Challenge
Comfortable automated solution for the determination of different carbon parameters (TC/TOC/TIC) in gypsum and limestone samples

Solution
Combustion elemental analysis – efficient high-temperature combustion coupled with NDIR detection

Intended audience
Gypsum production and recycling, cement production, industrial quality control, contract labs dealing with analysis of building materials

Determination of Total Organic Carbon in Limestone and Gypsum Samples by Combustion Elemental Analysis coupled with NDIR Detection in Accordance with EN 13639

Introduction

Gypsum, or chemically correct calcium sulfate dihydrate, is a naturally occurring mineral. It is considered an important raw material for many industrial, medical, and artistic applications, one of the most important of which is its use as a building material, e.g., anhydrite, plaster, stucco gypsum, screed, or plasterboard. Gypsum is also generated in large quantities as a by-product in industrially used technical processes, such as the production of organic and inorganic acids like oxalic acid, HF, H_2SO_4, the neutralization of sulfate containing process wastewaters and the flue gas desulfurization of the exhaust gases of coal-fired power plants, as FGD gypsum. Depending on the contained impurities, such materials can be used in the building materials industry. A high volume of FGD gypsum makes the mining of natural gypsum partly dispensable. If production is higher than demand, it can be used for other purposes, e.g., as a filler, or simply disposed of on landfills.

After utilization is before recovery – recycling takes an important place in the gypsum lifecycle. In industrial recycling, gypsum is usually ground and used to make new gypsum plaster board, as an absorber for drying processes, or in water treatment. Both dumping and recycling require compliance with maximum permissible values (e.g., for classification in a landfill class) and fulfillment of specified quality markers. Numerous physical and chemical parameters are important for this, including the TOC – a sum parameter that describes the total organically bound carbon content. Not all waste containing gypsum is suitable for recycling. The Federal Association of the Gypsum Industry in Germany specifies quality requirements for recycled gypsum. For example, the TOC for recycled gypsum must not exceed 1.00%[1]. Plant-specific deviations up to max. 1.50% are only possible by special agreement.

For the landfilling of gypsum waste, the criteria and limit values of the Landfill Ordinance (DepV) must be observed. Due to the elution behavior of gypsum waste (sulfate concentrations in the eluate of up to 1,500 mg/L), landfills from Class I (DK I) are suitable for the deposition of gypsum-based building materials. Increased TOC content may require a higher landfill class. A high organically bound carbon content supports the formation of hydrogen sulfide (H_2S) in the presence of high sulfur levels, which must be avoided. Organic contaminants (TOC) can originate from the manufacturing process (citric acid, cellulose glue, fiber material) but also from contamination accumulated during use (adsorption from air, fungal growth).
Methods for the determination of TOC and other carbon sum parameters in solids such as soil, gypsum, cement, waste, and related materials are described in many regulations, such as EN 13137, DIN EN 15936, or EN 13639. The reference and alternative methods described here are all based on three essential steps. First, the dried, homogenized sample must be freed of any carbonate-bound carbon (TIC) present by acidification with a non-oxidizing mineral acid. The TIC is released in the form of CO_2. Afterwards, the organically bound carbon (TOC) contained in the sample is completely converted to CO_2 by chemical or thermal oxidation. This is quantitatively determined in the final step using a suitable gravimetric or spectroscopic measuring method.
Due to the large quantity of samples and the need for complete monitoring, automation of the analysis process is essential. Elemental analyzers that have been specially optimized for the determination of carbon sum parameters are ideally suited for this purpose. These systems combine both wet-chemical reactors for the separate determination of inorganically bound (TIC) carbon and a furnace for high-temperature combustion for the determination of total carbon (TC) and organically bound carbon (TOC). Through intelligent gas management, even the determination of elemental carbon (EC) is possible through an additional pyrolysis step. The EC can falsify the TOC values if present. Thus, the determination of all relevant parameters is possible with only one analyzer, conveniently and fully automated. Advantages are the better comparability of the individual parameters, a noticeably increased sample throughput, and the minimization of error sources and dangers. The multi EA 4000 is an analytical system suitable for the determination of carbon sum parameters in a wide variety of matrices. Thanks to large possible sample quantities up to 3 g and very robust ceramic technology, there are hardly any limits to its use beyond gypsum analysis.

