Challenge

Is it possible to determine both, very small and large EOX contents, in solid waste and soil samples with good precision, in one and the same device?

Solution

The multi X 2500 with its HiPerSens coulometer detects ultra-low EOX traces reliably as well as large EOX quantities in shortest time, without interference and memory effects.

Determination of EOX in Waste and Soil Samples According to DIN 38414-17 and EPA 9023

Introduction

There are many substances that contribute to the total amount of environmentally harmful organic halogen compounds, such as detergents, disinfection byproducts, pesticides, varnishes, stain removers, flame retardants, cosmetics, pharmaceuticals, deodorants, etc. With wastewater, these compounds get distributed throughout environment. Some studies point out that even at low concentrations in soil, such substances can get enriched by soil-plant interactions (effects of assimilability, poor solubility, leaching, etc.). This can lead to extensive pollution and unpredictable phenomena over a long time.
Since it is very difficult to identify all individual organically bound halogens in environmental matrices such as water, sludge or soil, so-called sum parameters such as adsorbable organically bound halogens (AOX) and extractable organically bound halogens (also: extractable organic halides (EOX), or total organic halogens (TOX)) have become established as environmental indicators in many countries around the world (e.g., German substitute building materials ordinance).
While the AOX parameter is often used to detect halogen-bound organic contaminants in waters, the determination of the EOX is mainly applied to solid samples (soil, sediment, waste, etc.). EOX represents the total organic halogen compounds extracted by solvents from solid or liquid matrices, with liquid matrices typically represented by aqueous eluates from waste materials (e.g., Austrian landfill ordinance). Most of the organics included in this parameter have been classified as particularly hazardous pollutants (priority pollutants), so the measurement of EOX content in soil gives a good estimate of the environmental pollution level. Many solid samples often have very low EOX concentrations (< 1 mg/kg), besides there are only a few samples with extremely high EOX concentrations. The challenge is to reliably determine both extreme values in one instrument day after day.

Materials and Methods

Reagents

- EOX standard solutions of decachlorobiphenyl (PCB-209) in n-hexane
- EOX control standard: 4-chlorophenol in n-hexane
- n-hexane as solvent and extraction agent
- Hydrochloric acid, 0.01 mol/L
- Sulfuric acid, 98%
- 5 solid freeze-dried samples

Sample preparation

The extraction of EOX can be carried out by using n-hexane, iso-hexane, cyclo-hexane, petroleum ether (acc. to DIN 38414-17), or ethyl acetate (acc. to EPA 9023) as extraction solvents.

All samples were prepared according to the procedure described in the standard method DIN 38414-17 in the following steps. The freeze-dried samples (ca. 10 g) were crushed (0–2 mm particle size) and the organically bound halogens were extracted with 75 mL of n-hexane using a Soxhlet extractor for 8 hours. Finally, the extract volume was reduced to less than 10 mL in a rotary evaporator, transferred to a volumetric flask, and made up to the mark with n-hexane. Obtained extracts were used for the further analysis.

Instrumentation

The EOX content of the sample extracts was determined using the multi X 2500 halogen analyzer in horizontal operation mode. The sample introduction was performed automatically by an autoX 112 sampler with liquids kit, combined with automatic boat drive (ABD).

The sample aliquots were automatically injected by aid of a 100 µL syringe onto a quartz sample boat, covered with a quartz tissue for better sample distribution and moderate evaporation, placed in the ABD sample port. The boat transfer into the combustion furnace was controlled by the flame sensor, which automatically determines the optimal speed for sample feeding depending on the intensity of the combustion flame. This ensures safe, controlled sample evaporation and combustion, and prevents formation of soot and other incomplete combustion products.

Sample combustion took place in a two phasic process. In the first phase, the sample was heated to 1,050 °C in an argon atmosphere, which resulted in evaporation of volatile and pyrolysis of the heavier organic compounds. The organic-rich gases were digested in an oxygen-rich atmosphere. In the second process phase, the combustion tube was completely purged with oxygen to ensure all non-volatile pyrolysis products are converted to the detectable species. The gaseous combustion products were dried using concentrated sulfuric acid and finally transported to a micro-coulometric titration cell for halogen determination.

