Challenge

How can the landfill-relevant biodegradable organic carbon content (BOC) of ash and slag waste be determined with an automated and fast measurement method for reliable landfill class assignment?

Solution

With the pyrolysis option according to the VGB[1] method and the TIC automatic module, the multi EA 4000 offers reliable and automated analysis procedures for determination of the BOC and the TOC by differential method.

Determination of Landfill-Relevant Organic Carbon (OC) According to DIN EN 15936 and VGB Pyrolysis Method in Waste from High-Temperature Processes – Comparison to the TOC_{400} Method

Introduction

In waste recycling and landfilling, not all carbon is the same. For example, organic carbon components are decomposable and lead to the formation of landfill gases (methane) and the mobilization of heavy metals through the formation of organic acids. Inorganic and elemental carbon, on the other hand, behaves largely inert in the landfill body and must therefore be evaluated differently in terms of its environmental relevance.

In many regions around the world, waste disposal is carried out by landfilling in dumpsites of different landfill classes, which are suitable for different types of waste in terms of their design (e.g., special subsoil sealing for groundwater protection, leachate collection and treatment, landfill gas management). In addition to other parameters such as heavy metals, the parameter TOC (total organic carbon) is an important parameter in landfill class assignment. It is usually determined using method A (TOC difference method) or method B (direct method) of DIN EN 15936[2] by dry combustion in an oxygen atmosphere. Here, a distinction is effectively made between inorganic and organic carbon contents in the waste sample. However, since elemental carbon (EC) is part of organic carbon according to this definition, for a number of wastes with high carbon black contents the landfill-relevant organic carbon is strongly overestimated.

An alternative method for determining the TOC content in waste is the temperature gradient method according to DIN 19539[3] or prEN 17505[4] with the parameter TOC_{400}. Here it is assumed that at 400 °C oven temperature all organic components are catalytically oxidized to CO_2. Soot-like (elemental) carbon compounds can be determined as ROC (residual organic carbon) at 600 °C or 900 °C.

TIC is determined at 900 °C under oxidative (method A) or inert carrier gas conditions (method B). However, as comparison measurements have shown, this method resulted in significant excess findings to TOC_{400} for most of the examined wastes originating from high-temperature processes. This is due to the fact that also many soot-like carbon compounds already react to CO_2 at temperatures up to 400 °C. This is also supported by a scientific publication of the Karlsruhe Institute of Technology (KIT)[5].

A remedy for the correct determination of the landfill-relevant degradable organic carbon (BOC - biodegradable organic carbon) is offered by the VGB pyrolysis method[6]. Here, the elemental carbon content is determined in direct measurement, after pyrolytic removal of the organic carbon at 850 °C under inert gas conditions, by dry combustion in an oxygen stream. By difference TOC - EC = BOC, the landfill-relevant degradable organic carbon can be easily calculated from the TOC results according to DIN EN 15936 and the EC results according to the VGB method.

