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Determination of TOC in Solids

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Introduction

The determination of TOC (Total Organic Carbon) in solid samples such as waste, soils, sediments or manufacturing materials is steadily gaining importance. The (German) Technical Instruction on Residential Waste as revised in 1993 acknowledges the determination of the TOC content in the original sample as a valid alternative to the determination of the loss of weight on ignition. Organic carbon occurs in waste in various kinds of bond. Given the multitude of possible organic carbon compounds, the quantitative determination of every single organic compound of natural or anthropogenic origin would only be possible at prohibitive expense, if at all. The measurement of summary parameters such as TOC is the only sensible alternative, therefore.

Principles of the Method

All methods of determining total carbon (TC) in solids are based on the conversion of the carbon compounds into carbon dioxide by oxidation or pyrolysis. Thermal digestion is performed at a temperature of at least 1300°C. The resulting gas is then purified by filters, dried, and flushed into the detector by means of a carrier gas flow. The detector is usually of the non-dispersive infrared type (NDIR). Acidification and pretreatment of the sample before the measurement removes total inorganic carbon (TIC), so that the measurement ascertains the share of non-volatile organic carbon (NVOC) only.

Inorganic carbon in solids is determined by NDIR detection of the carbon dioxide formed by sample acidification and subsequent purging.

TOC Determination

TOC in solids can be determined by either of two methods: the direct and the indirect (differential) one. The latter is based on forming the difference between the TC and TIC parameters, while the direct method determines TOC as NVOC.

Differential method

The indirect (differential) method requires two separate measurements - TC and TIC - in order to ascertain the organic share as the difference of these. The method is applied if the inorganic carbon share is smaller than or equal to the organic carbon share in the sample.

Carbonates are decomposed in a suitable apparatus (TIC module) at a temperature of about 80 °C by addition of a mineral acid, and the resulting carbon dioxide is detected. In parallel, the untreated sample is thermally digested at ≥ 1300 °C, and the carbon dioxide determined. TOC is then given by the difference of the two measurements: $TOC = TC - TIC$.

The graph (Figure 1) shows an example of the retrieval of the TOC content of a certified standard by means of the TIC module. The repeatability of the TIC content greatly depends on the homogeneity of the solid sample.

