Application Note AN-CIC-035

固体品中的素和硫含量符合 EN 17813 准

Rapid analysis with combustion ion chromatography (CIC)

Organic halides constitute one of the largest groups of environmental pollutants [1] and should be monitored, especially during waste disposal (e.g., EU legislation 2000/76/EC and 99/31/EC). Sample preparation is crucial for the subsequent analysis of halogens. This step is susceptible to systematic errors, contamination, and analyte loss due to volatilization or adsorption [2]. Pyrohydrolytic combustion is a suitable method for decomposing both inorganic and organic material [2,3]. Halogens are efficiently separated from the matrix, lowering matrix effects and detection limits [2,4,5]. Combustion ion chromatography (CIC) combines the steps of pyrohydrolytic decomposition, adsorption of halogens and sulfur in solution, and their subsequent analysis by ion chromatography [6,7]. This method is preferred and validated for the simultaneous direct determination of fluorine, chlorine, bromine, and sulfur in solids according to EN 17813:2023. This Application Note focuses on analyzing solids (e.g., sludge, soil, wood) and polymers with CIC using a robust ceramic tube that extends the lifetime of consumables for samples containing high amounts of alkali metals and/or alkaline earth metals.

EXPERIMENTAL

This Application Note describes the experimental approach for determining halogens and sulfur via oxidative pyrohydrolytic combustion followed by ion chromatography according to EN 17813:2023. The complete validation dataset of the ISO standard is published on the webpage of VITO NV, Belgium [**8**].

SAMPLES

Five different types of samples (i.e., solid recovered fuel (SRF), wood, sludge, soil, and a polymer) were analyzed with CIC for their content of fluorine, chlorine, bromine, and sulfur. Four independent replicates were run for the validation study.

The solids were pre-dried at 105 °C and ground to a particle size of less than 250 m. The ground material was dried for a second time at 105 °C for two hours before being weighed out into the combustion vessels. Depending on the type, between 25 mg and 50 mg of each sample was weighed into appropriate ceramic cups (SRF: 50 mg, wood: 50 mg, sludge: 30 mg, soil: 30 mg, and polymer: 25 mg). The overall sample preparation procedure resembles that of EN 17813:2023.

The TEI oven used in this study has two temperature zones (T1, T2), offering more flexibility regarding the temperature gradient the sample is exposed to. This enables the use of one analytical method for various matrices like polymers, sludge, and soil. The final temperature where combustion took place in the presence of argon and oxygen was 1050 °C.
For pyrohydrolytic combustion, a water stream is essential as it converts the halogens into their hydrogenous form (**Figure 1**). The halogens (fluorine, chlorine, bromine) and sulfur are volatilized in the combustion step, transported into the absorber solution (hydrogen peroxide) with an argon/oxygen gas stream, and transferred into the liquid phase (**Figure 1**). Dosinos guarantee precise automated liquid handling, e.g., the transfer of the aqueous sample into the IC for analysis or water delivery essential for pyrohydrolytic combustion.