Materials and Methods

The determination of the parameter TOC (total organic carbon) was carried out by the TOC differential method in full compliance with DIN EN 15936. In this method, the TOC equals the subtraction of the TIC (total inorganic carbon) from the TC (total carbon): **TOC = TC – TIC**.
Therefore, the TC and the TIC have to be determined. Both measurements for each sample were performed using a multi EA 4000 with an applied TIC automatic solid module and the automatic solids sampler FPG 48. Two sample aliquots per analysis were weighed into ceramic boats. The first sample aliquot was acidified in the TIC reactor with 40% H_3PO_4, the CO_2 from the carbonate was released and the TIC was measured directly. For better wettability with the acid, few droplets of a TIC-free detergent solution were added after the sample was weighed into ceramic boats. This led to a hydrophilic slurry, even for hydrophobic samples. With a second boat, the sample was introduced into the ceramic combustion tube of the resistance furnace at 1,200 °C and was completely oxidized in a pure oxygen atmosphere. In both runs the measuring gas was dried and cleaned and the carbon content was measured by NDIR (non-dispersive infrared) spectrometry. The calculation of the TOC was performed automatically by the device's multiWin software.
The determination of the BOC was performed by a difference method as well: **BOC = TOC – RC**. Therefore, the determination of the RC (residual carbon) – equivalent to EC (elemental carbon) – was carried out according to the pyrolysis procedure of VGB standard 4.4.2.1.
For the analysis of residual (resp. elemental) carbon (RC/EC) the furnace temperature was set to 850 °C. Prior to the introduction of the sample into the furnace, the combustion tube was flushed with Ar (1.5 L/min). Argon as an inert gas can equivalently be used instead of nitrogen for the pyrolysis step. Samples were introduced into the hot inert atmosphere and were kept there for 300 s. Within this pyrolysis time the lighter components evaporated, and complex organic structures were pyrolyzed to lighter compounds. With a constant Ar flow these components together with the CO_2 from the also decomposed carbonates were flushed out into an exhaust. Following the pyrolysis phase, the system switched automatically to the combustion mode and the combustion tube with the hot boat still inside was flushed with an O_2 flow (2.5 L/min). The remaining carbon on the sample boat was immediately oxidized, which was followed by drying and purifying the sample gas and passing it into the NDIR detector for quantitative CO_2 determination. The calculation of the BOC was carried out with external tools.

Samples and reagents

- 6 samples were examined for this method comparison, including waste from a foundry (sample 1), aluminum production (sample 2), a recycling process (sample 3), coke from petroleum refining (sample 4), as well as fly ash (sample 5), and waste incineration slag (sample 6)
- 40% phosphoric acid for automatic TIC determination
- EC calibration standard glassy carbon
- Alumina (Al_2O_3) for the preparation of the solid dilutions of the calibration standards

Sample preparation

All samples were dried at 40 °C, cleaned from obvious impurities, and finally ground in order to receive fine powders in full accordance with EN 15936. All samples were measured directly without any further preparation, except for the automatic TIC determination, where few droplets of a detergent solution were applied onto the weighed sample to increase the acid wettability.

Calibration

The multi EA 4000 was calibrated for the determination of all parameters using a standard of constant concentration and applying different sample quantities. As calibration material for total carbon (TC) and residual carbon (RC) respectively elemental carbon (EC), glassy carbon was applied. This was diluted in Al_2O_3 if needed. TIC was calibrated with diluted calcium carbonate (1.2% $CaCO_3$ in Al_2O_3). Calibration curves are shown in figures 1–3. In table 1 the calibration ranges are described.

Table 1: Calibration of the different carbon species

Parameter	Standard	Content [%]	Weigth [mg]	Calibrated range [mg]
TIC	$CaCO_3$	1.2	16–141	0.2–1.7
TC (1,200 °C)	Carbon, glassy	9.91	14–86	1.4–8.6
TC (1,200 °C)	Carbon, glassy	9.91	86–509	8.6–51
RC/EC	Carbon, glassy	9.91	20–80	2–8
RC/EC	Carbon, glassy	9.91	80–378	8–38

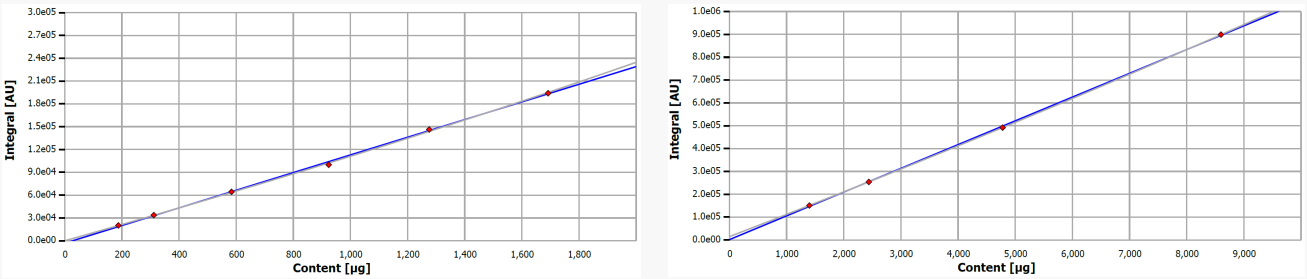

Figure 1: Calibration curves for the TIC (left, 1.2%) and TC (right, low range, 1,200 °C, 9.91%)