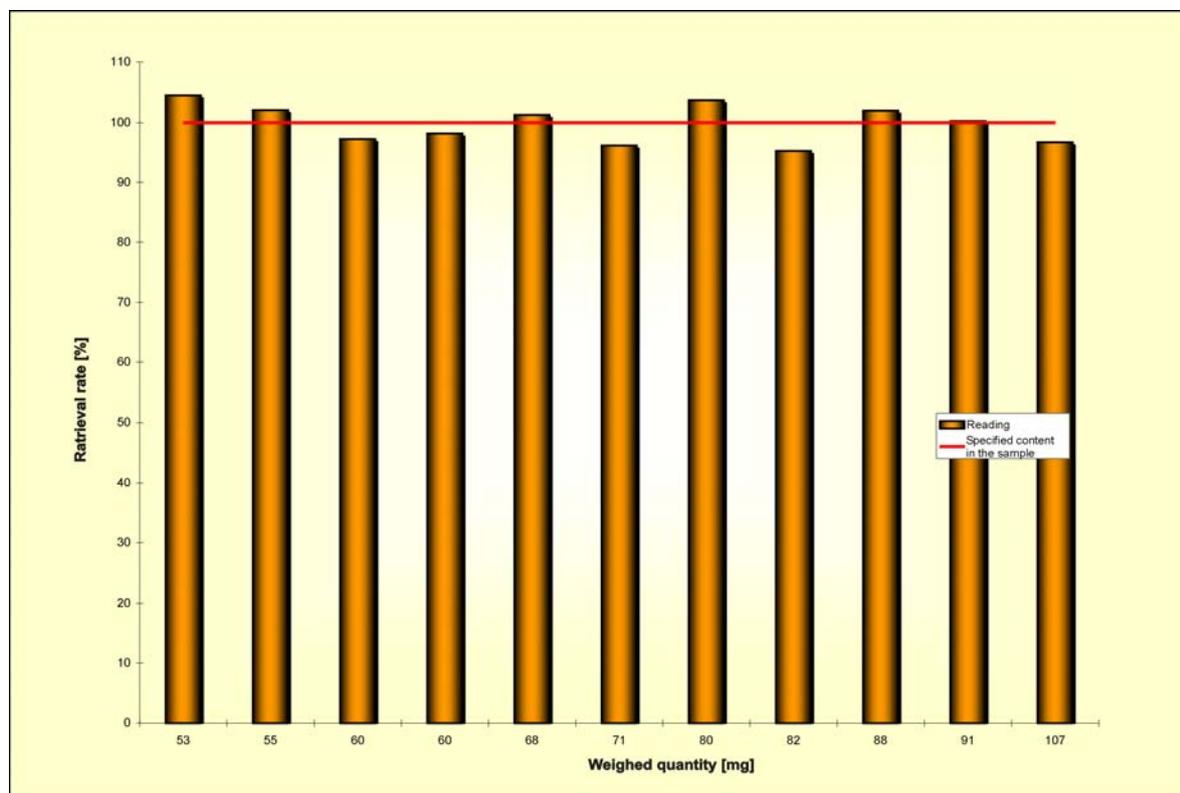


Fig.1

Other methods frequently mentioned in connection with indirect TOC determination in solids are detection of the residue on ignition or the running of temperature ramps.

In the first of these methods, the organic carbon share is combusted at about 600°C in a muffle furnace to which oxygen is fed, and TIC is measured in what is called the residue on ignition. Subsequently, a measurement of the original sample is made to determine total carbon. By forming the difference, one gets $TOC = TC - TIC$. This method suffers, however, from a number of uncertainties, which may cause errors. One is that a temperature of 600°C may cause carbonate portions to be decomposed into CO_2 , depending on the matrix, and thus to be lost for TIC analysis. Another uncertainty is that 600°C may not be sufficient to completely oxidize all organic compounds. The same problems also affect TOC determination by temperature ramping. Therefore, these methods should be judged critically, despite the advantage of not having to use wet chemical techniques.

Direct method

As an alternative to the differential method, the share of non-volatile organic carbon can be determined directly. Here, the sample is acidified, while the resulting carbon dioxide is not detected. 10% HCl is added to the sample drop by drop until the main reaction is over. The reaction is then completed by the dropwise addition of concentrated HCl until no more gas is seen

to develop. The sample thus pretreated is dried at 105°C for 2 hours. After drying, the sample should be kept in a desiccator until analysis to prevent it from taking up any water again. The sample, now free of TIC, is analyzed by thermal digestion and subsequent NDIR detection of the carbon dioxide formed.

Table 1 lists several sample matrices with the associated weighed quantities and results. The real samples were pretreated as described.

Sample	Weighed quantity [mg]	TOC [%]
Polluted soil	40 - 1000	6,68
Electroplating sludge, containing Cu	40 - 1000	1,28
Emulsion sludge	40 - 1000	19,92
Fly ash	40 - 1000	2,78
Ion-exchange resin	40 - 1000	24,98

Table 1: Determination of TOC in various sample matrices by the direct method

This method is suitable especially for TOC determination in solids with a TIC concentration greater than or equal to the TOC content. In such cases, use of the differential method would lead to erroneous results. It should be noted, though, that the direct method does not detect volatile organic carbon compounds.

Comparison of the direct and differential methods

Figure 2 compares the TC and TOC contents of a standard and of real samples, determined by different methods.

It can be seen that the TOC content determined from the residue on ignition deviates from the results obtained by the other two methods. This is due to the problems described above.

The TOC contents obtained by the differential and direct methods are about comparable.

Summary

TOC can be determined reliably even in difficult samples containing, for example, volatile organic carbon compounds or having an unfavourable TIC / TOC ratio. The method to be chosen depends on the proportions of the organic and inorganic carbon shares in the sediment samples. The direct method of TOC determination is recommendable where samples have high contents of inorganic carbon. Volatile organic constituents should be determined by the differential method using TIC module.

To characterize solids, TOC is a parameter that can be determined with certainty and convenience.

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