



Challenge

Fast and cost-effective total organic carbon determination over a wide concentration range in environmental analysis (soil, sediments, etc.).

Solution

Fully automated determination with multi EA 4000 using FPG 48 solids sampler and TIC solids automatic module. Flexible selection of TOC determination method for each sample.

Comparison of TOC Determination Methods in Soil Samples According to EN 15936

Introduction

The carbon (TC, total carbon) contained in soil has different sources and effects on the soil's quality. Total inorganic carbon (TIC), mainly carbonate and hydrogen carbonate, is a natural part of soil but can also derive from artificial addition and other sources. Total organic carbon (TOC) is generated by organic matter that is present from natural sources (plants, animals, degradation processes) and contaminations caused by humans and industrial and agricultural processes (oil residues, waste, overfertilization, etc.). Its content is influenced by erosion, biological decomposition (e.g., by bacteria), and farming. The TOC affects soil properties (e.g., color, fertility, toxicity). This makes TOC an important parameter in environmental protection, agriculture, waste management, and landfills, needing to be regularly monitored. For this purpose elemental analysis techniques based on sufficient high-temperature combustion of all

sample components have proven best suited, followed by NDIR detection of the formed CO₂ (e.g., DIN EN 15936^[1]). Depending on the soil type and its TOC/TIC ratio, two different TOC determination strategies are available. The direct method B is preferred in case of low TOC compared to the present TIC. It requires an extensive pretreatment of the sample to completely remove the interfering TIC (wet chemical acid digestion and drying of the treated samples). This method is also difficult to automate and negatively affects the hardware of the analyzer in terms of consumables and maintenance. Thus the difference method (indirect method A) is preferred whenever possible (equivalent or higher content of TOC compared to TIC). This method requires two analyses (TC and TIC determination) to obtain results. Still, additional measurement time is minimal compared to the pretreatment efforts for direct determination.

Materials and Methods

Samples and reagents

Four different soil samples were analyzed. All of them were solid fine powders.

Sample preparation

The samples were analyzed directly, no sample preparation was required.

Calibration

The multi EA 4000 was calibrated before the analysis. For the determination of total carbon (TC) pure CaCO_3 (12 % C) was used directly. For the determination of TIC, a standard, prepared by solids-dilution of CaCO_3 with SiO_2 (0.2 % C), was used. To cover a wide concentration range, the used quantities of the different standards were varied (calibration model: constant concentration – variable quantity). The resulting calibrations are suitable for evaluation of the different carbon parameters (TC, TOC, TIC) of inorganic or mainly inorganic sample matrices like soil and sediments. The quality of the calibrations was checked with different standards. Calibration curves for the TIC and TC determination are depicted in Figure 1 and 2.

Table 1: Calibration of the different carbon species

Parameter	Standard	Carbon content	Weight range	Calibrated range
TIC	CaCO_3 in SiO_2	0.20 %	7–200 mg	0.02–0.40 mg C absolute
TC	CaCO_3 (pure)	12.0 %	10–70 mg	1.2–8.4 mg C absolute