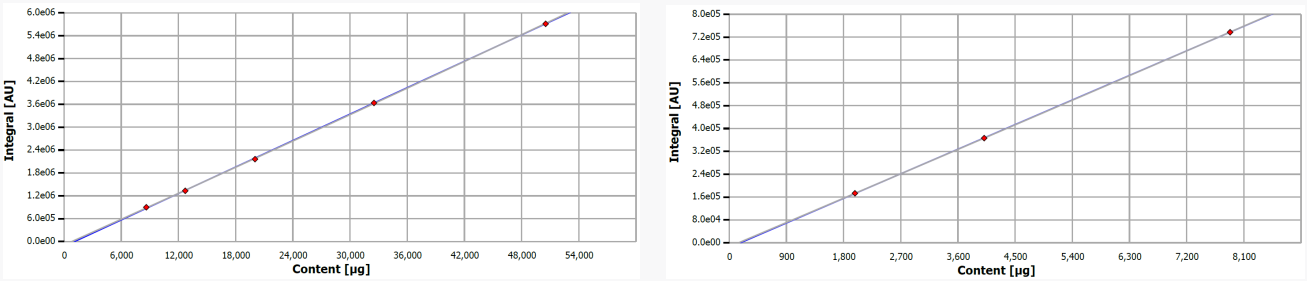

Figure 2: Calibration curves for the TC (left, high range, 1,200 °C, 9.81%) and RC/EC (right, low range, 850 °C, 9.81%)

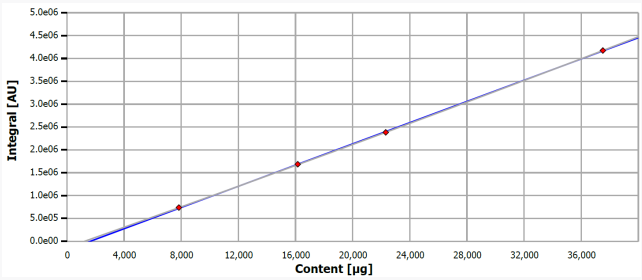

Figure 3: Calibration curve for the RC/EC (high range, 850 °C, 9.81%)

Results and Discussion

TOC difference

Analysis results of the measurements for TOC by differential method are shown in table 2. Typical measuring curves are shown in the following figures. Measurements were performed as triplicates for each sample. Check standards were measured as single value only. Typical weight of the samples varied from 20 to 300 mg depending on the expected content and parameter.

Table 2: Results of the TIC, TC (1,200 °C), and TOC determination

Sample ID	TIC [%] ± SD	TIC RSD [%]	TC [%] ± SD	TC RSD [%]	TOC [%] ± SD	TOC RSD [%]
Sample 1	0.018 ± 0.005	27.0	15.35 ± 0.63	4.1	15.34 ± 0.71	4.1
Sample 2	0.15 ± 0.009	5.7	32.97 ± 1.06	3.2	32.81 ± 1.07	3.3
Sample 3	0.97 ± 0.026	2.7	20.61 ± 0.28	1.4	19.63 ± 0.28	1.5
Sample 4	0.073 ± 0.023	30.7	94.9 ± 2.48	2.6	94.8 ± 2.48	2.6
Sample 5	3.40 ± 0.025	0.7	11.62 ± 0.06	0.5	8.22 ± 0.04	0.5
Sample 6	0.22 ± 0.029	13.1	35.06 ± 0.64	1.8	34.84 ± 0.65	1.9
TC 10	–	–	9.65	–	–	–
TC 100	–	–	101.86	–	–	–
$CaCO_3$ 0.12	0.15	–	–	–	–	–
$CaCO_3$ 1.2	1.12	–	–	–	–	–

