Challenge

Can a wide variety of TOC/DOC concentrations in aqueous waste eluates and landfill leachates with high matrix loads be determined quickly and reliably?

Solution

The multi N/C 3300 TOC analyzer with its integrated focus radiation wide-range detector and robust combustion system is ideally suited for eluate and leachate samples.

Waste Characterization for Landfill Classification – Determination of TOC/DOC According to DIN EN 1484 in Waste Eluates and Landfill Leachates

Introduction

The treatment, recycling, and disposal of waste are subject to strict regulations. "Residual waste" that can neither be recycled nor thermally recovered is ultimately landfilled. Prior to landfilling, the waste is usually pre-treated in order to keep the proportion of organically degradable substances and thus the formation of climate-damaging landfill gas (methane) as low as possible.

Landfills are generally divided into different classes in order to minimize the impact on the environment when storing different types of waste with different hazard potentials. To this end, landfills are appropriately designed and sealed structurally to prevent pollutants from entering groundwater. Open landfills are exposed to precipitation and temperature changes, causing microbial degradation processes to take place on organic compounds. During this process, what is known as landfill leachate is formed by the dissolution of chemical compounds from the landfill body.

The leachate is collected by appropriate drainage systems in a collection basin and is then to be treated in a wastewater treatment plant. Therefore, landfill leachates have to be analyzed regularly, focusing on heavy metals and poorly degradable organic compounds. Beside other criteria, the investigation of sum parameters like the total organic carbon (TOC) is also used to provide a quick overview of the hazard potential of the leachate.

According to the European landfill directive and the acceptance criteria of waste at landfills[1], the assignment of waste to a landfill class is done by characterizing the waste with the help of physical and chemical parameters. In addition to the solids, the aqueous eluates are also examined according to DIN EN 16192[2]. The determination of the material fractions that can be eluted under the respective process conditions serves to estimate the leaching behavior of the waste constituents due to weather influences. The preparation of the aqueous waste eluate must be carried

out in accordance with DIN EN 12457[3], sheets 1–4. Waste and water are brought into intensive contact in a specific ratio by shaking, after which the aqueous phase (the eluate) is separated from the waste phase by membrane filtration. The eluate obtained is then analyzed for specified criteria, parameters, and elements. In addition to heavy metal analysis, the determination of total organic carbon (here as DOC = dissolved organic carbon) is also mandatory.

Materials and Methods

The determination of TOC/DOC was carried out on the multi N/C 3300 in combination with the autosampler AS vario. The NPOC method was selected for determination. This method is preferably used whenever no volatile organic substances are present in the sample and the expected content of organic carbon (TOC) is less than or comparable to the content of inorganic carbon (TIC). In addition, the direct determination of TOC as NPOC (non-purgeable organic carbon) is widely used in routine labs because it allows a higher sample throughput, and the results are less subject to error compared to the difference method (TOC = TC-TIC). The analysis was performed in accordance with DIN EN 1484[4].

Samples and reagents

- 5 eluate samples from different types of waste
- 1 landfill leachate
- 2 M HCl to acidify the samples
- TOC calibration standard solutions (potassium hydrogen phthalate in water)
- TOC control standard solution (potassium hydrogen phthalate in water)

Sample preparation and measurement

The waste eluates were analyzed without further sample pretreatment within 24 hours after preparation of the aqueous eluate. All eluate samples were acidified to pH ≤2 using 2 M HCl immediately before their analysis. For the samples at hand, an acid amount of 0.5 mL per 100 mL sample volume was sufficient for this purpose. The landfill leachate sample, which was clearly brownish in color, was diluted with ultrapure water at a ratio of 1:10 prior to analysis and acidified to pH ≤2 in a manner analogous to the eluate samples. Since both the original and diluted leachate samples contained no visible particles, homogenization steps (such as treatment in a disperser) were omitted. All samples were filled into 40 mL sample vials and placed on the sampler tray. As an alternative to manual acidification, the autosampler can also be used for automatic acidification and dilution of the samples.

The next step was the automatic purging of the samples. Here, the CO_2 (from carbonates / hydrogen carbonates) released by the acid treatment is removed from the samples with the aid of a CO_2-free auxiliary gas (in this case O_2). Thanks to an advantageous arrangement of 2 needles on the AS vario autosampler, the injection / analysis of the current sample and the purging / preparation of the next sample could be performed simultaneously. This saves valuable analysis time and the sample throughput can be doubled.

The purged samples, freed from TIC, were then injected into a furnace with a quartz combustion tube, where the conversion of the remaining organic constituents (NPOC) to carbon dioxide takes place. For this purpose, a representative sample aliquot of 500 µL each was fed to the combustion tube. To ensure rapid and complete oxidation of the ingredients to CO_2, the conversion took place at 800 °C in the presence of a platinum catalyst. Pure oxygen was used as carrier gas (hydrocarbon and CO_2-free synthetic air is also possible). The sample gas was transferred to the detector after appropriate drying and purification. Quantification was performed using non-dispersive infrared spectrometry in a Focus Radiation NDIR Detector.

Calibration

The multi N/C analyzer was calibrated with potassium hydrogen phthalate standard solutions in the concentration range of 1 and 500 mg/L TOC. All calibration solutions were prepared according to DIN EN 1484.

