Challenge
Determine the TOC in inhomogeneous waste materials by the direct method.

Solution
With TOC analyzers, like the multi N/C duo systems TOC in waste samples can be determined fast, automated, cost-effective and reliably by the TOC direct method.

Determination of TOC in Solid Waste

Introduction

Depending on the origin of waste material, its composition can vary considerably. There are also numerous utilization possibilities for waste. From simply dumping the waste to a landfill, burning it for energy production, or the recycling of the material; various usages are employed and therefore numerous analytical techniques are applied to determine different parameters of interest.

When depositing domestic or industrial waste, sewage sludge, contaminated excavated soil, road waste (containing bitumen and tar), rubble from building sites, and many other materials the total organic carbon (TOC) content is an important measure for the waste classification. E.g., according to the European Landfill Directive among other parameters, the TOC concentration of waste determines the assignment to a landfill class. On dumping sites organic waste components are subject to microbial decomposition, which leads on one hand to the formation of landfill gases, causing a smell nuisance and contributing to the greenhouse effect. On the other hand, decomposition products such as organic acids contribute significantly to the mobilization of heavy metals by complexation reactions. This leads to their transfer into the lower soil layers and to serious seeping water or ground water contamination. To prevent this, waste materials with increased TOC content need to be treated differently.

The basics for the determination of the parameter TOC in solids are described in the DIN EN 15936 (also: EN 13137). Various techniques can be used, but all are based on a treatment of the sample with an inorganic non oxidizing acid as one step of the complete procedure. The carbonates react with the acid and form CO_2, which is either quantitatively determined using the approach of the so-called indirect method (TOC = TC - TIC) or the CO_2 is just eliminated from the sample with the aim to measure the TOC directly afterwards.

Materials and Methods

For all waste samples the determination of TOC was performed by the direct method according to EN 15936 resp. EN 13137. For this purpose, all samples were weighted into ceramic sample boats. Different sample amounts were chosen regarding the homogeneity of the particular sample. The more inhomogeneous appearance of the sample, the higher sample weight was applied. The weighing step was followed by an acidification step for removal of carbonates/hydrogen carbonates (TIC) and subsequently drying. The boats were then placed onto the sampler FPG 48 and automatically introduced into the furnace of the analyzer. Different method settings (temperature, sample introduction speed, hold positions) were applied for the different waste matrices. The combustion took place inside a robust and catalyst-free ceramic combustion tube at temperatures ≥ 1,000 °C in a pure oxygen atmosphere. The quantitative oxidation of all present organic compounds after TIC elimination is ensured on the one hand by the high combustion temperature and otherwise by an oxygen surplus. During combustion carbon dioxide is formed which is transferred by the carrier gas into the Focus Radiation NDIR detector. On the way from the furnace to the detection system the combustion gases were purified by passing several stages of particle removal, moisture and halogen absorption.

Sample preparation

The different waste samples were already homogenized (crushed or ground) to a satisfactory particle size of 1 to 3 mm. Especially road waste and industrial waste showed an erratic, non-uniform sample structure with uneven particle size and coloring. All sample were weighted into ceramic sample boats without further homogenization. Acidification was made by the aid of an acid dispenser, 500 µL of 10% HCl were added to each sample. Completeness of TIC elimination was verified by addition of a few drops of HCl 25% until no more gas (CO_2) was produced. All samples boats were then placed onto a heating plate (40 °C) and dried overnight for approx. 14 hours.
A set of three boats for each sample and an additional certified reference material were prepared in the way described above.

Calibration

Calibration of the solid TOC analyzer was performed by analyzing a single standard substance (Coal CRM) with different sample weights. The resulting calibration curve covers a wide concentration range. The coal standard (TC = 62.53%) was weighted in different portions starting with approx. 20 mg directly into ceramic sample boats. These boats were introduced into the furnace of the solid TOC analyzer by the FPG 48 autosampler and combusted. The calibration curve is shown in Figure 1.