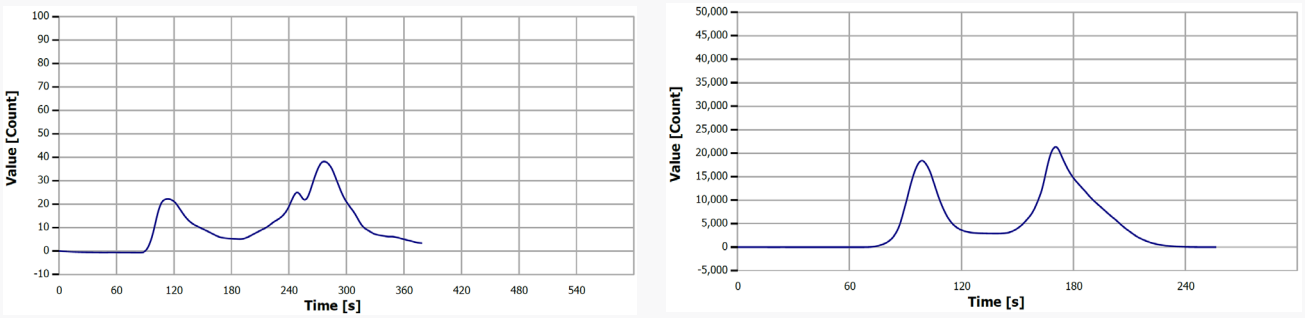

Figure 4: Measuring curve for the TIC (left) and TC (right) determination of sample 1

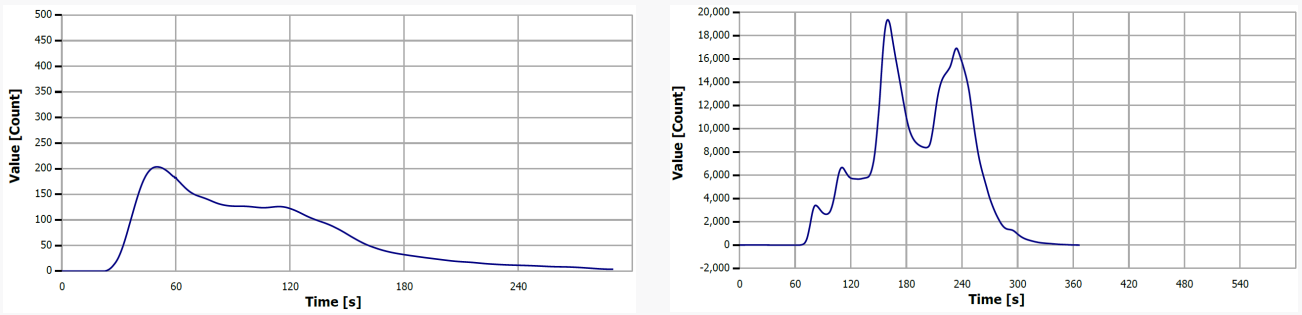

Figure 5: Measuring curve for the TIC (left) and TC (right) determination of sample 2

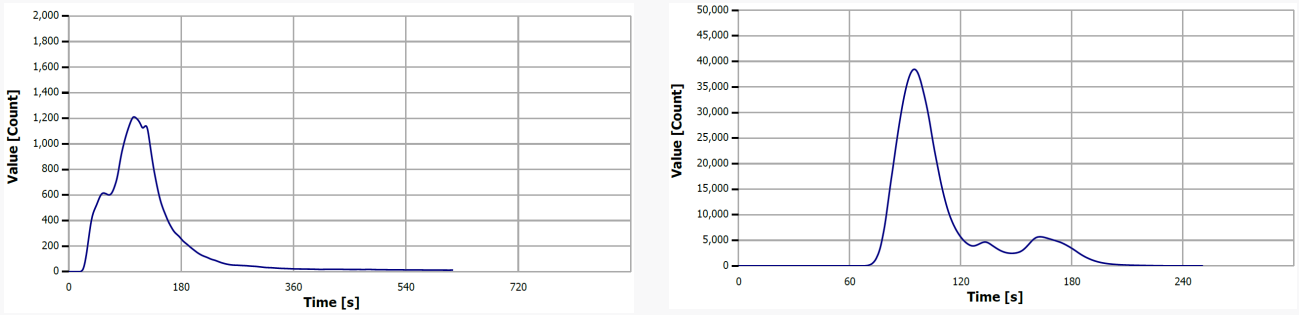

Figure 6: Measuring curve for the TIC (left) and TC (right) determination of sample 3

