Challenge
Automated solution for reliable and reproducible simultaneous determination of total carbon and sulfur contents in samples from cement production

Solution
Combustion elemental analysis – efficient high-temperature combustion coupled with NDIR detection for sulfur and carbon

Intended audience
Cement production, industrial quality control, contract labs dealing with cement and other building materials

Determination of Total Carbon and Total Sulfur Content in Cement and Related Samples by Combustion Elemental Analysis Coupled with NDIR Detection

Introduction

As an inorganic building material, cement belongs to the category of hydraulic binders. Due to its excellent properties and flexible usage, cement is the number one building material worldwide. In addition to its use in the construction of residential and industrial buildings, it is also used in road construction and other infrastructures (pipelines). The powder-shaped cement forms mortar by reacting with water (hydration), which hardens alone or with additional aggregates such as sand, gravel, porous solids, steel elements, and others to form solid, highly robust concrete. Calcium-, aluminum-, and silicon-containing natural raw materials such as limestone and clay minerals are used for its production. In addition to these main constituents, there are many additives that have a significant influence on the service properties and robustness of the cement. These materials include gypsum/anhydrite, slag sand, burnt shale, silica dust, fly ash, pozzolan, and blast furnace slag. Based on its composition, cement is categorized into various standardized types and sub-types. This makes it possible to find a product perfectly suited for each specific application in terms of its properties and resistance. It goes without saying that a building material, which must meet the highest quality requirements, is subject to close analysis throughout the entire production process. In addition to important physical properties such as loss on ignition and heat of hydration, chemical properties such as the content of metal oxides (CaO, Fe_2O_3) and non-metals such as carbon and sulfur are also required. The latter two non-metals are determined as the sum parameters TC and TS. They play an important role in process optimization, to assess environmental effects (CO_2 / SO_2 emission), potential risk in further use (sulfur corrosion), or to classify the final products

(sulfate resistance). Although the sulfur content can also be determined by XRF methods together with the also relevant metal oxides, this is not possible for the carbon. Since both, carbon and sulfur, are important for many different process-relevant matrices – solid combustibles, raw materials, intermediates, additives and the final product – combustion elemental analysis, which allows simultaneous and matrix-independent determination of both parameters in a single analytical step, is established.
The multi EA 4000 is such an elemental analyzer, designed for rapid simultaneous C/S determination over a wide concentration range in inorganic and organic sample matrices as needed in cement industry.

Materials and Methods

A combustion elemental analyzer type multi EA 4000 was used for the simultaneous determination of sulfur and carbon contents. The analyzer is based on high-temperature combustion for sample digestion, using a robust ceramic combustion tube. The multi EA 4000 is an open system, the combustion furnace is arranged in horizontal orientation. Samples are fed via a simple gas lock. This allows easy operation and automation of the analysis process. For the here described measurements a solids sampler type FPG 48 was used to transfer the samples, which have been filled in ceramic boats, into the furnace. The boats were removed with residue after analysis for fully automated disposal.
The total sulfur (TS) and total carbon (TC) contents have been determined by combustion of the untreated samples at 1,450 °C in a pure oxygen stream. Therefor the samples were weighted into ceramic boats and covered with vanadium pentoxide (V_2O_5) to enable a faster release of SO_2 during the process. This was done to increase the reaction speed and thereby safe valuable analysis time. The formed reaction gas is cleaned and dried sufficiently by integrated systems before it is transferred to the NDIR (non-dispersive infrared) detectors for sulfur and carbon determination.

Samples and reagents

- Different cement samples, powder-shape
- Cement standard I - 2.04% C (calibration and performance check)
- Cement standard II - 0.41% S (calibration and performance check)
- NIST 1889a cement (reference cement, 1.08% S)
- V_2O_5 (auxiliary material, oxidation aid)

Sample preparation

Due to the samples' good homogeneity no sample preparation was necessary.

Calibration

The analyzer has been calibrated before analysis. The applied calibration principle is constant concentration. Two solid standard materials of the same matrix type have been used, a cement standard with 0.41% S for the sulfur determination and a cement standard with 2.04% C for the carbon determination, see details in table 1. To cover a wide concentration range different quantities of these standards have been used to vary the absolute element content. The resulting calibration curves are shown in figure 1 and 2. Correctness of calibrations was checked with different standards.