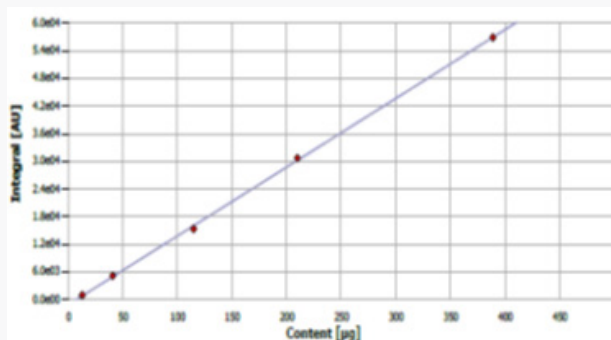


Figure 1: TIC calibration with 0.2 % C standard

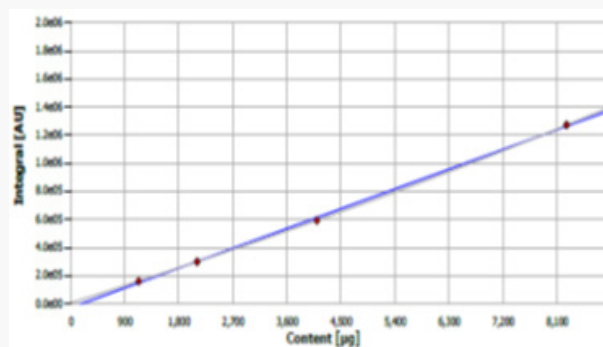


Figure 2: TC calibration with 12 % C standard

Instrumentation

The soil samples have been analyzed on a multi EA 4000 elemental analyzer, equipped with the automatic TIC solids module. The introduction of samples was realized with the FPG 48 solids autosampler. This configuration allows for the fully automated determination of different carbon parameters (TC, TOC, TOC). TOC determination was done using two different strategies.

Difference method (indirect method A)

TOC is not measured directly, only TC and TIC are measured. TOC is then calculated by subtracting TIC from TC.

For each sample, both measurements have been performed by a multi EA 4000 equipped with the automatic TIC solids module. Two portions of the same sample were weighted into two sample boats for each analysis. The first sample

boat was acidified automatically with 40 % H_3PO_4 in the reactor of the TIC module. The CO_2 from the carbonate was released and the TIC was measured directly. The second boat was then introduced directly into the resistance furnace. Inside, all C compounds were combusted at 1,200 °C in a pure oxygen atmosphere. In both runs, the measuring gas was dried and cleaned and the carbon content was measured by means of the wide-range NDIR detector. The TOC calculation was done automatically by the analyzer's multiWin software.

Direct method (method B)

With this approach, TOC is determined directly. Before the analysis, the interfering TIC has to be removed by means of a nonoxidative acid (e.g., HCl). For this determination, an aliquot of the sample was acidified directly on the ceramic

boat with 500 μL of a 10 % HCl in water solution. To dry the sample, the boats were placed on a heating plate at 40 °C. The complete reaction of the carbonate was tested with careful additional acidification until no more gas was produced. The TOC determination was then done by direct combustion of the treated sample at 1,200 °C. The formed combustion gases were filtered, dried and measured as described above.

Table 2: Process parameters TC/TOC/TIC determination

Parameter	Specification
Temperature	1200 °C
Introduction Speed Program	inorganic
O ₂ flow	2.5 L/min
Amount of acid	2 (difference) 1 (direct)

Method parameters

Standard method settings from the method library were applied. The parameter settings for the combustion (TOC, TC) and digestion (TIC) process and the sample transfer are summarized in Table 2. The evaluation parameters for the detection of carbon are given in Table 3.

Table 3: CO₂ detection parameters

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

Results and Discussion

The results of the four soil samples and the quality control standard summarized in Table 4 show the average of two replicate analyses. Due to high reproducibility, duplicate measurements were sufficient to gain reliable results. This is also depicted by the very low deviation of the measurements (SD). Typical measuring curves are shown in Figures 3–6.

Table 4: Results of the TC, TIC and TOC determination (direct and differential method)

Measurement	TIC \pm SD [%]	TC \pm SD [%]	TOC \pm SD [%] difference method	TOC \pm SD [%] direct method
AT-1	0.07 \pm 0.03	10.33 \pm 0.09	10.26 \pm 0.06	10.35 \pm 0.02
AT-2	0.26 \pm 0.01	1.37 \pm 0.01	1.11 \pm 0.02	1.12 \pm 0.03
AT-3	0.23 \pm 0.00	3.95 \pm 0.02	3.72 \pm 0.02	3.62 \pm 0.08
AT-6	0.09 \pm 0.02	1.81 \pm 0.03	1.72 \pm 0.04	1.62 \pm 0.00
QC standard CaCO ₃ 1.2 %	1.16 \pm 0.003	1.23 \pm 0.009	-	-

