Challenge
Comfortable automated solution for the differentiation between total sulfide and other sulfur species in cement and related samples

Solution
Combustion elemental analysis – high temperature combustion, acid digestion, coupled with NDIR detection, speciation of sulfur-bond types according to the differential method

Intended audience
Cement production, industrial quality control, contract labs dealing with analysis of building materials

Determination of Sulfur Species in Cement Samples by Combustion Elemental Analysis coupled with NDIR Detection according to Difference Method

Introduction

Cement is one of the most popular building materials of our time. This is mainly due to its flexible application possibilities, easy processing, and extraordinary stability and robustness. DIN EN 197-1 divides cement into five major types, according to its main constituents – Portland cement CEM I, Portland composite cement CEM II, blast furnace cement CEM III, pozzolanic cement CEM IV, and composite cement CEM V – which can be further subdivided into 27 special and sub-types. No matter how demanding the application, there is always a suitable cement type with optimum properties and robustness adapted to the type of use and environmental conditions. Despite all this, even cement does not have an eternal life. For example, acids, salts, and organic substances such as H_2SO_4, magnesium and ammonium salts, fats and oils can reduce its strength and attack it from the surface. Sulfates can penetrate low density concrete and cause so-called sulfate corrosion or sulfate attack by forming ettringite and gypsum with the calcium hydroxide and aluminate hydrates, which are cement components. By attaching numerous water molecules, the sulfate can increase its volume by up to 300%, this leads to disruption of the structure up to the formation of cracks and spalling of fragments, thus contributing to the loss of stability. In this process, environmental conditions such as moisture (e.g., composition, pH, flow velocity) and temperature play not insignificant roles. However, sulfur compounds contained in the cement and its aggregates (e.g., gypsum, anhydrite), also drive the destruction of concrete forward. Depending on the type of cement used, it can contain several mass percent of sulfur, which already results in 1% sulfate in the freshly prepared concrete. Initially, this does not pose any danger, but in the presence of increased moisture or permanent contact with water, the hydration of the sulfates, as described above, leads to sulfate corrosion and thus destruction of the concrete.

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Therefore, sulfur measurement in cement and feedstock materials used in the production of cement, such as limestone and fly ash, plays an important role in controlling the raw materials and ensuring the required quality of the final products. In addition to determining the total sulfur content, it is also important to determine the proportion of sulfur species, the sulfates, which are critical for sulfate concrete corrosion. This is used for quality assurance and classification of the cement. However, distinguishing between the different sulfur species is a demanding challenge for the analytical technique used. Traditional methods such as XRF or elemental analysis using induction furnace or classical elemental analysis cannot do both. They provide the total sulfur content as a sum parameter.

The sulfur bound in sulfates must be determined by further analysis using wet chemical methods (e.g., gravimetry, photometry, indirect potentiometric titration, or ion chromatography). A combination of high-temperature combustion and a simple sample treatment step offers an interesting alternative, which uses one and the same digestion and detection principle for the determination of both, the total sulfur and the sulfate-bound sulfur. This makes the results much more reliable and comparable in contrast to use of two completely different analytical methods. For the methodology described in this application note an elemental analyzer of the type multi EA 4000 was used.

Materials and Methods

Instrumentation

A combustion elemental analyzer type multi EA 4000 was used for determination of sulfur contents. The analyzer is based on high-temperature combustion principle 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 and to remove these boats with residue after analysis for fully automated disposal.

The total sulfur (TS) content has been determined by combustion of the untreated samples at 1,450 °C in a pure oxygen stream. Therefor the samples were weighed into ceramic boats and covered with vanadium pentoxide (V_2O_5). This was done to increase the reaction speed and thereby save 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) detection.

