Challenge
Determination of halides and sulfur, especially fluoride in solid samples from the environment requires combustion at high temperatures under pyrohydrolytic conditions and thus a special digestion system with water dosing unit

Solution
The ICprep pyrohydrolytic digestion system can be used to ensure a complete conversion of all halogen and sulfur compounds contained in solid samples

Intended audience
Environmental laboratories and regulatory authorities, contract laboratories for environmental analysis

Sample Digestion for the Determination of Fluorine, Chlorine, Bromine and Sulfur in Environmental Solids According to DIN EN 17813

Introduction

DIN EN 17813 describes a method that is suitable for the determination of the halogens fluorine, chlorine, bromine, and sulfur in environmental solids. These solids include plastic waste, secondary fuels, wood waste, other types of waste, soils, and much more. Why is the determination of halogens and sulfur in such solids relevant? Many residual materials are now fed into targeted recycling processes or energy recovery. For this purpose, these materials are processed in plants that need to be protected from corrosion by aggressive gases (such as HF, HCl, SO_2 etc.). Halogenated pollutants are also monitored during the landfilling of non-recyclable waste. The determination of the individual halogen species as total fluorine, total chlorine etc. facilitates the evaluation and classification of such waste.
DIN EN 17813 provides a conventional method describing the direct determination of the F, Cl, Br, and S content by oxidative pyrohydrolytic combustion at 1,050 °C ± 50 °C followed by ion chromatography (IC) although other detection methods are possible. Controlled dosing of water is crucial for the complete conversion of all compounds during combustion and for the loss-free transfer into the absorption solution. The water is added to the carrier gas oxygen in a constant quantity. The addition of water during combustion is not necessary for the determination of the elements chlorine, bromine, and sulfur, but does not interfere with the process. During sample combustion, gaseous products are formed which are collected in an aqueous absorption solution. For the determination of the elements bromine and sulfur, an oxidizing or reducing agent must be added to the absorption solution. Hydrogen peroxide is often used for this purpose. Finally, the absorption solution enriched with the analytes is made up to a defined volume and an aliquot of this solution is injected onto the separation column of the IC or fed to an alternative detection method. Digestion (pyrohydrolytic combustion) and detection (IC or an alternative detection method) of the analytes can take

place separately, in two independent systems. According to DIN EN 17813, furnaces or digestion systems operating between 1,000 °C and 1,100 °C are suitable for halogen and sulfur determination. These systems must allow controlled water dosing during combustion and enable the absorption of sample gases in an aqueous solution. For example, elemental analyzers specially upgraded for pyrohydrolysis or the ICprep system described in this paper. The separation of digestion and detection increases the application flexibility and utilization of any existing systems. The measurements presented below were carried out with ICprep automatic and an independently operated IC to demonstrate the standard compliant suitability of the digestion system for the determination of halogen species and sulfur in various solid samples.

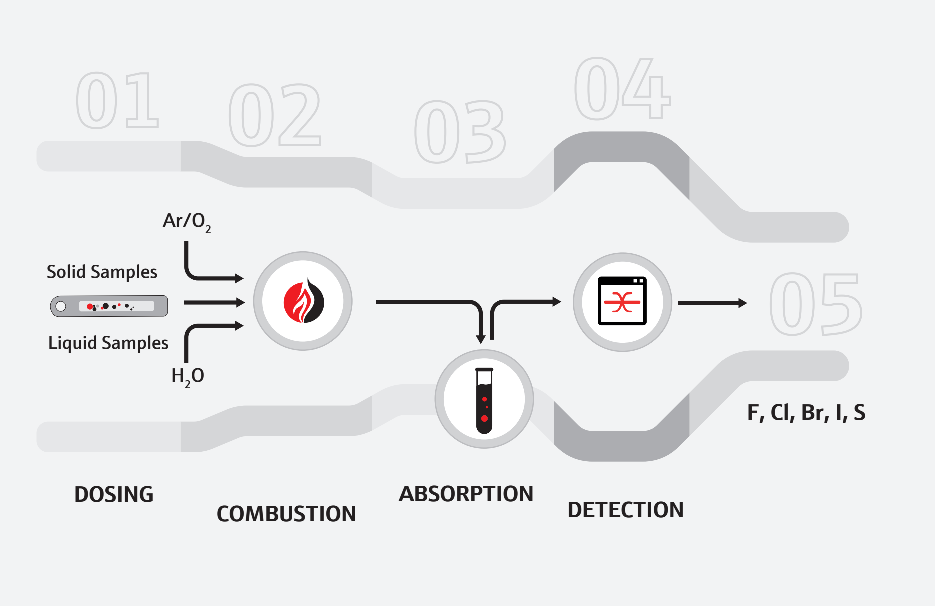

Figure 1: Schematic diagram of the procedure for halide and S determination in solid samples (ICprep is used for the step of sample digestion according to pyrohydrolysis)

Materials and Methods

Two systems were used to determine the halogen and sulfur content of several solid samples:

1. ICprep automatic, a high-temperature digestion system – for the combustion of samples under pyrohydrolytic conditions and for the absorption of the measured gases in the integrated fraction collector
2. Ion chromatograph (IC) with anion separation column and conductivity detector – for the detection of halide and sulfate ions.