Method settings

Sample extracts were analyzed using a liquids method for EOX. The process parameters are summarized in table 1 and table 2. The injection volume for the EOX determination was set to 100 µL.

Table 1: Process parameters of the method

Parameter	Setting
Furnace temperature	1,050 °C
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Draw up speed	2 µL/s
Injection speed	2 µL/s

Table 2: Detection parameters

Parameter	Setting
Max. integration time	1,200 s
Cell temperature	23 °C
Titration delay	1
Threshold	25
Threshold value	300

Calibration

Liquid calibration standards based on decachlorobiphenyl in n-hexane were used to calibrate the analysis system in the concentration range from 0.05 to 10 mg/L. The concentrations where calibrated by standards of different concentration and a constant volume. The calibration curves are shown in the following figures.

Table 3: Calibration data

Parameter	Standard	Concentration [mg/L]
EOX	decachlorobiphenyl (PCB 209) in n-hexane	0.05 - 1/1 - 10

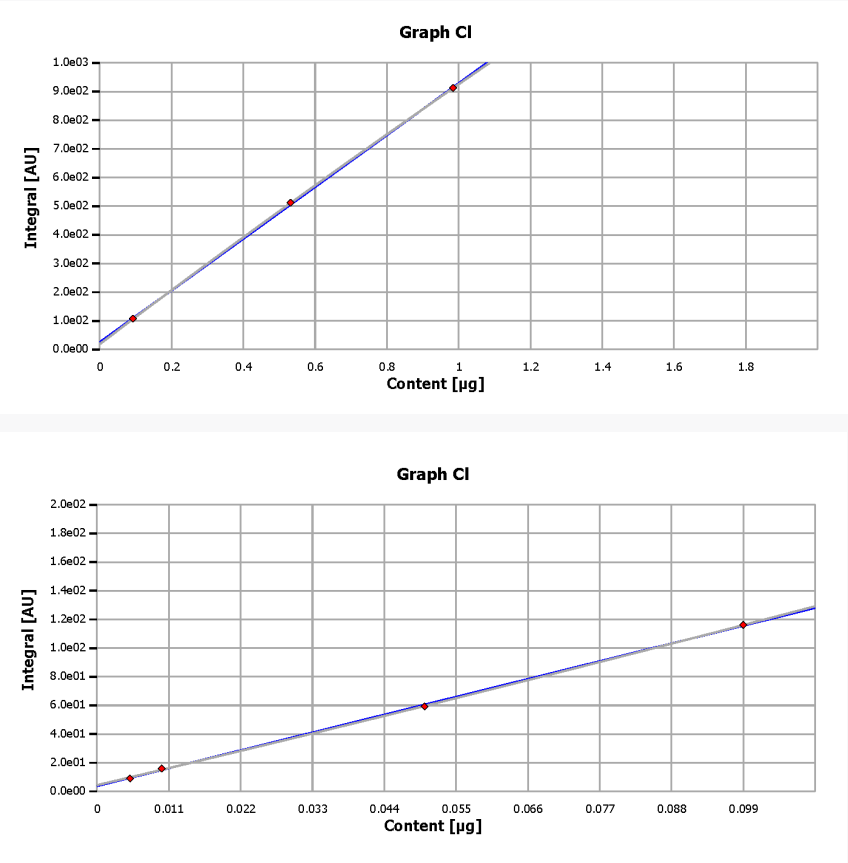

Figure 1: Calibration curves for the EOX determination (high and trace range)

Results and Discussion

Sample preparation and measurement was performed as described. Measurements were performed as multiple replicates with an outlier selection from two out of three for EOX. The results, as well as the corresponding standard deviations of samples and control standards are shown in Table 4 and 5. Representative measuring curves are depicted in the following figures.