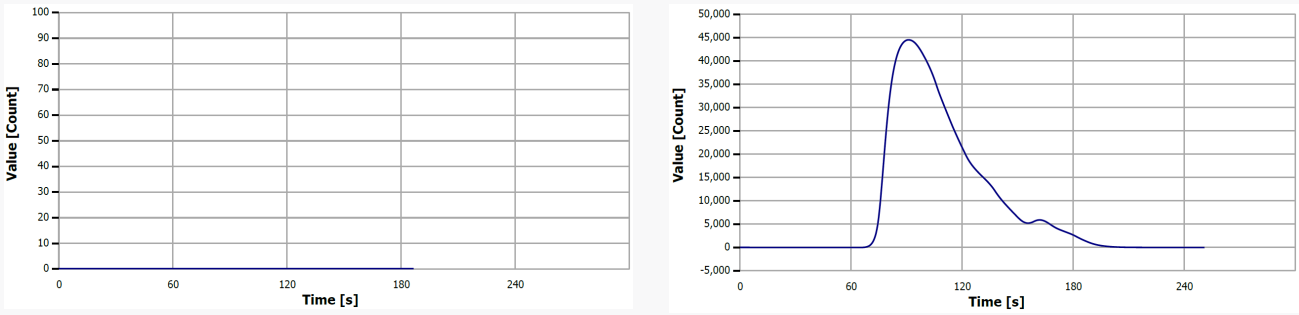

Figure 7: Measuring curve for the TIC (left) and TC (right) determination of sample 4

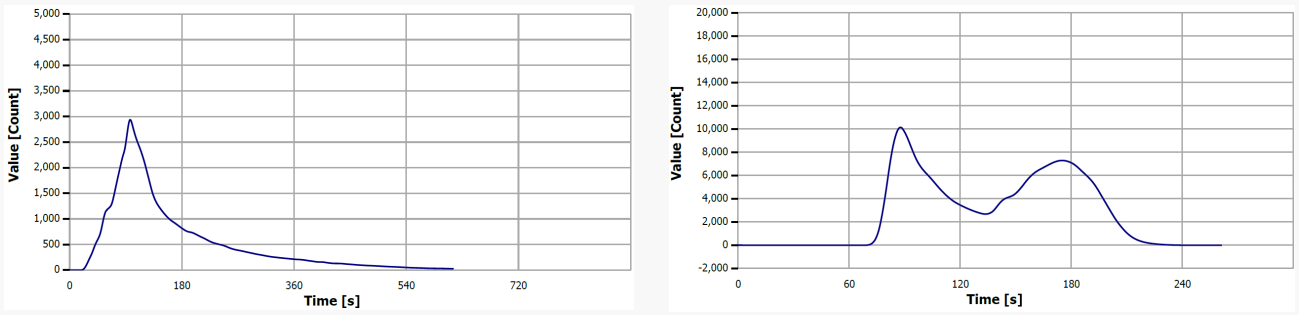

Figure 8: Measuring curve for the TIC (left) and TC (right) determination of sample 5

