



SLOVENSKI STANDARD
SIST EN 17813:2024

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Trdni matriksi v okolju - Določanje halogenov in žvepla z ionsko kromatografijo po oksidativnem pirohidrolitskem sežigu

Environmental solid matrices - Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography

Feststoffe in der Umwelt - Bestimmung von Halogenen und Schwefel durch oxidative pyrohydrolytische Verbrennung, gefolgt von Ionenchromatographie

Matrices environnementales solides - Méthode de dosage des halogènes et du soufre par combustion pyrohydrolytique oxydative suivie d'une analyse par chromatographie ionique

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European foreword

This document (EN 17813:2023) has been prepared by Technical Committee CEN/TC 444 “Environmental characterization of solid matrices”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2024, and conflicting national standards shall be withdrawn at the latest by April 2024.

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EN 17813:2023 (E)**1 Scope**

This document specifies an empirical method for the simultaneous direct determination of the fluorine, chlorine, bromine, and sulfur content in environmental solid matrices by oxidative pyrohydrolytic combustion at $(1\ 050 \pm 50)$ °C, followed by ion chromatography. The method is applicable for the determination of concentrations ≥ 10 mg/kg of each element based on dry matter. The upper limit and exact concentration range covered depends on the blank levels of the instrumentation and the capacity of the chromatographic separation column used for determination.

NOTE 1 Simultaneous determination of iodine content is possible but currently not validated.

NOTE 2 Other detection methods can be applied if validated.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

3.1 pyrohydrolysis

high temperature chemical reaction with water

3.2 test portion analytical portion

quantity of material, of proper size, for measurement of the concentration or other property of interest, removed from the test sample

Note to entry 1: The test portion can be taken from the primary sample or from the laboratory sample directly if no preparation of sample is required (e.g. with liquids), but it is usually taken from the prepared test sample.

Note to entry 2: A unit or increment of proper homogeneity, size, and fineness, needing to further preparation, can be a test portion.

[SOURCE: EN ISO 11074:2015, definition 4.3.15]

4 Principle

The homogenized sample is combusted under oxidative conditions. For the determination of fluorine, the combustion is performed under pyrohydrolytic conditions. The combustion gases are absorbed in an aqueous solution. For the determination of sulfur the absorption solution contains an oxidizing agent to ensure complete conversion to sulfate. Changes in the volume of the absorption solution are considered for concentration calculations.

The anions of interest (bromide, chloride, fluoride, and sulfate) are separated by ion chromatography, and detected with a conductivity detector. To reduce the total conductivity caused by the eluent a suppressor unit (cation exchange unit) is used [4].

NOTE A UV detector is not required to carry out this analysis, but can be used for the detection of bromide, if a higher detection selectivity is required or in case of a matrix interference observed in conductivity detection. Bromide can be detected directly at $\lambda = 205$ nm.

NOTE Additional information is available in [3].

5 Interferences

5.1 Interferences during combustion

Pyrohydrolytic conditions during fluorine determination are required to avoid a negative bias.

Sulfur present in inorganic compounds with melting points higher than 1 050 °C (e.g. earth alkali metal sulfates) can lead to a negative bias. In this case the determination of the sulfur content can be carried out by dry combustion in an oxygen stream at a temperature $\geq 1\ 250$ °C [7].

5.2 Interferences during absorption

For the determination of sulfur an oxidizing agent in the absorption solution is required to avoid a negative bias.

For the determination of bromine a reducing agent in the absorption solution is required, as elemental bromine can be formed during combustion, which may not be completely absorbed.

5.3 Interferences during ion chromatography

Any substance which generates a detector signal and from which the peak resolution R between the analyte ion and that substance is less than 1,3, can cause interference. A high concentration of ions can influence the peak resolution and the retention time of the analyte. A gradient elution can help to prevent these kind of interferences.

6 Reagents and gases

6.1 General

Use only reagents of recognized analytical grade. The purity of water, reagents and gases shall be confirmed. Unless otherwise specified, reagents shall be weighed to an accuracy of ± 1 % of nominal mass. Commercially available solutions may be used. If necessary, alternative volumes and concentrations may be prepared for the solutions described in this section.

Relevant reagents should be tested for their contribution to the blank value.

6.2 Reagents for ion chromatography

6.2.1 Eluents

Degas all water used for eluent preparation. During operation, the gas intake shall be purged, e.g. by applying an inert gas to the eluent bottles or use of an inline degasser.

