



BSI Standards Publication

## **Environmental solid matrices — Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography**

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# National foreword

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The UK participation in its preparation was entrusted to Technical Committee EH/4, Soil quality.

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Published by BSI Standards Limited 2023

ISBN 978 0 539 19546 0

ICS 71.040.40; 71.040.50

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 October 2023.

## Amendments/corrigenda issued since publication

| Date  | Text affected |
|-------|---------------|
| <hr/> |               |

English Version

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

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

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

This European Standard was approved by CEN on 23 July 2023.

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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of an identical text or by endorsement, at the latest by April 2024, and conflicting national standards shall be withdrawn at the latest by April 2024.

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## 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  $\geq 10$  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  $\lambda = 205 \text{ nm}$ .

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  $1\,050\text{ }^{\circ}\text{C}$  (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  $\geq 1\,250\text{ }^{\circ}\text{C}$  [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  $\pm 1\%$  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, 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.

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

**6.2.3 Sodium carbonate (anhydrous)**,  $\text{Na}_2\text{CO}_3$

**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<br>(105 ± 5) °C for at<br>least |
|----------|--------------------------|------------|---------------------------------------------|
| Fluoride | NaF                      | 2,210      | 1 h                                         |
| Chloride | NaCl                     | 1,648      | 2 h                                         |
| Bromide  | NaBr                     | 1,288      | 6 h                                         |
| Sulfate  | $\text{Na}_2\text{SO}_4$ | 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.