Table 1: Calibration

Parameter	Calibration Standard	Carbon Content [%]	Weight [%]	Calibrated Range [mg $C_{absolute}$]
TC	Coal Standard (CRM)	62.53	24 – 200	15 – 125

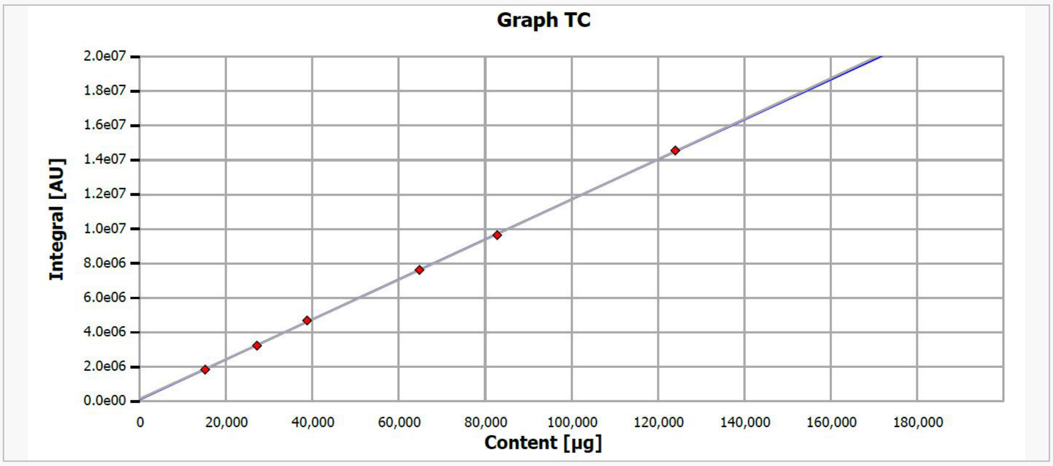

Figure 1: Calibration curve

Instrument settings

Measurements were performed with multi N/C 2100S duo consisting of the multi N/C 2100S basic unit equipped with AS 60 and HT 1300 solid furnace combined with the FPG 48 solid sampler.
The following instrument configurations may alternatively be used for the determination of TOC in waste samples of different origin 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 TCl (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 TCl (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 of alkali or earth alkali metals or acid vapors. Combustion temperatures of up to 1,300 °C (multi N/C duo systems) resp. 1,500 °C (multi EA 4000 configurations) ensure a quantitative digestion of all carbon compounds.

Method Parameters

Since waste samples of different origin may considerably vary in their compositions, they show different combustion behavior. For samples with a high content of organic matter (like biowaste) the expected vigorous combustion process needs to be controlled to avoid falsified results. This is done by a slower introduction of the sample into the hot furnace and by additional covering of the sample with an inert retarding material (e.g., annealed quartz sand).
The parameter settings for combustion and sample introduction of the different waste samples are summarized in Table 3.

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

Matrix	Parameter	Combustion temperature [°C]	Sample introduction speed [mm/min]	Holding position autosampler [mm]	Waiting period at holding position [s]	Additives
Biowaste	TC	1,000	300	100	60	Quartz sand
Contaminated soil	TC	1,200	500	-	0	-
Road waste	TC	1,200	100	100	60	Quartz sand
Industrial Waste	TC	1,200	300	-	0	-

Results and Discussion

Analysis results for the different waste samples are shown in Table 4. Measurements were performed as triplicates, the achieved standards deviations (SD) are in the expected range for heterogeneous matrices like waste. The reproducibility can be improved by putting more effort into sample homogenization (e.g., milling with cooled mills for samples like road waste containing tar). Routine labs often pass on laborious homogenization procedures and accept RSD values up to 5%.
Typical measuring curves are shown in the Figures 2 on the next page.

