APPLICATION NOTE

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EXCELLENCE IN ELEMENTS

Determination of carbon in soil, sediment, sludge, and solid waste

Introduction

The total organic carbon (TOC) content is an important indicator for a multitude of applications. In agricultural science, carbon is an important parameter to understand the element cycling of soils and sediments. Organic carbon enters through the decomposition of plant and animal residues and acts as the main source of nutrients for microorganisms and plants. TOC analysis, therefore, provides essential information about microbiological activity and organic matter to characterize and evaluate soil and sediment.

Directly measuring TOC is a non-trivial analysis. Often total carbon is measured, and then non-organic carbon sources are subtracted. In addition to organic carbon, inorganic carbon is also present in soils and sediments, typically in the form of carbonates. The two most common sources of carbonate in soils and sediments are the minerals calcite and dolomite. The corresponding bulk parameter, total inorganic carbon (TIC), includes these minerals as well as other carbonate derivatives, such as carbonic acid and bicarbonate. Inorganic carbon is distinguished from organic carbon because it is not an accessible form of carbon for biological systems, i.e. it is not bio-available.

Often it is not enough to just differentiate between TOC and TIC. Elemental carbon (ROC) is a further common source of carbon, which is also not bio-available. Especially in solid wastes, but in other applications as well, separately measuring this third type of carbon gives a much more accurate determination of bio-available, and thus environmentally relevant, carbon sources.

TOC IN SOLID SAMPLES
soli TOC® cube
vario MAX cube
acquray®
vario EL cube
rapid CS cube
UNICUBE®

Method of choice

For the analyses of TOC different methods can be used.

Method 1: Determination of TOC at combustion temperatures above 900°C with prior acidification.

The classic TOC determination in soil, sludge, sediment, and solid waste uses high temperature combustion at temperatures above 900°C. Carbon is converted into CO_2 in the presence of oxygen and then measured by a thermal conductivity or infrared detector. To remove the TIC, the sample is acidified prior to the measurement. In the presence of mineral acid, the carbonate in the sample is converted into CO_2, which is removed during a drying step over several hours at elevated temperatures. The principles and procedures are described in various standards, including ISO 10694, DIN EN 15936 and DIN EN 13137.

Method 2: Determination of TOC at lower combustion temperatures.

To overcome the time consuming acidification step to remove the carbonates, lower combustion temperatures can be used. By choosing an optimum combustion temperature it is possible to minimize inorganic carbon loss while maintaining full recovery of organic carbon. Combustion temperatures between 450°C and 650°C have been shown to give adequate results (e.g. Pitt et al, 2003). This method, however, only works for instruments with automated ash removal after each analysis (see Table 2).

Method 3: Determination of different forms of carbon using temperature programming.

When evaluating solid waste for example, it might be necessary to determine the ROC separately, since elemental carbon is not bio-available. For this purpose, a temperature ramp method is used: TOC is determined at 400°C, ROC between 400 and 600°C, and TIC between 600 and 900°C. The sample is heated at a rate of 70°C per minute to the designated temperature, and then maintained for a given hold time. The CO_2 produced at the different temperatures represents the different carbon fractions (see Figure 1).

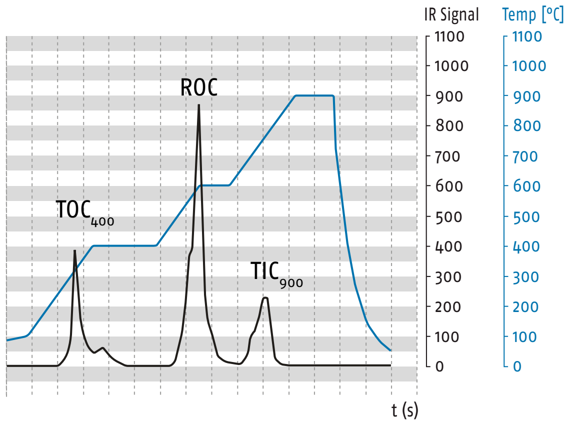

Figure 1. Three-step temperature program of the soli TOC cube using a Cambisol B Horizon soil sample.

The separation of ROC and TIC can be further improved by the use of an inert carrier gas. After the 400°C temperature step, the carrier gas is switched from oxygen to nitrogen and the sample is directly pyrolyzed at 900°C. Under these conditions, the ROC remains in the sample container while the TIC is converted to CO_2. After the TIC has been determined, the system is given oxygen again, to oxidize the ROC. In most cases, this technique results in a better separation of TIC and ROC (see Figure 2).

Both methods are conform to the new DIN 19539.