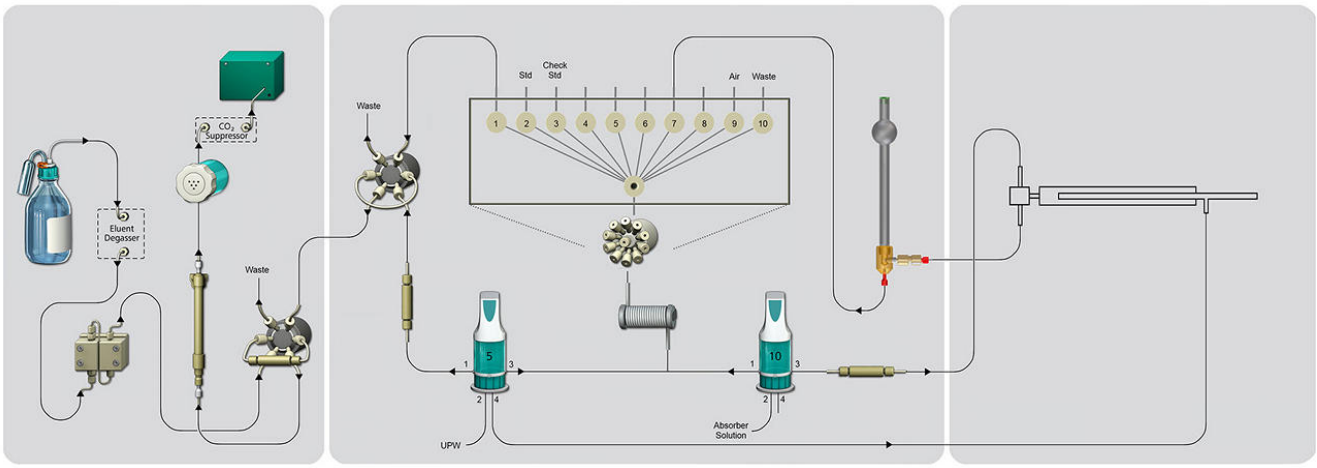

Figure 1. Schematic of the CIC system. The sample is introduced into the oven (right), where it is exposed to heat, water, argon, and oxygen for pyrohydrolytic combustion. The absorber solution is added directly to the combustion gases at the oven exit. All liquid handling of the sample, ultrapure water, and absorber solution is performed using Dosinos. This also enables very precise volume tracking. An aliquot of the sample (5–200 µL) is transferred to a preconcentration column for matrix elimination using ultrapure water. The eluent stream releases the adsorbed analyte ions for separation on the A Supp 19 - 150/4.0 separation column, followed by sequential suppression and conductivity detection. The complete CIC process is fully automated and controlled by MagIC Net chromatographic software.

The ceramic setup of the TEI CIC instrument enables stable combustion conditions and extends the lifetime of consumables which are more robust against high concentrations of alkali metals and/or alkaline earth metals (compared to quartz consumables, e.g., combustion tubes, boats, and cups).

The ion chromatographic separation of the studied anions was achieved on the high-capacity Metrosep A Supp 19 - 150/4.0 column in combination with the A Supp 19 Guard/4.0. A standard carbonate/bicarbonate eluent was used, prepared automatically from a self-made concentrate with the 941 Eluent Production Module.

Automatic system calibration with the Metrohm intelligent Partial Loop Injection Technique (MiPT) was performed using inorganic standards for fluoride, chloride, bromide, and sulfate (1 g/L standard solutions, TraceCert® from Sigma-Aldrich). Depending on the sample concentration, a high-low calibration is recommended. Two calibration ranges (low calibration 0.0125–0.500 mg/L, required to quantify fluoride and bromide in the wood sample, and high calibration 0.125–5.000 mg/L for the rest of the samples) were performed. MagIC Net automatically assigns the correct calibration depending on the analyte's concentration and calculates the concentration in mg/L. With special user-defined results, final concentrations in the samples were automatically calculated (in mg/kg, **Equation 1**) and summarized in a report.

Performance checks were done with inorganic quality control standards on the IC side (direct injection) as well as with a solid CRM material (ERM-EC681m, Polyethylene (elements, high level)) which is, amongst other elements, certified for chlorine, bromine, and sulfur content.

Additionally, blanks were run to qualify the system and to check for even minimal influence of carryover and high background values.

Because of the broad concentration range of the samples, analysis with different injection volumes was performed using MiPT to ensure that all measured analyte concentrations fell within the calibration.

RESULTS

Fluoride, chloride, bromide, and sulfate were determined in less than 20 minutes (**Figure 2**). Sample concentrations (**Table 1**) were calculated according to **Equation 1**. The formula was pre-defined in the MagIC Net software, allowing the summary of the final results in mg/kg in the final report.

Fluorine concentrations ranged from 14 mg/kg (wood) to 559 mg/kg (soil), chlorine concentrations were from 351 mg/kg (polymer) to 7676 mg/kg (SRF), bromine was from 9 mg/kg (wood) to 1304 mg/kg (polymer), and sulfur was found from 189 mg/kg (soil) to 8672 mg/kg (sludge). Relative standard deviations (RSDs) of less than 11% reveal a good reproducibility of the solid materials.

$$c_{sample} = \frac{c_{Abs} * V_{total}}{m_{sample} * \rho_{sample}} * 1000$$

Equation 1.

c_{sample}	analyte concentration in the sample, mg/L
c_{Abs}	analyte concentration in the absorber solution, mg/L
V_{total}	Total end volume in the absorber tube, mL
m_{sample}	sample amount that was weighed in (solids), mg
1000	factor for a result, mg/kg

Table 1. Results of fluorine, chlorine, bromine, and sulfur content determined in solid recovered fuel (SRF), wood, sludge, soil, and a polymer by pyrohydrolytic combustion using CIC.

Sample	Fluorine		Chlorine		Bromine		Sulfur	
	avg. conc. [mg/kg]	RSD [%]	avg. conc. [mg/kg]	RSD [%]	avg. conc. [mg/kg]	RSD [%]	avg. conc. [mg/kg]	RSD [%]
SRF	79.3	5.7	7676	11.0	455	26	714	3.0
Wood	13.5	8.5	522	9.2	8.60	10	406	5.4
Polymer	Not detected	—	351	2.6	1304	2.4	616	2.2
Soil	559	2.4	772	2.9	340	4.3	189	3.1
Sludge	256	4.9	3213	3.3	40.4	2.4	8672	2.2