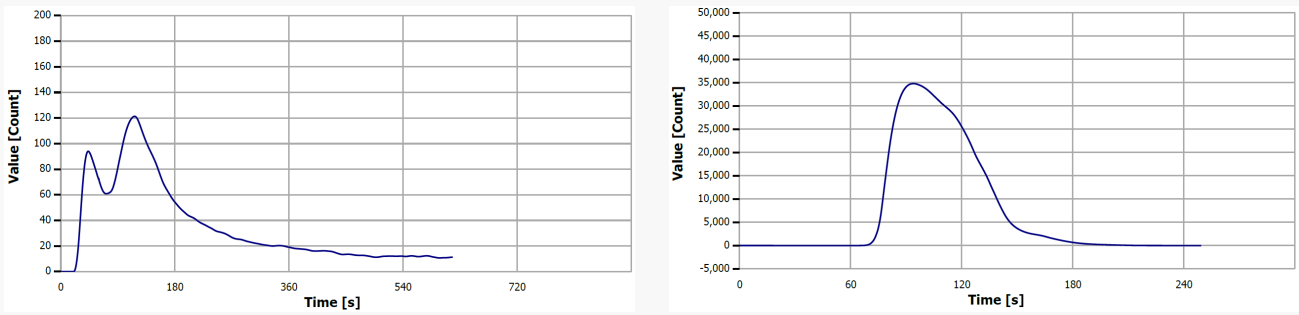

Figure 9: Measuring curve for the TIC (left) and TC (right) determination of sample 6

Since the samples originated from high-temperature processes (soot, slag, ash), the TIC content was very low for most samples. Acidification was possible for all samples except for sample 4. Even with detergent solution as wetting agent, the hydrophobicity of the sample was too high to obtain a trustworthy result. For all other samples and all TC measurements the determinations were performed successfully, and the standard deviations were in the expected range.

RC/EC determination (850 °C) for BOC calculation

Analysis results of the measurements for RC/EC determination are shown in Table 3. Typical measuring curves are shown in the following figures. Measurements were performed as triplicates for each sample. Typical weight of the samples varied from 50 to 300 mg depending on the expected content and parameter.

Table 3: Results of the RC/EC (850 °C) determination

Sample ID	RC/EC [%] ± SD	RC/EC RSD [%]
Sample 1	15.11 ± 0.24	1.6
Sample 2	16.56 ± 0.30	1.8
Sample 3	17.61 ± 0.06	0.3
Sample 4	95.70 ± 2.44	2.6
Sample 5	5.29 ± 0.28	5.2
Sample 6	30.74 ± 0.33	1.1
TC 10	9.92	–
TC 100	99.23	–

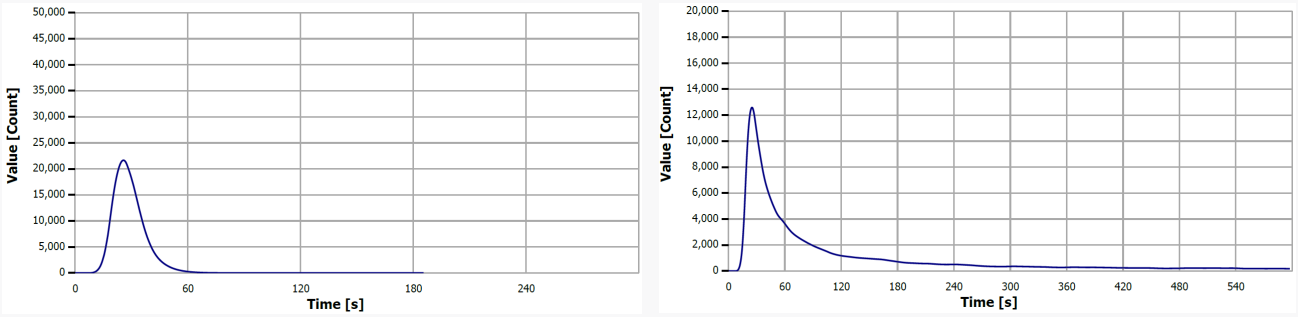

Figure 10: Measuring curves for the RC/EC for samples 1 (left) and 2 (right)