Table 1: Calibration of the instrument

Standard	Parameter	Concentration	Weight	Calibration range
Cement standard I	TC	2.04 % C	45–280 mg	11–87 mg C
Cement standard II	TS	0.41 % S	64–280 mg	0.23-0.57 mg S

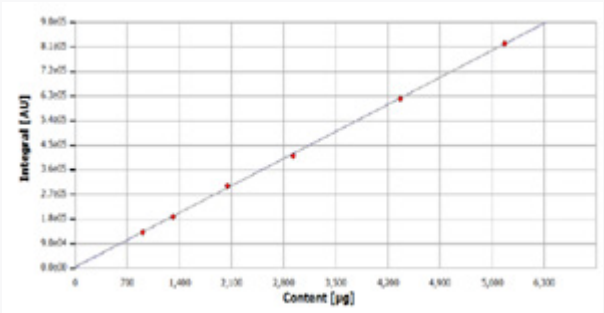

Figure 1: TC calibration with cement standard I - 2.04% C

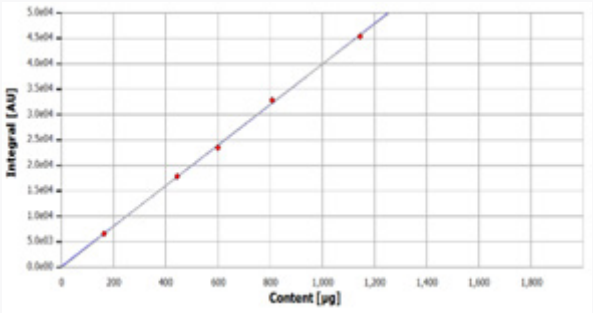

Figure 2: TS calibration with cement standard II - 0.41% S

Method parameters

The used process parameters for sample introduction and combustion are summarized in table 2 (below left).

Evaluation parameters

The used process parameters for detection and evaluation are summarized in table 3 (below right).

Table 2: Process parameters multi EA 4000 and FPG 48

Parameter	Specification
Temperature	1,450 °C
Oxygen flow	2.5 L/min
FPG 48 parameter set	TC_TS_inorg

Table 3: Process parameters for carbon detection (NDIR) and sulfur (NDIR)

Parameter	C detection	S detection
Max. integration time	600 s	600 s
Start	0.12 ppm	0.12 ppm
Stop	5 ppm	1.50 ppm
Block	3	3

Results and Discussion

Different cement samples and certified reference cements have been analyzed for their sulfur and carbon contents. For analysis quantities between 60 and 120 mg were used for both, standard and samples. The gained measurement results are summarized in table 4. They are average values of triplicate analysis.

Table 4: Results of determination of total carbon and total sulfur (TC, TS) in cement samples and reference materials

Sample	TC ± SD [%]	TS ± SD [%]
Cement 1	36.3 ± 2.24	0.32 ± 0.04
Cement 2	48.3 ± 1.07	0.41 ± 0.04
Cement 3	10.1 ± 0.03	0.09 ± 0.00
Cement 4	10.8 ± 0.04	0.29 ± 0.02
Cement 5	2.07 ± 0.02	1.33 ± 0.00
Reference cement	0.70 ± 0.01	1.27 ± 0.00
Cement standard I (2.04% C)	2.00 ± 0.04	
Cement standard II (0.41% S)		0.38 ± 0.01
NIST 1889a cement (1.08% S)		1.13 ± 0.00

The results are reproducible, and the standard deviations are low. Slight deviations from the reference values are to be expected and the differences are in the familiar range. The obvious differences in their carbon and sulfur contents are based on their different composition (cement type). Measurement results are available in short time. For simultaneous determination, even for higher contents 4 to 6 minutes are sufficient for a simultaneous C/S analysis.
To depict this, exemplarily selected measuring curves for the determination of carbon and sulfur are shown in figures 3 to 8.

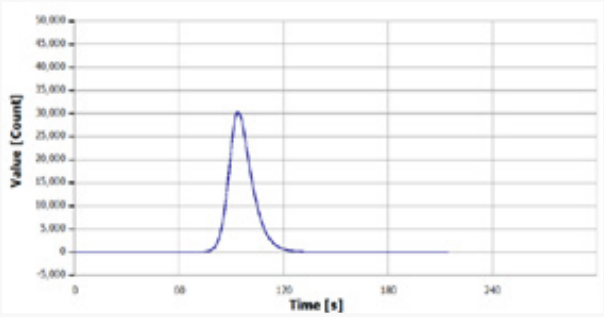

Figure 3: TC measuring curve of sample "cement 1"

