Challenge
Fast, reliable, and cost effective determination of the total organic carbon in environmental analysis (soils, sediments, ...) over a wide concentration range

Solution
Fully automatic determination with the multi EA 4000 with applied solids sampler FPG 48 and an automatic TIC solids module

Intended audience
Contract and environmental laboratories, state agencies, academia and agricultural institutes

DIN EN 15936 Method A – Using the Difference Method for Automatic and Trustworthy TOC Results in Soils and Other Solids

Introduction

Carbon is present in soils and sediments in various forms and and is considered in a very differentiated manner. A precise analysis of the various compounds is very time-consuming and laborious due to their diversity and requires complex separation and analysis techniques. The sum parameters of carbon provide control laboratories with a quick and cost-effective method to assess soil quality without precisely identifying the individual components.

The total carbon (TC) contained in the soil is subdivided into further parameters:

- Inorganic carbon (TIC, total inorganic carbon), mainly in the form of carbonate and hydrogen carbonate, is a natural component of soil, but can also come from artificial additives and other sources.
- Total organic carbon (TOC) is mainly produced by organic matter from natural sources (plants, animals, microbial decomposition processes), but also man-made pollution and industrial and agricultural processes (e.g., oil residues, waste, over-fertilization) contribute to TOC. Its content is influenced by erosion, biological decomposition (e.g., by bacteria) and agriculture. TOC has an influence on soil properties such as color, fertility, or toxicity. This makes it an important parameter in agriculture, environmental protection, waste management, and for landfills, which must be monitored regularly.

Separation of these parameters is very important, as it enables to estimate the suitability for landfilling, carbon sequestration capacity, and general soil quality. For this purpose, elemental analysis techniques based on complete high-temperature combustion of all sample components followed by detection of the CO_2 formed using non-dispersive infrared (NDIR) spectrometry (e.g., in accordance with DIN EN 15936[1]) have proven effective.

Depending on the type of soil and its TOC/TIC ratio, two different TOC determination methods are available. Direct method (B) is used if the TOC is low compared to the TIC. It requires extensive sample preparation to completely remove the interfering TIC (wet-chemical acid digestion and drying of the treated samples). This method is also difficult to automate and has a negative impact on the hardware of the analyzer in terms of consumables and maintenance. Therefore, the difference method (indirect method A) is preferable if the TOC content is equal to or higher than the TIC. This method requires two analyses to determine the result (TC and TIC determination). Nevertheless, the additional measuring time is negligible compared to the sample preparation effort for direct determination.

Material and Methods

Samples and sample preparation

In addition to internal standard materials and standardized control mixtures, eight certified reference materials (CRM) with certified reference or informative values were analyzed. All samples were dry, fine powders. They were measured directly, without any sample preparation.

Calibration

The multi EA 4000 was calibrated in advance, using a standard of constant concentration and applying different sample quantities. As calibration material for carbon, pure calcium carbonate (12% C) and diluted calcium carbonate (1.2% C and 0.12% C in Al_2O_3) was applied.

For standard preparation, one part $CaCO_3$ and nine parts Al_2O_3 were mixed in a ball mill to obtain a homogeneous 1 in 10 dilution with a concentration of 1.2% C. This standard was checked and characterized. It was the base for a second 1 in 10 dilution step in Al_2O_3 for the 0.12% C Standard. These calibration standards were used for TIC and TC determination.
Used calibration curves are shown in Figures 1 and 2 below. In Table 1 the calibration ranges are described.

Table 1: Calibration of the multi EA 4000 for the different carbon parameters

Parameter	Standard	Content C (%)	Weight (mg)	Calibrated range (µg C)
TIC	$CaCO_3$ in Al_2O_3	0.12	14–265	18–310
TIC	$CaCO_3$ in Al_2O_3	1.2	17-228	200–2,850
TIC	$CaCO_3$	12	13–49	1,600–6,000
TC	$CaCO_3$ in Al_2O_3	1.2	38–330	450–3,950
TC	$CaCO_3$	12	16–131	1,900–15,500