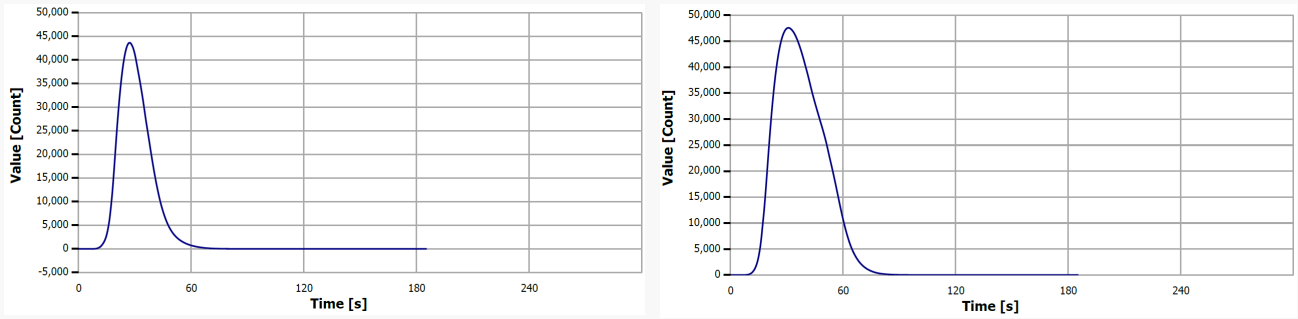

Figure 11: Measuring curves for the RC/EC for samples 3 (left) and 4 (right)

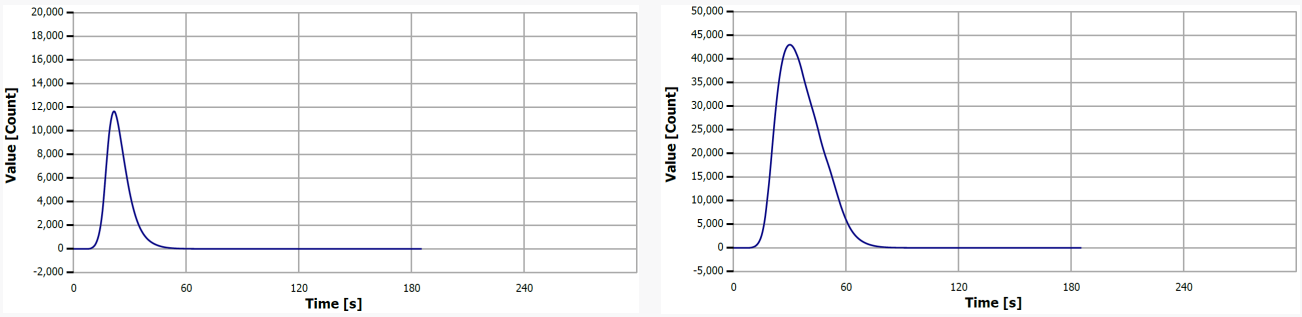

Figure 12: Measuring curves for the RC/EC for samples 5 (left) and 6 (right)

The measurements for the RC/EC determination were successful. The deviations are in the expected range.

Calculation of BOC – Comparison to TOC_{400}

Within this set of samples, the content of elemental carbon, derived from the pyrolysis approach according to VGB standard 4.4.2.1 was expected to be rather large, considering the sources of the samples, derived from high-temperature processes. To determine the real organic carbon, accessible to microbes on landfills, it is possible to subtract the RC/EC from the TOC. This is the biodegradable organic carbon (BOC), according the definition. The result of the calculation is given in Table 4 and compared to the results obtained by the TOC_{400} method (prEN 17505)).

Table 4: Calculation of BOC and comparison to TOC_{400}

Sample ID	TC [%] ± SD	TIC [%] ± SD	TOCdiff [%] ± SD	RC/EC [%] ± SD	BOC [%] ± SD	TOC_{400} [%] ± SD**
Sample 1	15.35 ± 0.63	0.018 ± 0.005	15.34 ± 0.71	15.11 ± 0.24	0.23 ± 0.54	0.8 ± 0.037
Sample 2	32.97 ± 1.06	0.15 ± 0.009	32.81 ± 1.07	16.56 ± 0.30	16.25 ± 0.77	2.7 ± 0.18
Sample 3	20.61 ± 0.28	0.97 ± 0.026	19.63 ± 0.28	17.61 ± 0.06	2.02 ± 0.34	17.9 ± 0.62
Sample 4	94.9 ± 2.48	0.073 ± 0.023	94.8 ± 2.48	95.70 ± 2.44	-0.92* ± 4.36	90.1 ± 1.12
Sample 5	11.62 ± 0.06	3.40 ± 0.025	8.22 ± 0.04	5.29 ± 0.28	2.93 ± 0.24	6.6 ± 0.31
Sample 6	35.06 ± 0.64	0.22 ± 0.029	34.84 ± 0.65	30.74 ± 0.33	4.10 ± 0.89	31.9 ± 0.83