Table 4: Summarized results of the sample measurements

Sample ID	Sample weight [g]	Result EOX ± SD [mg/kg]
Soil 1	9.89	0.33 ± 0.024
Soil 2	10.57	0.23 ± 0.023
Soil 3	10.11	0.19 ± 0.008
Waste 1	9.96	16.22 ± 0.36
Waste 2	9.74	6.35 ± 0.10

Table 5: Summarized results of the reference standard measurements

Control standard	Nominal value EOX [mg/L]	Result EOX ± SD [mg/L]
4-chlorophenol in n-hexane	10	9.91 ± 0.215
4-chlorophenol in n-hexane	1	1.04 ± 0.017

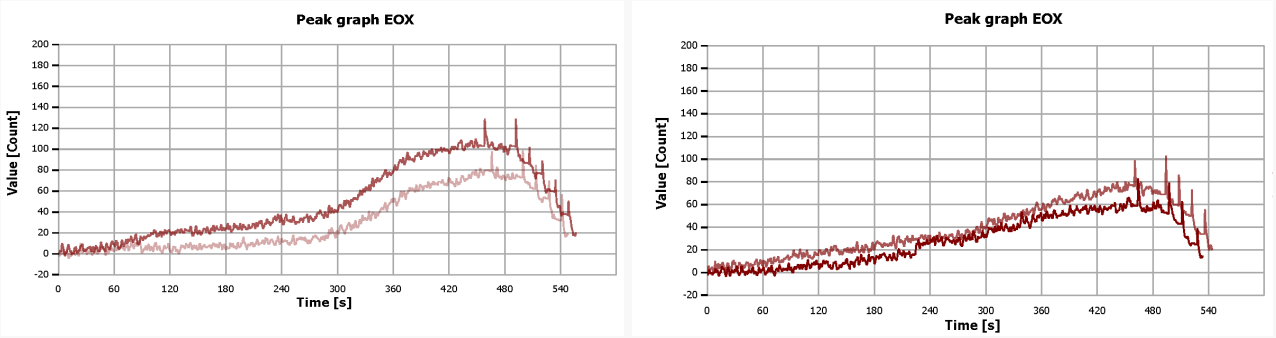

Figure 2: EOX measurement curves of sample Soil 1 (left) and Soil 2 (right)

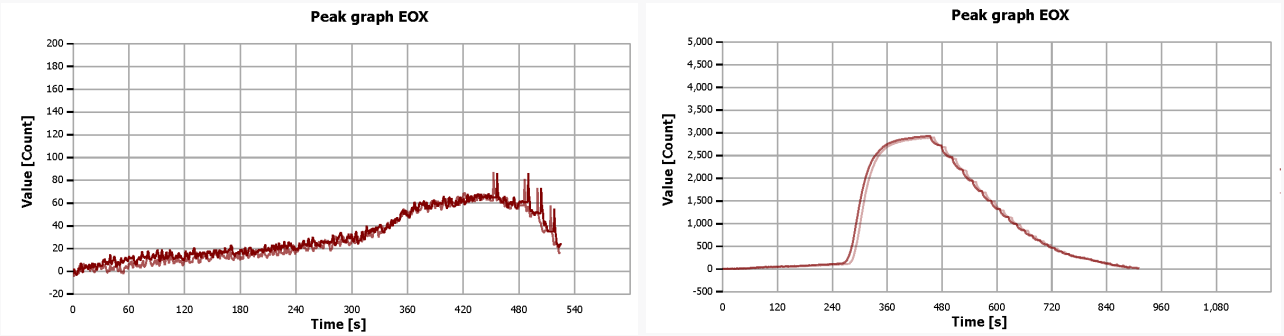

Figure 3: EOX measurement curves of the sample Soil 3 (left) and Waste 1 (right)