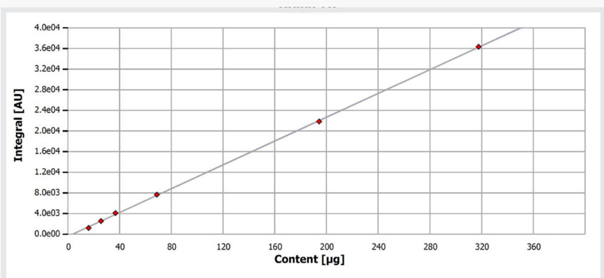

Figure 1: TIC calibration with 0.12% C standard

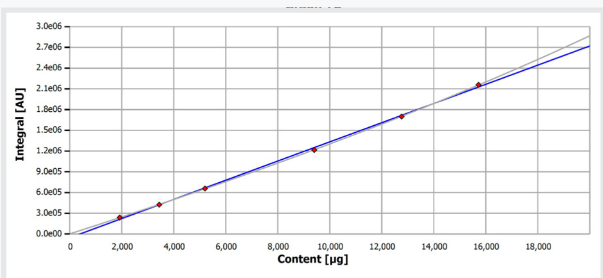

Figure 2: TC calibration with 12% C standard

System parameters

For the determination of the TOC, a TOC difference method was applied. The TOC equals the difference between TC and TIC: TOC = TC – TIC. Therefore, the TC and the TIC had to be determined for each sample. Both measurements were performed by means of a multi EA 4000 C with TIC solids module "automatic" and the automatic solids sampler FPG 48. Two weighed sample aliquots were used per analysis. The first sample aliquot was acidified automatically in the TIC reactor with 40% H_3PO_4, the CO_2 from the carbonate was released and the TIC was measured directly. With a second boat, the second sample aliquot was introduced into the resistance furnace at 1,200 °C and completely digested in a pure oxygen atmosphere. In both runs the measuring gases were dried and cleaned and the carbon content was measured by NDIR spectrometry. The calculation of the TOC was performed automatically by the device's multiWin software.

Method parameters

Standard settings from the integrated method library were applied to perform the measurements. Parameter settings for the combustion are shown in Table 2, detection settings in Table 3.

Table 2: Process parameters for the TOC difference method

Parameter	Setting
Furnace temperature	1,200 °C
FPG program	TOC_IC/OC_inorg
O_2 flow	2.5 L/min
Amount of acid	2 (=800 µL)

Table 3: Detection parameters

Parameter	Setting
Max. integration time	600 s
Stability	3
Start	0.12
Threshold	5

Results and Discussion

Analysis results for the measurements of the samples are shown in Table 4. Typical measuring curves are shown in Figure 3 and following. Measurements were performed as triplicates for each sample. Carbonate standards were measured as duplicates. Sample weights varied, depending on the parameter and concentration; for TIC determinations between 50 mg and 300 mg, for TC determination about 100 mg were used.

Table 4: Results of the TOC difference determination

	TIC ± SD (%)		TC ± SD (%)		TOC difference
$CaCO_3$ 12% C	11.51	± 0.13	11.61	± 0.02	
$CaCO_3$ 1.2% C	1.16	± 0.00	1.28	± 0.03	
$CaCO_3$ 0.12% C	0.13	± 0.00	0.14	± 0.00	
DC73326	1.71	± 0.02	2.02	± 0.03	0.31
GSS-3	0.005	± 0.001	0.57	± 0.01	0.56
DC73319	0.31	± 0.02	2.10	± 0.00	1.79
Nutrients in Sand	0.003	± 0.000	0.56	± 0.01	0.55
Clean Sand	0.54	± 0.01	1.76	± 0.05	1.22
B2188	0.92	± 0.01	4.55	± 0.04	3.64
B2186	0.04	± 0.02	2.63	± 0.02	2.59
B2176	0.41	± 0.06	15.04	± 0.13	14.64
Control mixture A	4.97	± 0.03	10.04	± 0.31	5.07