Materials and Methods

A combustion elemental analyzer type multi EA 4000 equipped with the TIC solids module “automatic” was used for determination of the parameters TC, TIC, and TOC. The analyzer is based on the high-temperature combustion principle for sample digestion, using a robust ceramic combustion tube for direct TC and TOC determination, and a wet-chemical reactor for TIC determination. The multi EA 4000 is an open system, the combustion furnace is arranged horizontally, the TIC solids module is installed in front of the furnace entrance. Samples are fed via a simple gas lock. This allows easy operation and automation of the entire analysis process. For the here described measurements a solids sampler type FPG 48 was used to transfer the TC and TIC samples, which have been filled in ceramic boats, into the furnace resp. the TIC reactor. The boats were removed with residue after analysis for fully automated disposal.
The total organic carbon (TOC) content was determined according to the difference method. Therefor the total carbon (TC) and the total inorganic carbon (TIC) have been measured, afterwards the TOC was calculated as difference of both.

TC-TIC = TOC

Therefor two aliquots of each sample were weighed in two sample boats. The first was acidified in the TIC reactor with 40% H_3PO_4, the CO_2 from the carbonates was released and the TIC was measured directly. With a second boat, the sample was introduced into the resistance furnace, where combustion took place at 1,200 °C in a pure oxygen stream, to ensure complete digestion. In both runs the measuring gas was dried and cleaned and the carbon content was measured by NDIR (non-dispersive infrared) detection. The calculation of the TOC was performed automatically by the multiWin operation and data evaluation software.

Samples and reagents

- Different gypsum samples, powder-shape derived from recycling gypsum process
- Control standard (5% TIC, 10% TC, 5% TOC)
- H_3PO_4, 40% (acid for digestion)
- Al_2O_3 (diluent)
- Glassy carbon (TC, standard material)
- $CaCO_3$ (TIC, standard material)

Sample preparation

Due to their good homogeneity no sample preparation was necessary.

Calibration

The analyzer was calibrated before analysis. The applied calibration principle is constant concentration. To cover a wide concentration range, different quantities of the standards have been used to vary the absolute carbon content. For determination of the parameter TC, a dilution of glassy carbon was applied. Therefor the glassy carbon was diluted with Al_2O_3 to generate a 9.91% TC standard. For determination of TIC, $CaCO_3$ was used. Therefor calcium carbonate was diluted[2] with Al_2O_3 to generate a concentration of 1.2% C. The resulting calibration curves are shown in figure 1 and 2. The calibration ranges are given in table 1.

For calibration of TC instead of glassy carbon also $CaCO_3$ or a dilution of it like for TIC could be used to avoid utilization of two calibration standards.

Table 1: Calibration of the instrument

Standard	Parameter	c_C	Weight	Calibration range
$CaCO_3$	TIC	1.2% C	16–142 mg	0.2–1.7 mg C
Glassy carbon	TC	9.91% C	14–86 mg	1.4–8.5 mg C

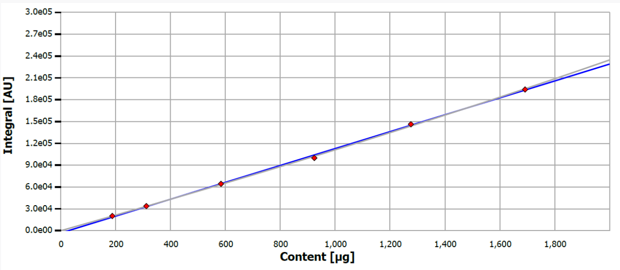

Figure 1: TIC calibration

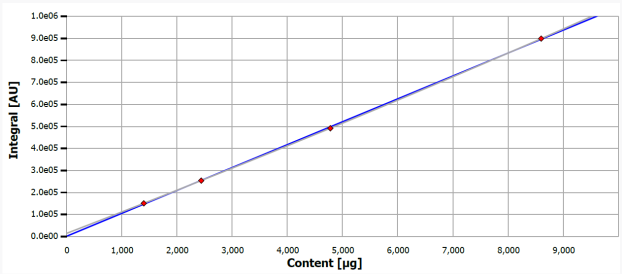

Figure 2: TC calibration

Method parameters

The used process parameters for sample introduction and combustion according to TOC difference method are summarized in table 2.

Table 2: Process parameters multi EA 4000 and FPG 48

Parameter	Specification
Temperature	1,200 °C
Oxygen flow	2.5 L/min
Amount of acid	800 µL
FPG 48 parameter set	TOC_IC/OC_inorganic

Evaluation parameters

The used process parameters for detection and evaluation are summarized in table 3.