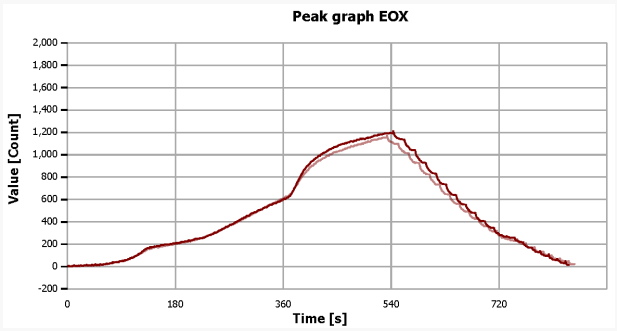

Figure 4: EOX measurement curve of the sample Waste 2

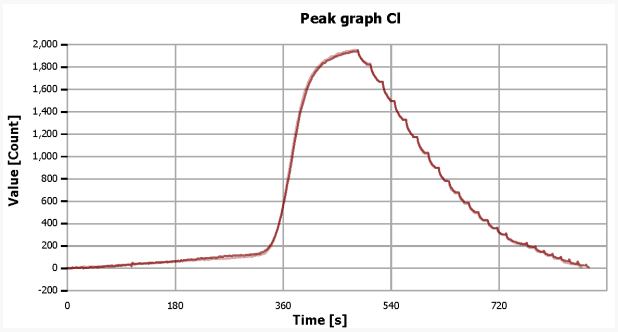

Figure 5: Control standard 10 mg/L 4-chlorophenol in n-hexane

The results illustrate the very good reproducibility of the EOX measurements in the concentration range below 0.5 mg/kg. The higher EOX contents in the contaminated waste samples were determined with even better precision.
Thanks to the very good sensitivity of the analyzer (LOD: 10 ng Cl absolute), it is not necessary to further concentrate the sample by evaporating the extracts obtained to the dryness and recovering them in a very small volume. Last but not least, the stability and the low signal drift of the coulometric system contribute to the reliable determination of these low concentrations. Measurement in the horizontal operation mode also offers the advantage that any kind of organic sample is quantitatively combusted by aid of the flame sensor technology. This applies to very light volatile or high-boiling and viscous samples. Even when analyzing highly loaded sample extracts, clogging of injection cannulas is prevented effectively by utilization of the boat inlet, allowing sample injection into cooled sample boats. Canulas often clog when samples are injected from the top into a vertically arranged combustion tube.
There is a wide range of EOX limits for different matrices (soils, sediments, various types of waste) and their recovery purposes (landfilling, incineration, farm land, land application, etc.). A value of 0.1 mg/kg EOX is the most stringent requirement, with the standard DIN 38414-17 describing a range of application starting at 0.2 mg/kg EOX. The measured values illustrate that these requirements can be met with the multi X 2500.

Conclusion

This work has successfully demonstrated that the multi X 2500 equipped with autoX 112, automatic boat drive (ABD) and flame sensor technology provides a fast, safe, and reliable solution for the analysis of EOX in soil and waste extracts. Both very low and very high concentrations can be reliably determined by using one and the same method in a single analysis cycle.
Due to the time- and matrix-optimized flame sensor controlled sample oxidation, the quantitative combustion of any sample component is ensured. No formation of soot or other undesired residues is observed. In combination with the efficient auto protection system, this enables superior reproducibility even if smaller quantities are of interest.
A high sample throughput is easily achieved using the autoX 112 multi matrix sampler, which can introduce solids, liquids, AOX, and EOX samples fully automatically either by quartz boats in horizontal operation mode or by direct syringe injection into the vertically arranged combustion tube.

Figure 6: multi X 2500 with automatic boat drive (ABD) and autoX 112.

References

[1] DIN 38414-17: Determination of the organically bound halogens amenable to extraction (EOX)

[2] EPA 9023: Extractable organic halides (EOX) in solids

[3] Ersatzbaustoffverordnung, 09.07.2021, BGBl. 2598, Jg. 2021, Teil I Nr. 43

[4] Deponieverordnung 2008 - DVO 2008, BGBl. II Nr. 39/2008 i.d. Fassung von 2021

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