Carbonate, hydrogen carbonate, or hydroxide salts can be used to prepare eluents. Eluents can be prepared manually, by mixing from stock solutions or electrochemically *in situ*. The choice of the eluent depends on the column chosen and the detector. Follow instructions of the column manufacturer. The selected combination of separation column and eluent shall fulfil the requirement for resolution according to 7.2.9. The eluents may be used as long as the requirements of 7.2.9 are met. An example of a suitable eluent is described in 6.2.3.2.

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6.2.2 Water, with a resistivity of $\geq 18 \text{ M}\Omega \text{ cm}$ (25 °C)

6.2.3 Sodium carbonate (anhydrous), Na_2CO_3

6.2.3.1 Sodium carbonate concentrate, $c(\text{Na}_2\text{CO}_3) = 0,09 \text{ mol/l}$

Dissolve 9,54 g anhydrous sodium carbonate (6.2.3) in water in a 1 000 ml volumetric flask and bring to volume with water.

The solution is stable for six months if stored at 2 °C to 8 °C.

6.2.3.2 Sodium carbonate eluent, $c(\text{Na}_2\text{CO}_3) = 0,009 \text{ mol/l}$

Pipette 100 ml of sodium carbonate concentrate (6.2.3.1) into a 1 000 ml volumetric flask and bring to volume with water.

Prepare the eluent freshly after 3 days.

6.2.4 Bromide, chloride, fluoride, and sulfate stock solutions, $c = 1\ 000 \text{ mg/l}$ of each anion

Single anion and mixed anion stock solutions are commercially available in sufficiently high quality. These solutions are considered stable for several months. Alternatively, stock solutions may be prepared manually according to Table 1.

Salts are dried appropriately and dissolved according to the weights stated in the table. For calibration, use mixed multi component standard solutions with at least five different concentrations.

Table 1 — Weight and salt pre-treatment for stock solutions

Anion	Salt	Weight (g)	Dry salt at (105 ± 5) °C for at least
Fluoride	NaF	2,210	1 h
Chloride	NaCl	1,648	2 h
Bromide	NaBr	1,288	6 h
Sulfate	Na_2SO_4	4,439	3 h

Other salts with corresponding weights and pre-treatment specifications may be used.

6.2.5 Bromide, chloride, fluoride, and sulfate standard solutions

6.2.5.1 General

Depending on the concentrations expected, prepare single or mixed calibration solutions with different bromide, chloride, fluoride, and sulfate concentrations from the stock standard solution (6.2.4). The example in 6.2.5.3 describes the preparation of mixed calibration solutions.

The standard solutions can be stored in e.g. polyethylene containers.

6.2.5.2 Example of a bromide, chloride, fluoride, and sulfate mixed standard solution, $c = 100 \text{ mg/l}$ of each anion

Pipette 10 ml of each stock solution (6.2.4) into a 100 ml volumetric flask and bring to volume with water.

The solution is stable for one week if stored at 2 °C to 8 °C.

6.2.5.3 Example of bromide, chloride, fluoride, and sulfate mixed calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (6.2.5.2) to prepare e.g. 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

For example, proceed as follows for the range 1 mg/l to 10 mg/l of each anion:

Into a series of 10 ml volumetric flasks, pipette the following volumes: 100 µl, 200 µl, 300 µl, 400 µl, 500 µl, 600 µl, 700 µl, 800 µl, 900 µl, and 1 000 µl of the standard solution (6.2.5.2). Bring to volume with water.

The concentrations of the anions in these calibration solutions are: 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, 6 mg/l, 7 mg/l, 8 mg/l, 9 mg/l, and 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

For the assessment of any chromatographic interference by co-eluting ions it is recommended to add further relevant anions, e.g. nitrite, nitrate or sulfite to the calibration solution.

6.3 Reagents and gases for combustion

6.3.1 Inert gas, for example argon, $\geq 99,9\%$ (v/v) purity

6.3.2 Oxygen, $\geq 99,9\%$ (v/v) purity

6.4 Control standard

6.4.1 General

Control standards are used to check the performance of the overall process. This section describes the preparation of liquid control standards. If a suitable solid control standard or Certified Reference Material (CRM) is available, this may be used. Standard substances, solvents and concentrations stated in this section are suitable examples. Other substances containing the desired element and other solvents may be used. Commercially available solutions may be used. When preparing mixed standard solutions, standard substances of elements that are not of interest may be omitted. Mixtures may be prepared from single element stock solutions by dilution into a common flask.