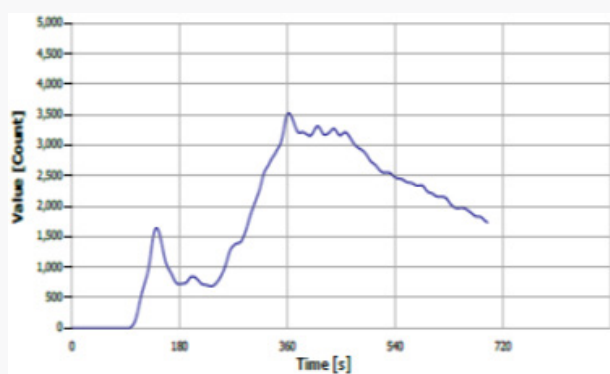


Figure 3: TIC measurement curve for AT-1

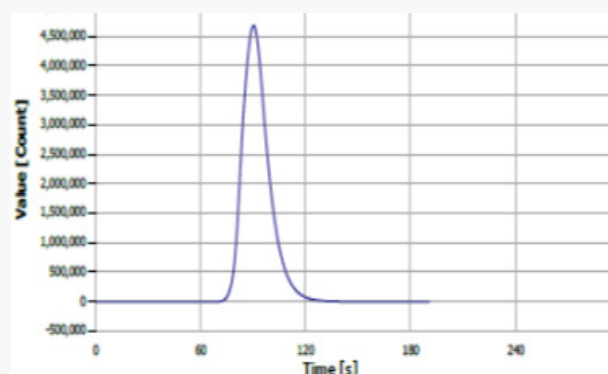


Figure 4: TC measurement curve for AT-1

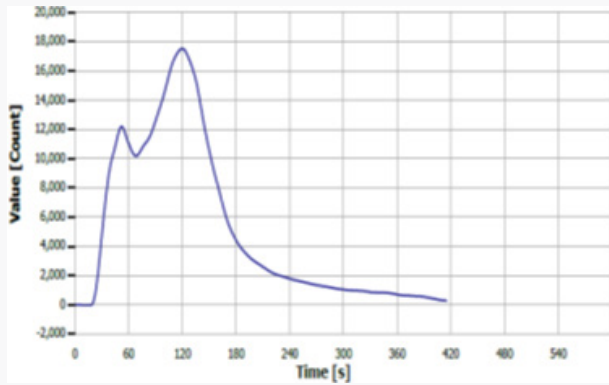


Figure 5: TIC measurement curve for AT-2

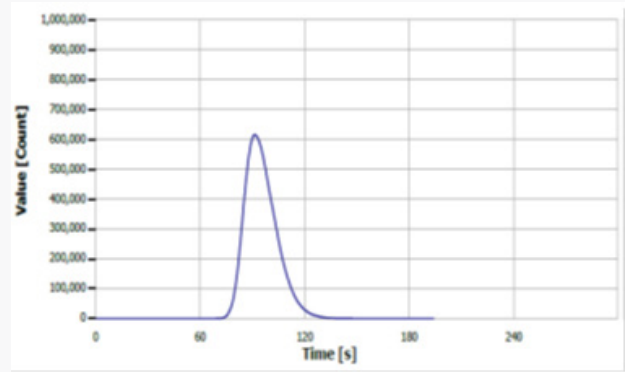


Figure 6: TC measurement curve for AT-2

For both methods, the difference and direct method, the SD values gained were rather low, thus a good reproducibility was obtained. To support the TIC measurement (as part of the TOC difference method), the sample aliquots were mixed with a detergent solution before acidification. This prevented hydrophobic behavior of the soil samples and enabled fast analysis times. By creating homogeneous slurry, the TIC digestion was accelerated and even, the CO₂ was fast released. Differences between the TOC difference method and the TOC direct method are only recognizable for the sample AT-6, but these were only very little.

Conclusion

The multi EA 4000 facilitates fast and efficient determination of different carbon species in soil and sediment samples. Depending on the special needs of the sample matrix and the throughput requirements, either the direct or difference method for TOC determination is possible. The analysis can be done manually or through a fully automated process using the FPG 48 solids sampler. Due to the flexible software, difference and direct TOC methods can be combined freely, if needed, for special applications. Both methods deliver equivalent results. Nevertheless, the difference method is to be preferred due to its lower impact on consumables (drier, filter, combustion tube).

Sample amounts up to 3 g (depending of the specific density) allow for the best results, even for trace analysis. Additionally, the system can be upgraded with optional detectors for sulfur and chlorine, extending the application possibilities of the multi EA 4000.



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

References

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

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Headquarters

Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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