Thanks to the separation of combustion (ICprep) and detection (IC), the respective determination steps could be carried out flexibly in terms of time without waiting or downtimes.

Samples and reagents

- Two Certified reference materials: ERM - EC680m (LDPE pellets for [Cl], Br, S) and BCR 038 (fly ash for F, Cl)
- Three solid samples: plastic waste, solid recovered fuel (SRF), wood waste

Sample preparation

All samples were dried in a drying oven at 105 °C ± 3 °C for approx. four hours and then stored in a desiccator. The dried samples were weighed into quartz glass boats (m: 10–30 mg) and placed on the tray of the ICprep's MMS autosampler.

Instrument and method settings

A boat drive (ABD) automatically fed the samples into the furnace. The combustion process took place in two phases, whereby in the first phase the volatile sample components were vaporized in an argon flow, followed by combustion of the gaseous products formed in an oxygen-rich atmosphere. In the second process phase, all remaining sample components were oxidized in a pure oxygen atmoshere. Here, the integrated flame sensor ensured safe and complete combustion by adapting the feed rate of the samples to their combustion behavior. The creation of matrix-dependent sample feed parameters and the associated time-consuming method development is not necessary thanks to the flame sensor control. A high-resolution syringe pump ensured controlled and constant water dosing during the entire combustion process. The gaseous analytes formed were absorbed in an aqueous solution with the addition of hydrogen peroxide (approx. 100 mg/L). Before the start of the measurement, the absorption solution was fed automatically into the collection vessels (15 mL centrifuge tubes) of the integrated fraction collector using a syringe pump. Integrated rinsing processes ensured complete transfer of the analytes and carry-over-free work.

Table 1: Settings on ICprep automatic

Parameter	Setting
Furnace temperature	1,050 °C
O_2 main flow	300 mL/min
Ar flow (1st phase)	150 mL/min
O_2 flow (2nd combustion)	150 mL/min
Second combustion	300 s
Water dosage	0.2 mL/min
Absorber supply	2 mL
Post-purge volume	1 mL

Results and Discussion

The use of a certified reference material is recommended to check the performance of the overall process. For the initial test of the suitability of the system, at least three blank value measurements are carried out using empty sample carriers (quartz or ceramic boats). If additives or accelerators are subsequently used in the analysis of samples, these should also be used in advance for the blank value determination. Furthermore, if possible, solid control standards with certified contents of F, Cl, Br, and S should be analyzed, too, at least three repeat measurements per solid standard are required. The system is suitable for use in accordance with DIN EN 17813 if the measured values obtained fall within a recovery interval of 90–110% compared to the certified values. Two CRMs were used for this purpose: spiked LDPE pellets (ERM - EC680m) with certified bromine and sulfur contents and an indicative (non-certified) chlorine content (target values are documented in Table 2). In order to provide proof of performance for fluorine and chlorine as well, another solid reference material was used: fly ash from pulverized coal (certified values also in Table 2).

The analysis results of all samples tested are summarized in Table 2 and represent mean values from three to four individual combustions.

Table 2: Results of the halogen and sulfur determination

Sample ID	Fluorine ± SD [mg/kg]	Chlorine ± SD [mg/kg]	Bromine ± SD [mg/kg]	Sulfur ± SD [mg/kg]
Blank (empty sample boat)	< LOD	< LOD	< LOD	< LOD
EC680m LDPE-Pellets	-	NV: 84 ± 11 (not cert.) MV: 75.3 ± 0.3 WFR: 90%	NV: 181 ± 9 MV: 173 ± 5 **Rec.: 96%**	NV: 86 ± 9 MV: 88.7 ± 5.1 **Rec.: 103%**
BCR 038 Fly ash	NV: 538 ± 13 MV: 531 ± 2.5 **Rec.: 99%**	NV: 323 ± 22 MV: 320 ± 6.7 **Rec.: 99%**	-	-
Plastic waste	2.6 ± 1.1	360 ± 73	3.9 ± 0.8	74 ± 21
Solid recovered fuel	130 ± 28	2110 ± 450	15 ± 3.6	2000 ± 390
Wood waste	12 ± 3.1	750 ± 150	4.5 ± 1.1	1100 ± 100