6.4.2 4-Bromobenzoic acid, $C_7H_5BrO_2$, $\geq 99\%$ (m/m) purity, CAS no. 586-76-5

6.4.3 4-Chlorobenzoic acid, $C_7H_5ClO_2$, $\geq 99\%$ (m/m) purity, CAS no. 74-11-3

6.4.4 Dibenzothiophene, $C_{12}H_8S$, $\geq 99\%$ (m/m) purity, CAS no. 132-65-0

6.4.5 4-Fluorobenzoic acid, $C_7H_5FO_2$, $\geq 99\%$ (m/m) purity, CAS no. 456-22-4

6.4.6 Xylene, C_8H_{10} , analytical grade, CAS no. 1330-20-7

6.4.7 Example of a bromine, chlorine, fluorine, and sulfur control standard solution, $c = 1\ 000\ mg/l$ of each element

Weigh 251,6 mg 4-bromobenzoic acid (6.4.2), 441,0 mg 4-chlorobenzoic acid (6.4.3), 574,5 mg dibenzothiophene (6.4.4), and 737,5 mg 4-fluorobenzoic acid (6.4.5) into a 100 ml volumetric flask. Add xylene (6.4.6) to dissolve and bring to volume with xylene. The solution contains 1 000 mg/l of fluorine, chlorine, bromine, and sulfur respectively.

6.4.8 Example of a bromine, chlorine, fluorine, and sulfur control standard solution, $c = 10\ mg/l$ and $100\ mg/l$ of each element

Pipette 1 ml and 10 ml respectively of the control standard solution (6.4.7) into separate 100 ml volumetric flasks and fill up to mark with xylene.

EN 17813:2023 (E)**6.5 Reagents for absorption****6.5.1 General**

Ultrapure water is suitable as an absorption solution and recommended for the determination of fluoride. A composition similar to that of the eluent can reduce interferences at the beginning of the chromatogram. Hydrogen peroxide as additive acts as an oxidizing agent to convert dissolved combustion gases to a uniform ionic species, e.g. sulfur dioxide to sulfate or elemental bromine to bromide. Sodium methane sulfonate may be used as internal standard for determination of the final absorption solution volume. Reagents stated here are suitable examples and may be combined, replaced by other substances or used at different concentrations.

6.5.2 Hydrogen peroxide solution, H₂O₂, approx. 30 % (m/m), electronic grade**6.5.2.1 Absorption solution containing hydrogen peroxide, $c(\text{H}_2\text{O}_2) \approx 330 \text{ mg/l}$**

Pipette 1 ml of hydrogen peroxide solution (6.5.2) into a 1 000 ml volumetric flask and bring to volume with water.

Hydrogen peroxide concentration in the absorption solution should be less than 1 %, as higher concentrations potentially damage the analytical column of the ion chromatography when the solution is injected. Matrix elimination before injection into the ion chromatography can help to prevent this effect.

6.5.3 Sodium methane sulfonate, CH₃SO₃Na**6.5.3.1 Sodium methane sulfonate solution, $c(\text{CH}_3\text{SO}_3\text{Na}) = 500 \text{ mg/l}$**

Weight 500 mg of sodium methane sulfonate (6.5.3) into a 1 000 ml volumetric flask and bring to volume with absorption solution.

6.5.3.2 Absorption solution containing sodium methane sulfonate, $c(\text{CH}_3\text{SO}_3\text{Na}) = 1 \text{ mg/l}$

Pipette 2 ml of sodium methane sulfonate solution (6.5.3.1) into a 1 000 ml volumetric flask and bring to volume with absorption solution.

7 Apparatus

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7.1 Combustion apparatus**7.1.1 Combustion furnace**

A device consisting of a furnace, capable of heating to at least 1 050 °C, and equipped with a combustion tube made of quartz glass. Ceramic inserts to the combustion tube can be used. Both vertically and horizontally arranged combustion tubes are suitable. For the determination of fluorine the apparatus needs to be equipped with a device suitable for pyrohydrolysis. Combustion gases are to be delivered at a controlled rate.

NOTE Flow rates of combustion gases are typically between 50 ml/min and 1 000 ml/min.

EXAMPLE See Figure 1.