



Determination of TOC in Agricultural Soil, Dried Manure, and Sediments

Introduction

The 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 e.g., fertilizers. Total organic carbon (TOC) is generated by organic matter that is present from natural sources (plants, animals, microorganisms, degradation processes) and is a precondition for soil formation and for the preservation of its fertility. On the other hand, contaminations caused by humans, as by industrial and agricultural processes (oil residues, waste, overfertilization, etc.) can also be an origin of elevated TOC levels.

The TOC content in soil is also mainly influenced by erosion, biological decomposition and farming and affects soil properties (e.g., color, fertility, but also toxicity). For example, topsoil rich in humus is subject to special protection. The humus content in such soils typically ranges from 1 to 8%, which equals a TOC range from 0.5 to 4%, meaning the humus content is typically twice the TOC concentration.

This makes TOC an important parameter in agricultural soil classification and environmental protection, needing to be regularly monitored. For this purpose, elemental analysis techniques based on high-temperature combustion of all sample components have proven best suited, followed by NDIR detection of the formed CO₂ (e.g., EN 13137 or DIN EN 15936, ISO 10694). According to these norms the differential or direct TOC method can be applied to measure the TOC concentrations in solids. The direct method is of advantage especially with samples of high TIC and low TOC content because here, the error affected

Challenge

Is it possible to determine lower and higher concentrations of TOC in agricultural soils, dried manure, and sediments by automated direct method?

Solution

With TOC analyzers like multi N/C duo systems the direct determination of TOC in soils can be performed fully automated, fast and with good precision.

subtraction of two big numbers ($TC - TIC = TOC$) is avoided and a higher sample throughput can be achieved, since only one measurement for one parameter has to be conducted instead of two measurements in TOC difference method.

Materials and Methods

The determination of the parameter TOC (total organic carbon) was performed using the direct method. With this approach, the interfering TIC had to be removed by means of a nonoxidative acid treatment before the sample was combusted. Samples were directly weighed into ceramic sample boats and manually acidified with 500 μL of a 10% HCl. The complete reaction of the carbonates and hydrogen carbonates was tested by careful additional of 50 μL of 25% HCl until no more gas was produced. Afterwards the sample boats were placed on a heating plate at 40 $^{\circ}\text{C}$ and dried for at least 12 h (overnight). The TOC determination was then done by direct and catalyst-free combustion of the treated sample at 1200 $^{\circ}\text{C}$ in a ceramic combustion tube in a pure oxygen atmosphere. The formed combustion gases were filtered and dried, the formed CO_2 was detected by an NDIR (non-dispersive infrared) detector.

Sample Preparation

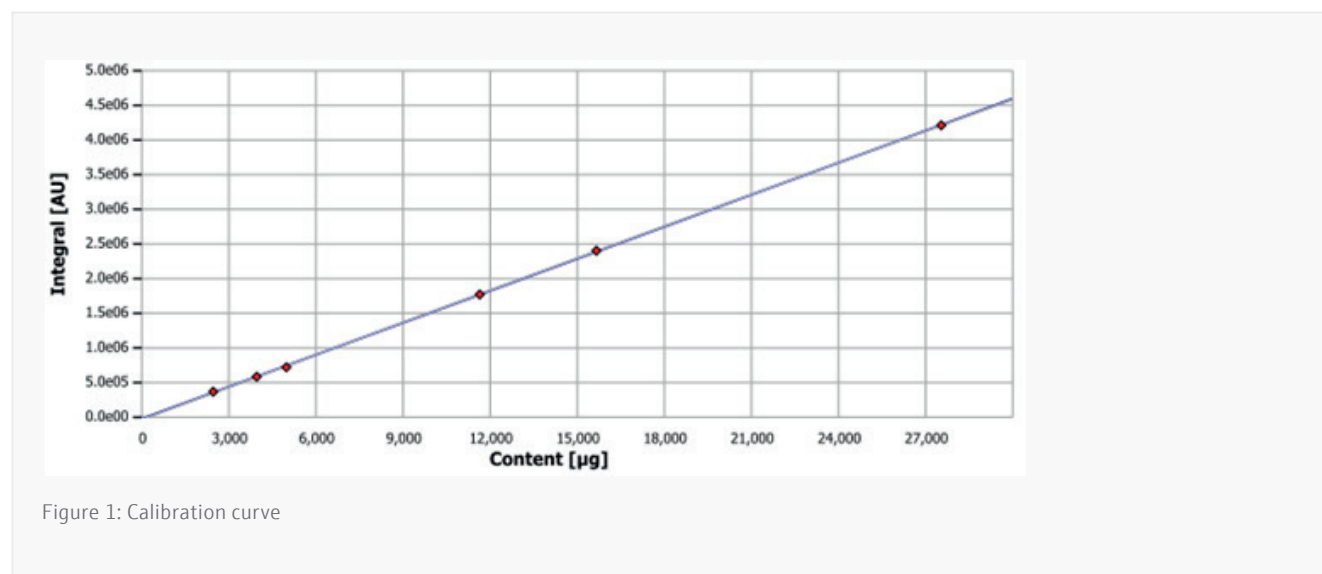
All dried and ground soil, manure and sediment samples (grain size < 2 mm is recommended) were treated with acid (HCl 10%, HCl 25%) and dried directly inside the sample boat as described above.