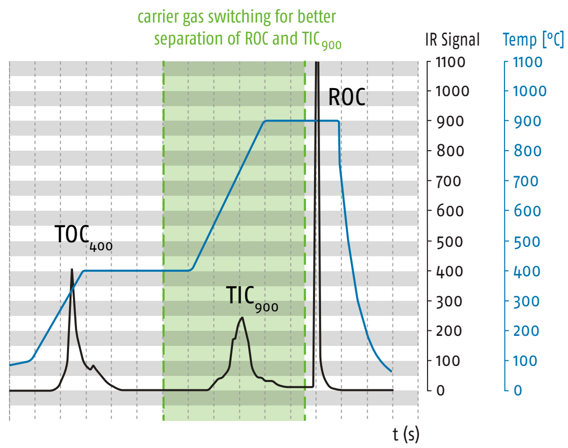

Figure 2. Two-step temperature program with gas switching of the soli TOC cube using a Cambisol B Horizon soil sample.

Experimental results

The TOC content has been determined in six different solid samples according to the methods described before.
It can be stated that the TOC contents according to method 1 (acidification and combustion at 900°C) and method 2 (combustion at 650°C) are in the same range for all analyzed materials. The TOC contents detected by method 3 (combustion at 400°C: TOC_{400}) are the lowest among all used method.

As sludge and fluvisol show the lowest relative ROC contents, TOC_{400} is similar compared to the TOC content determined by using the other methods. In contrast at higher ROC contents, results for TOC_{400} are obviously different from the results of the other methods. However, the sum of TOC_{400} and ROC is always in line with the other TOC results.

Interestingly, the sum of TOC_{400} and ROC of slag and recycled building material show the largest difference between the sum of TOC_{400} + ROC and the TOC contents determined by the other two methods among all samples.

In conclusion, the comparability of the TOC results of the different methods highly depends on the carbon fractions that prevail in the sample. It is important to keep this in mind when choosing the correct method to determine the TOC content.

Table 1. Determination of TOC contents in six different samples according to three different methods. The analyses according to method 1 and 2 are performed using the vario MAX cube with a combustion temperature of 900°C and 650°C, respectively. The soli TOC cube has been used for the analyses of TOC_{400}, ROC and TIC_{900} by the temperature ramp method 3.

	METHOD 1	METHOD 2	METHOD 3				
SAMPLE	TOC [%]	TOC [%]	TOC_{400} [%]	ROC [%]	TIC_{900} [%]	TC [%]	TOC_{400} + ROC [%]
Fluvisol	4.02	4.12	3.64	0.25	0.04	3.93	3.89
Excavated soil	0.40	0.57	0.23	0.15	0.42	0.80	0.38
Recycled building material	0.95	1.18	0.34	0.42	0.90	1.66	0.76
Slag	0.17	0.28	0.03	0.09	0.16	0.28	0.12
Waste incinerator ash	0.80	1.25	0.57	0.56	0.18	1.31	1.13
Sewage sludge	2.24	2.29	2.06	0.12	0.03	2.21	2.18

Instrument solutions

Elementar offers the most dynamic range of products to serve all the different customer demands based on their application tasks.

With the vario MAX cube, soli TOC cube and the acquray series, larger samples, on the order of grams, can be reliably analyzed. This makes them perfect instruments for the accurate analysis of inhomogeneous samples. The measurements of the TOC according to method 2 and method 3 is remarkable simple. For the analysis, the samples are weighed into crucibles and delivered immediately to the instrument. In case of method 1, the sample is acidified directly in the crucible and after drying delivered to the instrument.

When using the vario EL cube and the rapid CS cube, the sample is weighed into silver foil cups, acidified, and dried prior to the measurement. Both are limited to method 1 but they are also able to determine additional elements. The typical sample weight used for these instruments is 100–200 mg.

To directly determine the TIC of solid samples, the soliTIC module has been developed to provide precise and accurate results. It is an additional device that can be easily connected to almost all cube models that can measure carbon, e.g. vario MAX cube, vario EL cube and rapid CS cube.

Table 2. Instrument solutions for the determination of carbon in soil, sludge, sediment, and solid waste.

INSTRUMENT	METHOD 1	METHOD 2	METHOD 3	N	S	H	AUTOMATED SAMPLE FEEDING	AUTOMATED ASH REMOVAL
vario MAX cube	✓	✓		✓	✓*		✓	✓
soli TOC cube	✓	✓	✓	✓**			✓	✓
acquray TOC + acquray solid	✓	✓	✓					✓
UNICUBE / vario EL cube	✓			✓	✓	✓	✓	
rapid CS cube	✓				✓		✓	

*in CNS mode only, **with optional EC detector.

References

DIN EN 15936 – Sludge, treated biowaste, soil and waste – Determination of total organic carbon (TOC) by dry combustion.
DIN 19539 – Investigation of solids — Temperature-dependent differentiation of total carbon.
DIN EN 13137 – Characterization of waste – Determination of total organic carbon (TOC) in waste, sludges and sediments.
ISO 10694 – Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis).

Pitt, J.L., T.L. Provin, F.M. Hons, F. Dou, and J.S. Waskom. Use of a total carbon/nitrogen analyzer for the determination of organic and inorganic carbon in soils, manure, and composts. Abstracts, 2003 Meeting of ASA, Denver, CO.

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