furnace temperature are the use of a less expensive and more robust Quartz combustion tube and a lower detection limit of the instrument.