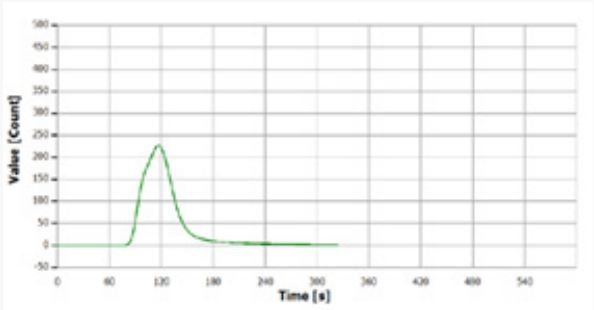

Figure 4: TS measuring curve of sample "cement 1"

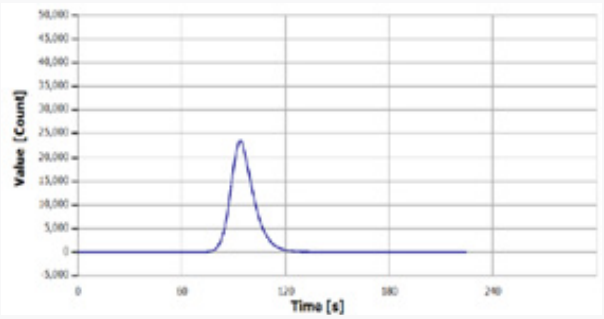

Figure 5: TC measuring curve of sample "cement 2"

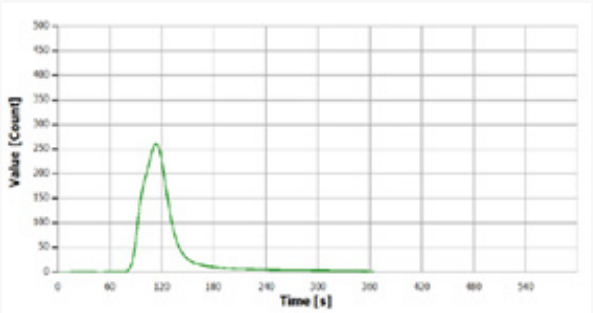

Figure 6: TS measuring curve of sample "cement 2

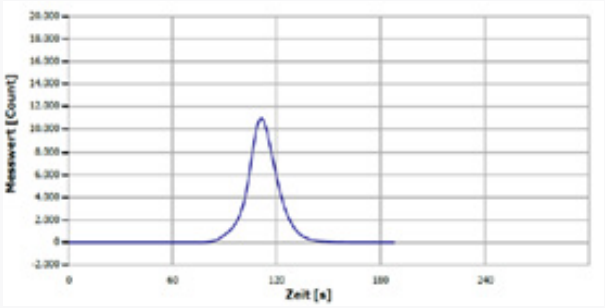

Figure 7: TC measuring curve of sample"cement 3"

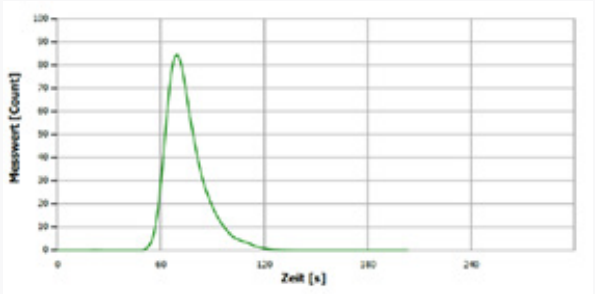

Figure 8: TS measuring curve of sample "cement 3"

Summary

The combustion based elemental analysis coupled with element-selective infrared (NDIR) detection offers an easy to use measurement principle for determination of the total sulfur and total carbon contents. The versatility of the analysis technique is essential, as it allows to also measure other relevant carbon sum parameters like TIC and TOC for feedstocks and the produced cement with one and the same system.
The multi EA 4000 used in this application note is well suited for the quick and simultaneous determination of total sulfur and total carbon contents in cement and related materials from cement production. In routine applications the solids autosampler with its 48 positions and boat deposition station enables high sample throughput at minimum operation effort. For small sample numbers manual sample supply is possible as an alternative. Thanks to the resistant heated furnace, also pure organic matter, such as solid fossil and derived fuels – crucial aids in the production of cement clinker – can be analyzed for their environmentally hazardous content of sulfur and chlorine. The system can easily be upgraded for Cl analysis. This unique element combination and carbon speciation capabilities make the multi EA 4000 the most versatile and widest applicable elemental analyzer in production and recycling of cements and other building materials.

Figure 9: multi EA 4000 CS analyzer

Recommended system configuration

Table 5: Overview of devices and accessories

Article	Article number	Description
multi EA 4000 CS	450-126.440	Combustion elemental analyzer for determination of Sulfur and carbon contents in solids
FPG 48	450-126.574	Solids autosampler for multi EA 4000
Boat deposition station for FPG 48	450-889.728	For FPG 48, for automatic disposal of used sample boats

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