Table 3: Process parameters for carbon detection (NDIR)

Parameter	Specification
Max. integration time	600 s
Start	0.12 ppm
Stop	5 ppm
Block	3

Results and Discussion

Different samples derived from gypsum production and recycling processes were analyzed for their total organic carbon (TOC), total carbon (TC), and total inorganic carbon (TIC) contents. For TOC determination the difference method by means of the automatic TIC solid module was applied.
The gained analysis results for the measured gypsum samples and control standards are summarized in table 4. They are average values of triplicate analysis. For analysis, quantities between 50 and 300 mg were used for both, standards and samples. The results are reproducible, and the standard deviations are low. Exemplarily the measuring curves for the sample gypsum 1 are shown in figures 3 and 4.

Table 4: Results of determination of different carbon sum parameters (TC, TIC, TOC) in gypsum samples, and reference materials

Standard	TIC ± SD [%]**	TC ± SD [%]**	TOC_{diff}*
Gypsum 1	3.88 ± 0.11	4.36 ± 0.15	0.48
Gypsum 2	0.09 ± 0.00	0.20 ± 0.01	0.11
Gypsum 3	0.22 ± 0.04	0.49 ± 0.04	0.27
Gypsum 4	1.21 ± 0.01	1.37 ± 0.08	0.16
$CaCO_3$ (1.20% C)	1.22 ± 0.01	1.25 ± 0.01	n.a.
Control standard (5% TIC, 10% TC, 5% TOC)	4.93 ± 0.10	10.38 ± 0.26	5.45

** measured directly, * calculated as difference TC – TIC

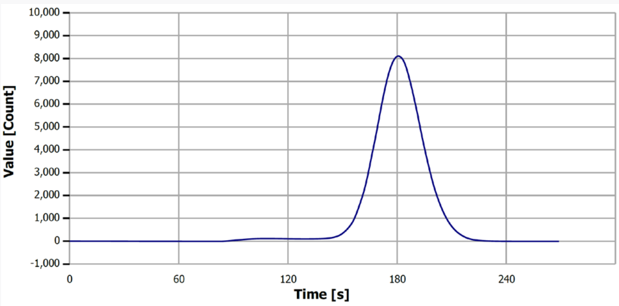

Figure 3: TC measuring curve of sample "gypsum 1"

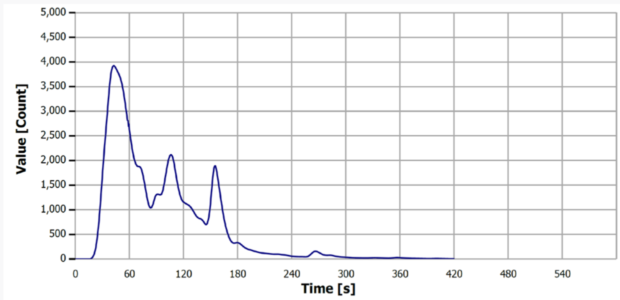

Figure 4: TIC measuring curve of the acid treated sample "gypsum 1"

Summary

Especially in the field of construction material production, recycling, and disposal, many different methods are accepted for TOC determination. EN 13639, for instance, refers to gravimetric methods with wet oxidation as reference method. Such manual methods are time-consuming and cannot be automated. Alternative methods are applicable, if their suitability and equivalent performance has been approved.
The multi EA 4000 carbon analyzer with TIC module is such an approved alternative and well suited for fully automated determination of different carbon parameters in gypsum and related sample materials. Compared to other reference methods, e.g., wet-chemical digestion with gravimetric determination, the high-temperature combustion with infrared (IR) detection is clearly superior due to its possibilities for high sample throughput and flexibility in carbon speciation. Thanks to the TIC solids module automatic, the TOC can be determined directly or according to the difference method. This allows easy adaptation of the analysis process to specific regulatory requirements or sample needs. Analysis is fully automated from sample introduction to the disposal of the acid contaminated sample boats. This prevents potential risks for the operator (minimization of acid contact) and the hardware by the used acid and allows for easiest operation.
The multi EA 4000 can be further upgraded to determine sulfur contents and organically bound chlorine.

Figure 5: multi EA 4000 with carbon detector

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 4000 C	450-126.564	Combustion elemental analyzer for determination of carbon contents in solids
FPG 48	450-126.574	Solids autosampler for multi EA 4000
TIC solids module "automatic"	450-126.576	Accessory module for multi EA 4000, enabling fully automated determination of TIC, and TOC acc. direct and difference method

References

[1] Umweltbundesamt, Gips – Factsheet, page 8, https://www.umweltbundesamt.de/sites/default/files/medien/3521/dokumente/factsheet_gips_fi_barrierefrei.pdf

[2] Analytik Jena – LabGuide Sample Preparation Strategies, page 14 ff, https://www.analytik-jena.de/wissen/whitepaper/labguide-sample-preparation/

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