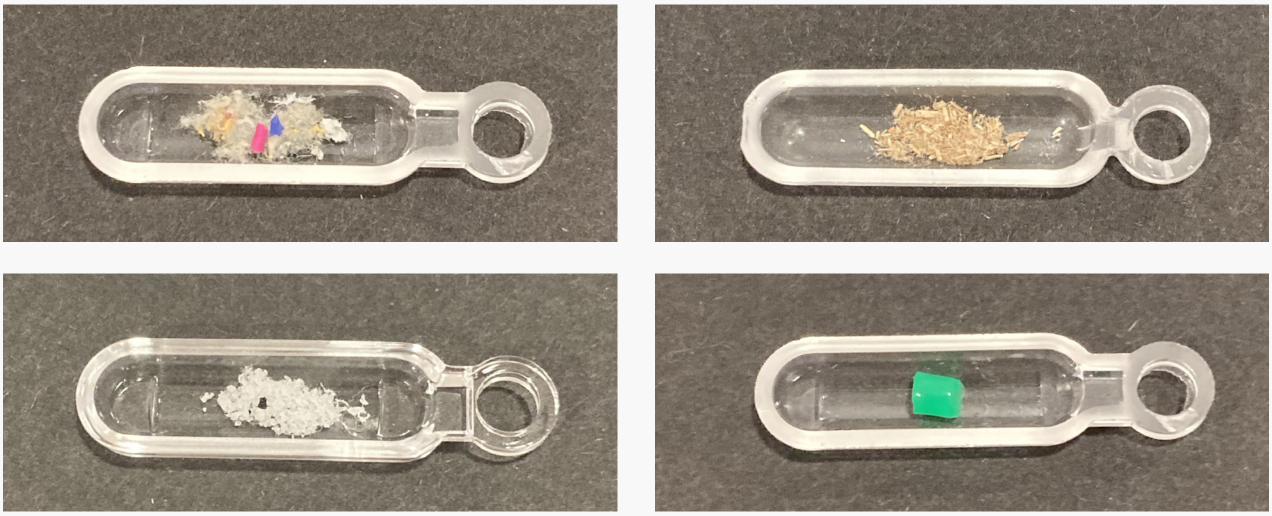

Figure 2: Pictures of the samples in quartz boats

Both the blank value determinations and the very good recovery rates for all certified element contents in the range of 96% to 103% confirm that the ICprep can be used to completely digest and absorb solid samples in accordance with DIN EN 17813. This pyrohydrolytic digestion system thus lays the foundation for accurate and reproducible results.
The measured values of the samples show above all that homogeneity of the individual types of waste was not guaranteed. At this point, the standard procedure recommends a grain size reduction to < 125 µm, especially for sample quantities of < 50 mg, a better milling and homogenization of the starting material can help to improve the repeatability.

Summary

With the help of ICprep, digestion for halogen and sulfur determination in accordance with DIN EN 17813 can be carried out easily, quickly, and reliably. A separate pyrohydrolytic digestion system can be advantageous, especially for smaller sample numbers that do not yet justify the purchase of a cost-intensive coupled CIC (combustion ion chromatography) system. An ion chromatograph already present in the laboratory can then be loaded with the digested samples (enriched absorption solutions) at any time and thus experience higher utilization.
In addition to ICprep, the described digestion can also be carried out with an AOX analyzer multi X 2500 or an elemental analyzer multi EA 5X00, if these are equipped with a corresponding kit for pyrohydrolysis and absorption. In this way, these analyzers can also be used for fluorine, chlorine, bromine, or sulfur determination, thereby increasing utilization.

Figure 3: ICprep automatic

ICprep can also be operated with a ceramic combustion tube, which can be particularly advantageous when analyzing samples rich in alkali and earth alkaline metal ions.

Recommended device configuration

Table 3.1: Overview of required devices, accessories and consumables – fully automated solution

Article	Article number	Description
ICprep automatic	450-300.102	Flexible system for sample digestion using pyrohydrolytic high-temperature combustion
Solid kit for MMS	450-300.034	MMS accessory for automated dosing of solids
Boat sensor	450-889.204	Sensor for additional safety when analyzing saline samples for MMS
multiWin software	450-011.803	Control software

Table 3.2: Overview of required devices, accessories and consumables – extension of a present analysis system

Article	Article number	Description
Extension kit ICprep basic	450-300.110 or	Kit for expanding a multi X 2500 or multi EA 5X00 for sample preparation for solid, liquid, EOF and AOF samples after pyrohydrolytic high-temperature combustion, absorption and collection of the reaction gases formed for further analysis steps
Extension kit ICprep automatic	450-300.111	Inclusive automatic collection of absorption solutions by fraction collector

References

[1] DIN EN 17813 “Environmental solid matrices - Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography“

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 · Author: BW
en · 06/2025
Picture p. 1: iStock/Imagesines