Calibration

The solid TOC analyzer has been calibrated using a single standard (CaCO_3) using in different quantities. This way a calibration curve covering a wide concentration range can be established very easily. Pure calcium carbonate (TC = 12%) was weighed in different portions starting with approx. 20 mg directly into ceramic sample boats. These boats were introduced into the furnace of the TOC solid analyzer. The calibration curve is shown in Figure 1.

Table 1: Calibration

Parameter	Calibration Standard	Carbon Content [%]	Weight [%]	Calibrated Range [mg C_{absolute}]
TC	CaCO_3	12	21 – 230	2.5 – 28



Instrumentation

Measurements were performed with multi N/C 2100S duo consisting of the main instrument multi N/C 2100S with AS 60 combined with a high temperature furnace HT 1300 and a solid sampler FPG 48. Alternative instrument configurations as shown in Table 2 may be used for the determination of TOC in soil by direct or differential method:

Table 2: Further Instrument configurations

Instrument configuration	Operation mode	Additional parameters /benefits
multi N/C 3100 duo (multi N/C 3100 + AS vario ER + HT1300 + FPG 48)	Automated determination of TOC, direct method	NPOC/TOC/TIC/TC determination in water samples, upgradable with TN _b option (CLD, ChD) for water samples
multi N/C 2100S + HT 1300 multi N/C 3100 + HT 1300	Manual determination of TOC, direct method	NPOC/TOC/TIC/TC determination in water samples, upgradable with TN _b option (CLD, ChD) for water samples
multi EA 4000 + FPG 48	Automated determination of TOC, direct method	Upgradable for TS (Total Sulfur) and TCI (Total Chlorine) determination in solid samples
multi EA 4000 + FPG 48 + TIC auto	Automated determination of TOC and/or TIC, difference or direct method, automatic acidification	Upgradable for TS (Total Sulfur) and TCI (Total Chlorine) determination in solid samples

All instruments listed above are equipped with a robust ceramic combustion tube which is not affected by high amounts alkali or earth alkali metals. Combustion temperatures of up to 1300 °C (multi N/C configurations) resp. 1500 °C (multi EA 4000 configurations) ensure a quantitative digestion of all carbon compounds.

Method Parametersp

Soil samples are not very reactive and thus do not require sophisticated method settings regarding sample introduction speed or hold positions. The addition of special combustion additives is not necessary. The parameter settings for the combustion and sample introduction are summarized in Table 3.

Table 3: Method settings multi N/C 2100S duo

Parameter	Combustion temperature [°C]	Sample introduction speed [mm/min]	Holding position autosampler [mm]	Waiting period at holding position [s]
TC	1200	500	-	-

Results and Discussion

Analysis results of all soil samples including a certified reference material are shown in Table 4. Measurements were performed as triplicates, the achieved standards deviations (SD) were very low. Typical measuring curves are shown in the Figure 2 below.

