



SLOVENSKI STANDARD
oSIST prEN 17813:2022
01-januar-2022

Matriksi z vidika okolja - Določevanje halogenov in žvepla z ionsko kromatografijo ali komplementarnimi/dopolnilnimi metodami po pirohidrolitskem sežigu

Environmental matrices - Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection and complementary determination methods

Umweltbezogene Charakterisierung fester Matrices - Halogene und Schwefel durch oxidative pyrohydrolytische Verbrennung, gefolgt von ionenchromatographischer Detektion und komplementären Bestimmungsmethoden

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Environmental matrices - Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection and complementary determination methods

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 444.

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COMITÉ EUROPÉEN DE NORMALISATION
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prEN 17813:2022 (E)

European foreword

This document (prEN 17813:2022) has been prepared by Technical Committee CEN/TC 444 “Environmental characterization of solid matrices”, the secretariat of which is held by NEN.

This document is currently submitted to the CEN Enquiry.

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1 Scope

This document specifies a method for the simultaneous direct determination of the total fluorine, chlorine, bromine and sulfur content in environmental solid matrices. 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 depend on system blank levels of instrumentation and capacity of the chromatographic separation column used for determination.

NOTE Simultaneous determination of total iodine content is possible but currently not 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

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4 Principle

The homogenized sample is combusted under oxidative conditions. For the determination of total fluorine the combustion is performed under pyrohydrolytic conditions. The combustion gases are absorbed in an aqueous solution. For the determination of total sulfur the absorption solution contains an additive 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, sulfate) are separated by liquid chromatography, applying an anion exchange resin as stationary phase, and aqueous solutions of salts of weak mono- and dibasic acids as eluents for isocratic or gradient elution. Detection is carried out using a conductivity detector (CD). When using a CD the eluents shall show a sufficiently low conductivity. For this reason, a CD is usually combined with a suppressor device (cation exchanger), which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

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.

5 Interferences

5.1 Interferences during combustion

Missing or too low water supply to establish pyrohydrolytic conditions during total fluorine determination can lead to negative bias. Sulfur present as inorganic compounds with high melting points (e.g. earth alkali metal sulfates) can lead to negative bias if combustion temperatures are too low.

5.2 Interferences during absorption

Missing or too low amount of oxidizing agent in the absorption solution can lead to negative bias on the determination of total sulfur. Missing or too low amount of reducing agent in the absorption solution can lead to an underestimation of total bromine, as elemental bromine can be formed during combustion.

5.3 Interferences during ion chromatography

Any substance that has a retention time similar to that of the analyte ion and generates a detector signal can cause interference. A high concentration of ions can influence peak resolution and retention time of the analyte. A gradient elution can help to prevent many such 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 $\pm 1\%$ 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, gas intake shall be prevented, e.g. by applying inert gas to the eluent bottles or use of an inline degasser.

Carbonate, hydrogen carbonate, or hydroxide salts may be used to prepare eluents. Eluents can be prepared manually, by low pressure mixing from stock solutions or electrochemically *in situ*. The choice of 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 7.2.8. The eluents may be used as long as the requirements of 7.2.8 are met. An example of a suitable eluent is described in 6.2.3.2.

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.

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

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 — Weighing and salt pretreatment for stock solutions

Anion	Salt	Weighing (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 ₂ SO ₄	4,439	3 h

Other salts with corresponding weights and pretreatment 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 preparation of mixed calibration solutions.

The standard solutions are typically stored in polyethylene containers.

6.2.5.2 Example of a bromide, chloride, fluoride and sulfate mixed standard solution, c = 100 mg/l of each element

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 element:

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, 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, ≥ 99,9 % purity

6.3.2 Oxygen, ≥ 99,9 % purity

prEN 17813:2022 (E)**6.3.3 Control standard****6.3.3.1 General**

Control standards are used to check the performance of the overall process. This section describes 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.

6.3.3.2 Bromobenzoic acid, ≥ 99 % purity

6.3.3.3 Chlorobenzoic acid, ≥ 99 % purity

6.3.3.4 Dibenzothiophene, ≥ 99 % purity

6.3.3.5 Fluorobenzoic acid, ≥ 99 % purity

6.3.3.6 Xylene, analytical grade

6.3.3.7 Example of a total bromine, chlorine, fluorine and sulfur control standard solution, $c = 1000$ mg/l of each element

Weigh 251,6 mg bromobenzoic acid (6.3.3.2), 441,0 mg chlorobenzoic acid (6.3.3.3), 574,5 mg dibenzothiophene (6.3.3.4) and 737,5 mg fluorobenzoic acid (6.3.3.5) into a 100 ml volumetric flask. Add xylene (6.3.3.6) to dissolve and bring to volume with xylene. The solution contains 1000 mg/l of total fluorine, chlorine, bromine and sulfur respectively.

6.3.3.8 Example of a total 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 (6.3.3.7) into separate 100 ml volumetric flasks and fill up to mark with xylene.

6.4 Reagents for absorption**6.4.1 General**

It is recommended to use an absorption solution that has a similar composition as the eluent of the ion chromatography. For the determination of fluoride, pure water as the absorption solution is recommended to reduce possible interferences. 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.

6.4.2 Hydrogen peroxide solution, H_2O_2 , approx. 30 %, electronic grade

6.4.2.1 Absorption solution containing hydrogen peroxide, $c(H_2O_2) \approx 330$ mg/l

Pipette 1 ml of hydrogen peroxide solution (6.4.2) into a 1000 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 IC can help prevent this effect.