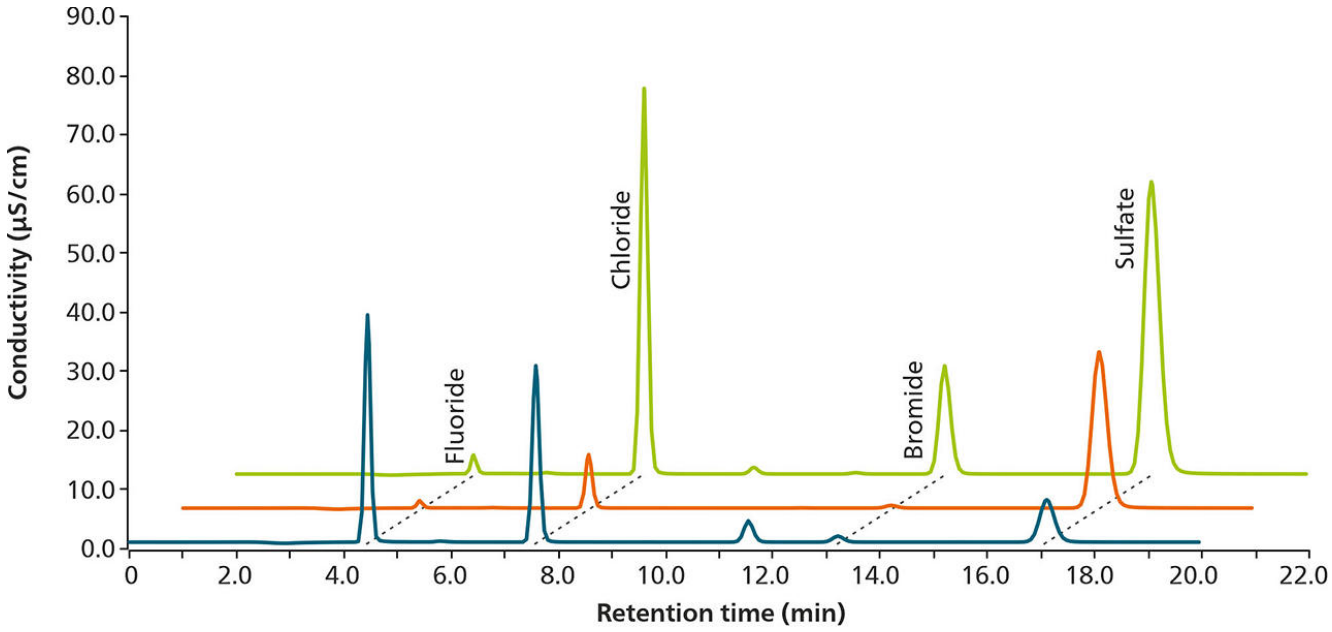

Figure 2. Chromatogram overlay of a soil sample (blue), sludge sample (orange), and wood sample (green). Separation of fluoride, chloride, bromide, and sulfate was achieved on a Metrosep A Supp 19 - 150/4.0 column using the standard carbonate/bicarbonate eluent. Using a flow rate of 0.7 mL/min, all analyte peaks were eluted within 20 minutes and detected using sequential suppressed conductivity.

CONCLUSION

Combustion ion chromatography is a straightforward analytical technique to determine halogens and sulfur in environmental and solid matrices. The ceramic setup is especially suitable for CIC analysis of sample matrices with high amounts of alkali metals and/or alkaline earth metals. With the ceramic setup, the robustness of the analysis and the lifetime of consumables is drastically improved. The ease-of-use is further advanced by the possibility to inject different sample volumes – depending on the analyte concentration in the samples – to guarantee that these fit into the calibration range.

Overall, users of this whole validated procedure profit from easy and standardized handling, the precise determination of the analytes, automatic eluent production, calibration, and results calculation, low maintenance, and a single-manufacturer setup.

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CONFIGURATION

Metrosep A Supp 19 - 150/4.0

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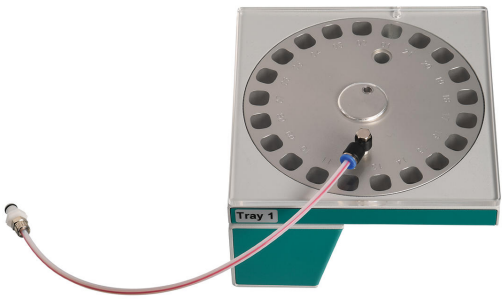

Solid Autosampler CIC (TEI)

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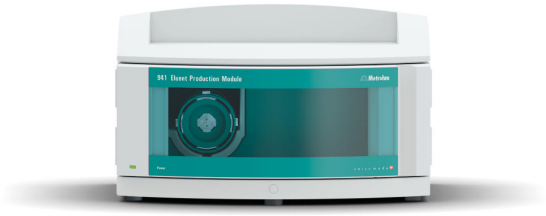

941 Eluent Production Module

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