Table 4: Results

Sample ID	Sample weight [mg]	TOC Average ± SD [%]	RSD [%]
Biowaste	approx. 300	7.46 ± 0.21	2.8
Contaminated Soil	approx. 500	5.23 ± 0.10	1.9
Road Waste	approx. 500	27.1 ± 0.81	3.0
Industrial Waste	approx. 500	14.4 ± 0.49	3.4
CRM (coal) 56.23 % TC NCS FC 28009J	approx. 50	55.9 ± 0.45	0.8

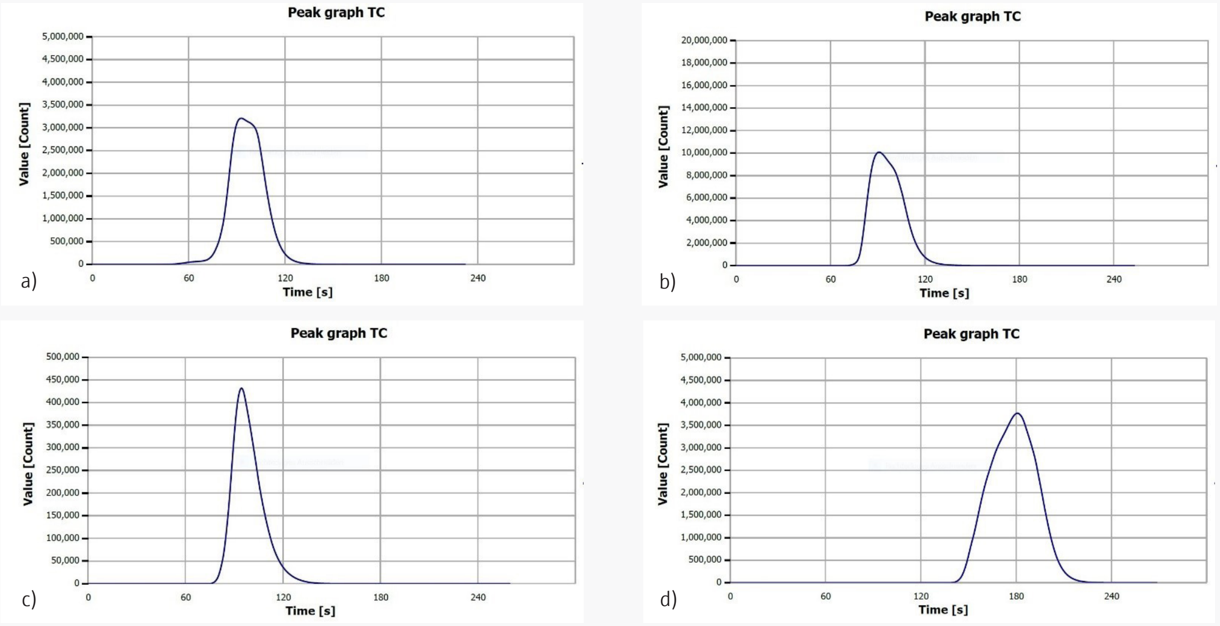

Figure 2: Typical measurement curves of a) biowaste, b) contaminated soil, c) road waste, d) industrial waste

Summary

The multi N/C duo systems are very well suited to analyze waste samples of different origin in a fast and reliable way by applying the direct method of TOC determination. Sample preparation can be performed for a batch of samples directly inside the sample boats, thus preparation time and man power effort are reduced to a minimum. Subsequent sample analysis is fully automated, the sampler FPG 48 can run a sequence of up to 48 samples, where different method settings for different sample matrices can be utilized. Simple calibration routines and the included wide range Focus Radiation NDIR detector enable a broad measuring range of up to 500 mg C absolute for all multi N/C duo instruments. This makes repeated analysis for samples with unexpected high concentrations unnecessary.
The preparation and measuring procedures are in full compliance with EN 15936. Furthermore, the multi N/C duo systems are suitable for the automated analysis of TOC (TIC, TC), NPOC, POC and TN_b in water samples without any laborious hardware modifications of the instrument. Changing the configuration setup in the software and loading the desired method are simply done by a few mouse clicks and the solid TOC analyzer is convert into a fully automated liquid analyzer or vice versa.

Figure 3: multi N/C 2100S duo

References

EN 13137 Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments

EN 15936: Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion

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