Table 1: Method settings

Parameter	multi N/C 3300
Method of determination	NPOC
Sample digestion	Catalytic high-temperature combustion (Pt) at 800 °C
Number of replicates	min. 2, max. 3
Autosampler, rack and vial size	AS vario ER, 72 positions rack, 40 mL sample vials
Rinse cycles with sample	3
Injection volume	500 µL
NPOC purge time (removal of TIC)	300 s

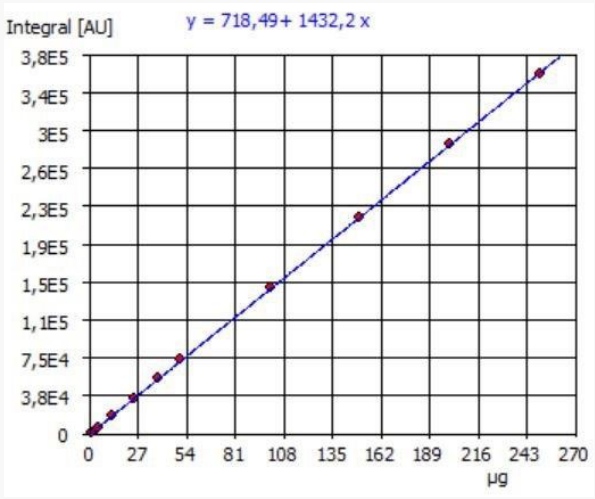


Figure 2: Calibration curve TOC 1 – 500 mg/L

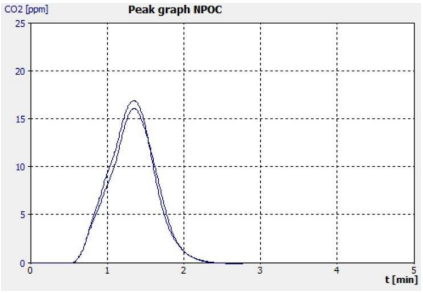
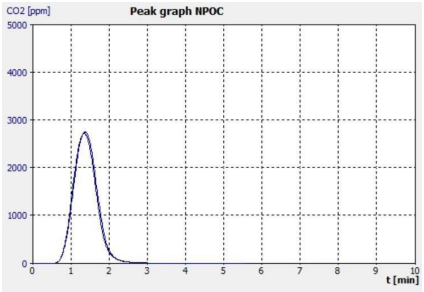
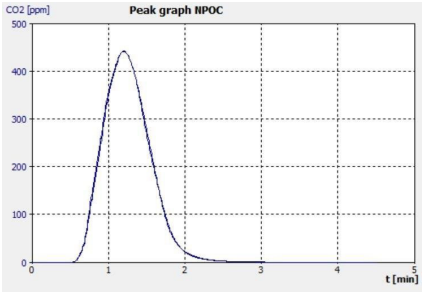
Results and Discussion

The analytical results of all samples and of the TOC/DOC control standard (potassium hydrogen phthalate) are summarized in Table 2. The measurements were each carried out as multiple injections from a sample vessel.
The results of the determination of the organic carbon in the aqueous eluates and in the leachate show, as expected, a certain range with regard to the determined concentrations. The TOC/DOC content of each sample could be determined with very good repeatability, the relative standard deviation (RSD) obtained is ≤ 2% for all results.
The example measurement curves illustrate the excellent reproducibility of the measured values within a multiple injection from a sample vessel.

Table 2: Results eluate and leachate samples

Sample ID	Result DOC/TOC ± SD [mg/L]	RSD [%]
Eluate 1	46.6 ± 0.28	0.6
Eluate 2	2.01 ± 0.04	2.0
Eluate 3	51.4 ± 0.56	1.1
Eluate 4	322 ± 5.51	1.7
Eluate 5	51.3 ± 0.58	1.1
Landfill leachate	561 ± 3.03	0.5
QC control 50 mg/L TOC (potassium hydrogen phthalate)	49.8 ± 0.62	1.2

Table 3: Examples of measurement curves for eluate and leachate samples

Eluate 2	Eluate 4	Landfill leachate (1:10 diluted)
		

Conclusion

The multi N/C 3300 is a universally applicable TOC/DOC analyzer that is very well suited for the determination of different sample matrices and concentrations. Both very low and very high TOC concentrations can be reliably determined in one sample sequence. Thanks to the large dynamic detector range for the focus radiation NDIR detector and the ability to calibrate a large working range within the same method, the need for internal sample dilution is eliminated. External sample dilution is possible at any time using the AS vario autosampler. Furthermore, the instrument features durable and robust components as well as intelligent rinsing mechanisms that reliably minimize sample carry-over and necessary maintenance interventions even for complex samples with high matrix loads.

The multi N/C 3300 is ideally suited for the determination of TOC/DOC according to DIN EN 1484. Fast, reliable and standard-compliant routine analysis is guaranteed at all times with this instrument. For additional TOC determination in solid waste the multi N/C 3300 duo system offers full automation solutions for both, liquid and solid samples.

Figure 1: multi N/C 3300 with autosampler AS vario

References

[1] DIRECTIVE (EU) 2018/850 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, of 30 May 2018, amending Directive 1999/31/EC on the landfill of waste and the COUNCIL DECISION of 19 December 2002, establishing criteria and procedures for the acceptance of waste at landfills

[2] DIN EN 16192:2012-02 Characterization of waste - Analysis of eluates

[3] DIN EN 12457-4:2003-01 Characterization of waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with limited size reduction)

[4] DIN EN 1484: 2019-04 Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

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