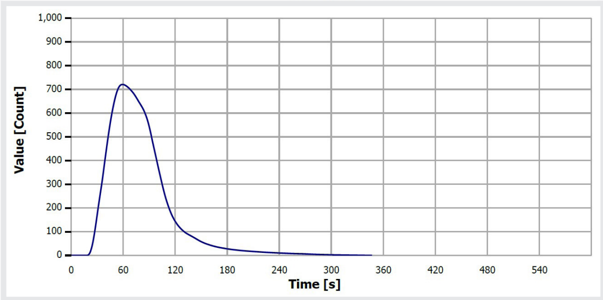

Figure 3: TIC measuring curve for sample DC73326

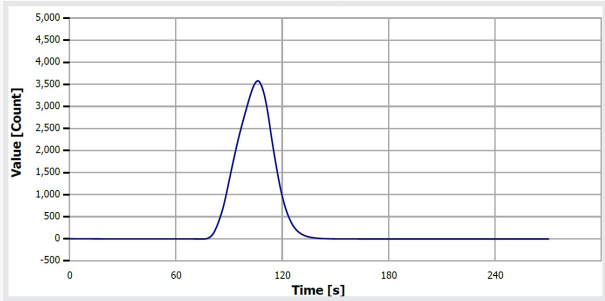

Figure 4: TC measuring curve for sample DC73326

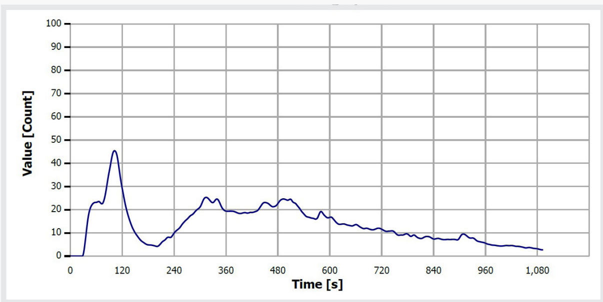

Figure 5: TIC measuring curve for sample B2176

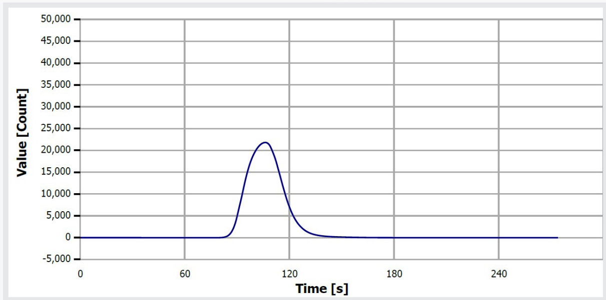

Figure 6: TC measuring curve for sample B2176

The good reproducibility and low standard deviations underline the quality of the analysis. In Table 5 the results are shown alongside the reference or informal values provided by the CRM supplier. The reference soils were measured with good accordance with the expected reference values. This shows that reliable analysis in accordance with DIN EN 15936 has been proven. The sources for the CRMs are given in Table 7 at the end of the document.

Table 5: Comparison measured vs. reference values

	TIC (%)		TC (%)		TOC (%)	
	Measured	Reference	Measured	Reference	Measured	Reference
DC73326	1.71	1.63*	2.02	1.91 ± 0.07	0.31	0.31*
GSS-3	0.005	0.13*	0.57	0.55 ± 0.05	0.56	0.51 ± 0,03
DC73319	0.31	0.306 ± 0.025	2.10	2.11 ± 0.19	1.79	1.80 ± 0.16
Nutrient in Sand	0.003	n.a.	0.56	n.a.	0.55	0.57 ± 0.07
Clean Sand	0.54	0.55	1.76	1.77	1.22	n.a.
B2188	0.92	0.95	4.55	4.64 + 0.77	3.64	3.69
B2186	0.04	0.08*	2.63	2.75 + 0.12	2.59	2.67*
B2176	0.41	0.38*	15.04	15.95 + 0.30	14.64	15.57*
Control A	4.97	5.00	10.04	10.00	5.07	5.00

* Informal value only

Summary

The multi EA 4000 is capable of a fast and efficient determination of the TOC in soils, sediments, and related matrices by difference method in accordance with EN 15936. The analysis can be carried out fully automatically using the FPG 48 autosampler and the TIC solids module "automatic" for solids. A full configuration list is given in Table 6.

The approach for TOC measurement using acidification provides much more reliable results than a temperature gradient approach (EN 17505), as the carbonate content in the soil is correctly evaluated. The difference method should not be applied for soils with a high content of TIC in comparison to TOC (ca. TIC > 5 x TOC); in this case the direct approach (EN 15936 method B) should be used, which can be easily performed with the given setup as well.
The high maximum sample mass of up to 3 g (depending on the specific density of the sample) enables best results even for low concentrations or inhomogeneous sample material. Additionally, the multi EA 4000 with pyrolysis option can be used for the determination of elemental carbon following a pyrolysis approach. An extension by detectors for sulfur and chlorine is possible at any time, further extending the application capabilities of the analysis system.

Figure 7: multi EA 4000 C with automatic TIC solids module and FPG 48 autosampler

Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 4000 C*	450-126.564	Elemental analyzer for the carbon determination in solids
FPG 48 solids autosampler for multi EA 4000	450-126.574	Autosampler for up to 48 solid and paste like samples
TIC solids module "automatic" for multi EA 4000	450-126.576	Unit for the automatic determination of TIC (TOC difference method) in solids

* multi EA 4000 C with pyrolysis option (402-126.568) can be used alternatively in case pyrolysis resp. EC determination is of interest too

Table 7: List of reference materials

ID	Reference	
DC73326	NCS certified Reference Material Soil	NCS DC73319 (GBW07401)
GSS-3	Geochemical Standard Reference Soil IGGE RIMA	GSS - 3 (550221) GBW – 07403
DC73319	NCS certified Reference Material Soil	NCS DC73326 (GBW07408)
Nutrient in Sand	Sigma-Aldrich, CRM, Nutrients - Sand	CRM092-100G (Lot # LRAA7716)
Clean Sand	Sigma-Aldrich, CRM, Clean Sediment #2	CLNSED2-100G (Lot # LRAA9874)
B2188	Elemental Microanalysis, Soil Standard Chalky	B2188 (Certificate No 326156)
B2186	Elemental Microanalysis, Soil Standard Loamy	B2186 (Certificate No 133505)
B2176	Elemental Microanalysis, Soil Standard Peaty	B2176 (Certificate No 133519)
Control mixture A	According to DIN EN 15936	44.13 g Na_2CO_3 + 18.83 g Na_4-EDTA x 4 H_2O + 37.04 g Al_2O_3

References

[1] EN 15936:2022 Soil, waste, treated biowaste and sludge - Determination of total organic carbon (TOC) by dry combustion

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