* negative results can be considered as 0
** results were obtained externally by a contract lab

For some samples the BOC (= TOC - RC) would be negative and is therefore defined as 0. This is a statistic phenomenon caused by the error ranges of the two big readings for TOC and RC/EC. In this case the RC/EC can be considered equal to TC.

Conclusion

The multi EA 4000 is well-suited to analyze the provided samples derived from high-temperature processes for the different carbon species. The results are reproducible and the standard deviations are low. All three parameters TIC, TC, and EC/RC are needed to determine the parameters TOC and finally BOC, which is a measure to assign the different waste materials to the appropriate landfill class. The multi EA 4000 determines the different carbon parameters by the chemical properties of the carbon compounds in the sample (reaction to acid, behavior in inert gas atmosphere and oxygen atmosphere at elevated temperatures). As confirmed by the comparison with the externally measured TOC_{400} values, the approach of BOC determination by combination of the TOC measurement according to DIN EN 15936 and the VGB pyrolysis method for the EC results provided comprehensible and correct results for the landfill-relevant degradable organic carbon content of the examined waste samples compared to overestimated TOC_{400} results.

The samples showed widely varying concentrations of the different carbon species. Therefore, calibration can be performed with low-concentrated reference materials or self-diluted standards as well as pure calcium carbonate or other higher concentrated reference material. With the capability of the multi EA 4000 to hold up to 3 g of sample (depending on the specific density) in combination with the wide-range NDIR detector it is possible to feed higher total carbon quantities for analysis. This feature can optimally be used to respond to typically occurring sample inhomogeneities.
With the applied FPG 48 solid sampler and the TIC automatic module, the process can be performed with a high degree of automation. The operator only weighs in the samples and places them onto the sampler. Additionally, the measurement system can be further upgraded to determine total sulphur (TS) and total halogens (TX).

Figure 13: multi EA 4000 with TIC automatic module, pyrolysis function, and FPG 48 solids sampler

Table 5: Configuration multi EA 4000

Module	Order number	Description
multi EA 4000 C BU with Pyrolysis Option	450-126.568	Elemental analyser for carbon determination in solids (with pyrolysis function)
TIC-solid module „automatic“	450-126.576	For direct and automated determination of TIC in solids
FPG 48 solid autosampler	450-126.574	Autosampling unit for the multi EA 4000

References

[1] VGB PowerTech is an international interest group of companies from the electricity and heat supply industry, more information on www.vgbe.energy

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

[3] DIN 19539 Investigation of solids - Temperature-dependent differentiation of total carbon (TOC_{400}, ROC, TIC_{900})

[4] prEN 17505:2022 Soil and waste characterization - Temperature dependent differentiation of total carbon (TOC_{400}, ROC, TIC_{900})

[5] Catalytic effects in heterogeneous combustion and gasification reactions of carbons with respect to thermal waste treatment, Forschungszentrum Karlsruhe - KIT, Table 5.1, Scientific Reports FZKA 6077, Z. I. Meza-Renken, 04-1998

[6] VGB-B 401: Handbuch “Chemie im Kraftwerk“ – Band II: Analysenverfahren, Blatt 4.4.2.1, 1/1993, Bestimmung von organischem Kohlenstoff in Müllverbrennungsschlacken unter Berücksichtigung des Kokskohlenstoffgehaltes / VGB-B 401: Manual “Chemistry in Power Plants” - Volume II: Analytical Methods, Sheet 4.4.2.1, 1/1993, Determination of organic carbon in waste incineration slags taking into account the coking carbon content

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