To obtain the sulfide content an additional measurement is necessary. Therefor an aliquot of the same sample was filled in a ceramic boat, but before analysis this was acidified by addition of 10% HCl to remove possibly included sulfides (S^{2-}). Sulfides react with a strong inorganic acid; the reaction generates gaseous hydrogen sulfide (H_2S) which escapes from the sample. To ensure completeness of the process, the samples were kept under a fume hood for a sufficient time (e.g., overnight). Afterwards the samples have been dried on a hot plate (approx. 70 °C) for one hour. From this point, the treated samples underwent the same analysis process as the untreated. The gained sulfur parameter is the total sulfur without the sulfide-bound sulfur portion. In this application the abbreviation TS_t (total sulfur after treatment)

is used. The content of sulfide-bound sulfur (TS_d) now can be calculated by differential method from the two measured results.

$$TS_d = TS - TS_t$$

As an alternative for HCl, a mixture of formic acid and phosphoric acid can be used for acidification. This is the preferable approach in case of a high content of sulfides and therefor addition of a huge amount of HCl, preventing strong halogen scrubber consumption.

Samples and reagents

- Different cement samples, powder-shape
- Cement standard 0.41% S (calibration and performance check)
- Cement standard 1.31% S (calibration and performance check)
- HCl, 10%
- V_2O_5, (auxiliary material, oxidation aid)

Sample preparation

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

Calibration

The analyzer has been calibrated before sulfur 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 lower concentrations and a cement standard with 1.31 % S for the higher contents. To cover a wide concentration range different quantities of these standards have been used.

Table 1: Calibration of the instrument

Standard	Parameter	Concentration	Weight	Calibration range
Reference cement 1	TS	0.41% S	64–280 mg	0.26–1.15 mg S
Reference cement 2	TS	1.31% S	76–296 mg	1.00–3.88 mg S

The resulting calibration curves are shown in figure 1 and 2. Correctness of calibrations was checked with different standards.
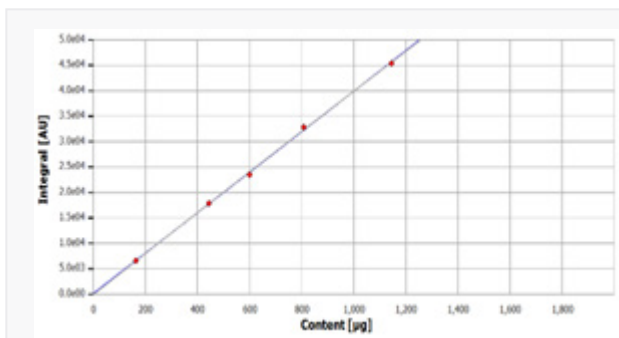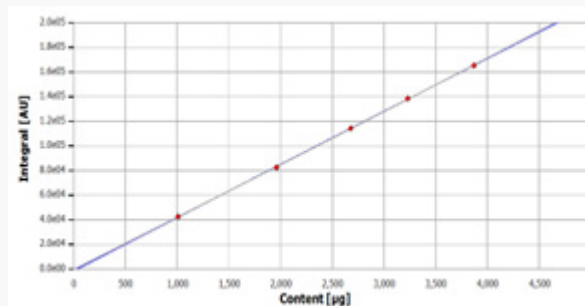

Figure 1: TS calibration with cement standard 0.41% S

Figure 2: TS calibration with cement standard 1.31% 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	TS_inorg_auto

Table 3: Evaluation parameters for sulfur detection (NDIR)

Parameter	Specification
Max. integration time	600 s
Start	0.12 ppm
Stop	1.50 ppm
Block	3

Results and Discussion

Analysis results for the measurements cement samples and control standards are summarized in table 4. They are average values of triplicate analysis. For analysis quantities between 70 and 200 mg were used for both, standards and samples.