Table 4: Results

Sample ID	Sample weight [mg]	TOC Average ± SD [%]	RSD [%]
Dried manure	approx. 100	33.1 ± 0.40	1.1
Soil A	approx. 200	2.35 ± 0.03	1.3
Soil B	approx. 300	1.62 ± 0.03	1.8
Sediment	approx. 300	1.32 ± 0.02	1.5
CRM (Soil) 1,8% TOC (NCS DC 73319)	approx. 200	1.85 ± 0.03	1.6

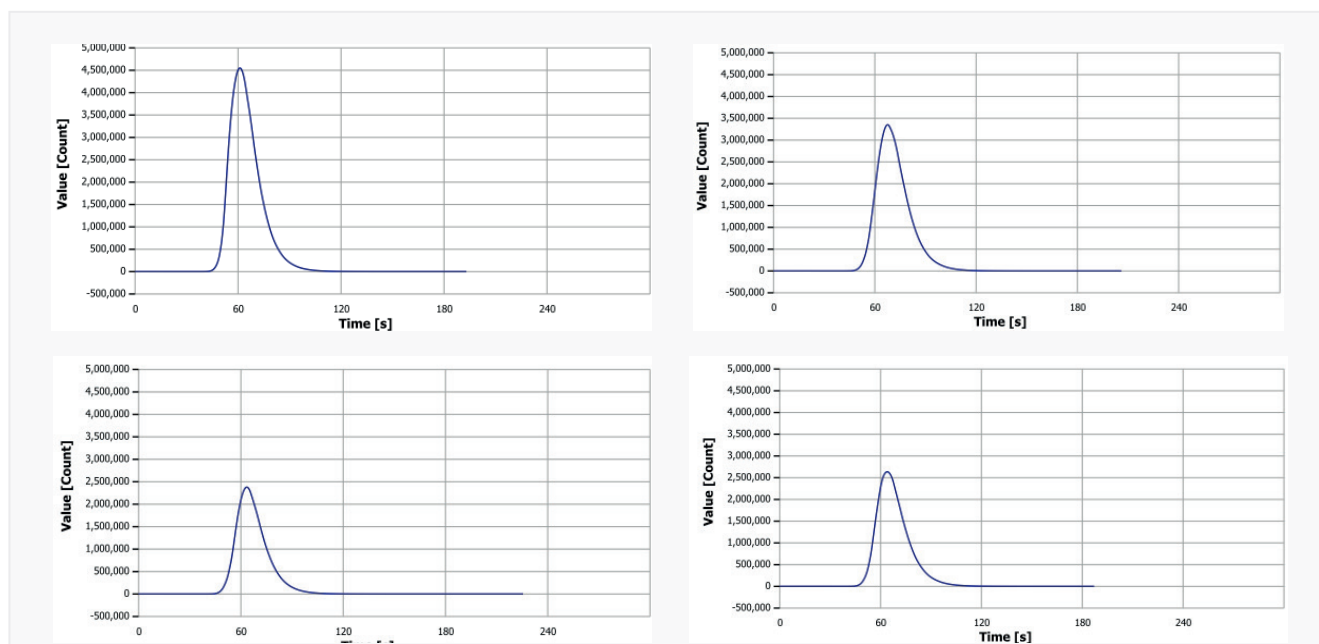


Figure 2: Typical measurement curves

Conclusion

The multi N/C duo systems are very well suited to analyze agricultural soil samples or related matrices like sediments or dried manure/ sludge samples according to the direct method of TOC determination described in EN 15936.

Soils or sediments are predominantly homogeneous sample matrices, so that sample weights in a range between 100 mg up to 300 mg are sufficient to achieve precise and reproducible results. Higher sample weights of up to 3 g are possible to apply what is beneficial in case of inhomogeneous samples or very low carbon concentrations.

Manual sample preparation (acidifying and drying) is recommended to do in batch, so that preparation time is reduced to a minimum. Sample analysis is fully automated, the dried samples just need to be placed onto the sampler FPG 48 and a sequence of up to 48 samples can be started.

Simple calibration routines and the included wide range NDIR detector enable a broad measuring range of up to 500 mg C absolute for all multi N/C duo systems. This makes repeated analysis for samples with unexpected high concentrations unnecessary.

The multi N/C duo series systems offer the possibility to determine TOC (TIC, TC) also in water samples without the necessity for a conversion/modification of the instrument hardware. Changing the configuration setup in the software and loading the desired method are the only actions to be done by only a few mouse clicks, to convert the solid analyzer into a fully automated liquid TOC analyzer.

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Version 1.0 | Author: BB
en · 12/2020

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