Table 4: Results of determination of different sulfur species (TS, TS_d, TS_t) in cement samples, results for TS determination in reference materials

Standard	TS ± SD [%]*	TS_t ± SD [%]*	TS_d**
Cement 1	0.81 ± 0.004	0.33 ± 0.01	0.48
Cement 2	1.19 ± 0.011	0.06 ± 0.00	1.13
Cement 3	1.06 ± 0.002	0.31 ± 0.02	0.75
Cement 4	1.65 ± 0.025	0.66 ± 0.04	0.99
Cement 5	1.53 ± 0.002	0.85 ± 0.04	0.68
Standard cement 0.41% S	0.40 ± 0.005	na	na
Standard cement 1.31% S	1.31 ± 0.001	na	na

*   measured
**   calculated as difference TS − TS_t

The results are reproducible, and the standard deviations are reasonably low. Exemplarily the measuring curves for the sample "cement 1", treated and untreated, and one standard for system check are shown in figures 3 - 5.
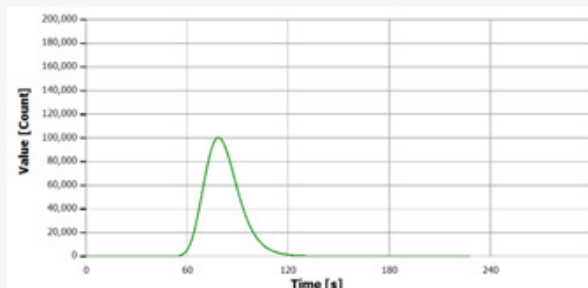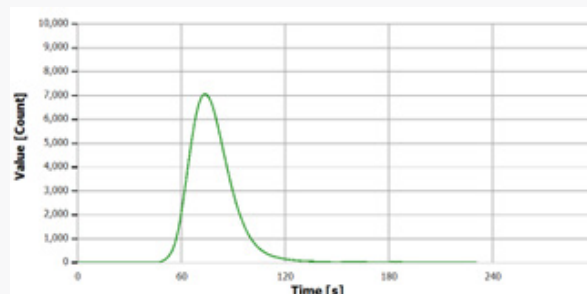

Figure 3: TS measuring curve of sample "cement 1"

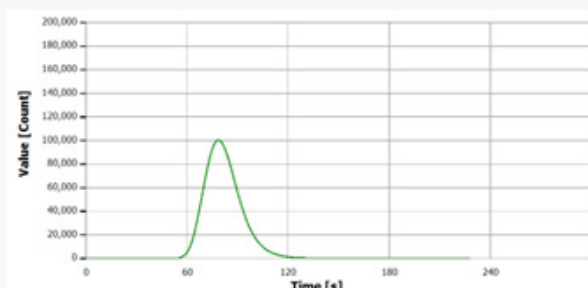Figure 4: TS_t measuring curve of the acid treated sample "cement 1"

Figure 5: TS measuring curve of standard "cement 0.41% S"

Summary

For risk assessment and quality control of cements, besides many other physical and chemical parameters also the determination of the sulfur bond types plays an important role. The gained results are also used for classification of the cement types.

Combustion based elemental analysis is the most efficient solution. The multi EA 4000, based on high temperature combustion coupled with selective infrared (IR) detection, is well suited for a reliable quantification of total sulfur and sulfide sulfur by difference method in cement and related materials. It offers ease of use and matrix-flexibility. Acid digestion releases sulfides in the shape of H_2S and is a simple treatment step that can be easily performed by the operator, enabling the speciation of sulfur bond types. With its capability to measure up to 3 g of sample weight (depending on the specific density) the multi EA 4000 allows for reliable analysis result even in the trace range. In routine applications the solids autosampler with its 48 positions and boat deposition station, enables high sample throughput at minimum operation effort.

Figure 6: multi EA 4000 with sulfur detector

Besides sulfur analysis, the system can be upgraded for determination of total carbon and related sum parameters like TIC, TOC, or total chlorine determination, e.g., for quality control of solid derived fuels as commonly used in cement industry.

Overview of devices and consumables

Table 5: Recommended device and accessories

Article	Article number	Description
multi EA 4000 S	450-126.565	Combustion elemental analyzer for determination of Sulfur contents in solids
FPG 48	450-126.574	Solids autosampler for multi EA 4000

References

[1] F. W. Locher, Chemischer Angriff auf Beton, Betontechnische Berichte Vol. 67