



# SLOVENSKI STANDARD

## SIST EN 14582:2017

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Nadomešča:  
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### Karakterizacija odpadkov - Vsebnost halogena in žvepla - Sežig s kisikom v zaprtem sistemu in metode za določevanje

Characterization of waste - Halogen and sulfur content - Oxygen combustion in closed systems and determination methods

Charakterisierung von Abfällen - Halogen- und Schwefelgehalt - Sauerstoffverbrennung in geschlossenen Systemen und Bestimmungsmethoden

Caractérisation des déchets - Teneur en halogènes et en soufre - Combustion sous oxygène en systèmes fermés et méthodes de dosage

Ta slovenski standard je istoveten z: **EN 14582:2016**

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#### **ICS:**

13.030.40	Naprave in oprema za odstranjevanje in obdelavo odpadkov	Installations and equipment for waste disposal and treatment
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EUROPEAN STANDARD

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## Characterization of waste - Halogen and sulfur content - Oxygen combustion in closed systems and determination methods

Caractérisation des déchets - Teneur en halogènes et  
en soufre - Combustion sous oxygène en systèmes  
fermés et méthodes de dosage

Charakterisierung von Abfällen - Halogen- und  
Schwefelgehalt - Sauerstoffverbrennung in  
geschlossenen Systemen und Bestimmungsmethoden

This European Standard was approved by CEN on 17 June 2016.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

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EN 14582:2016 (E)

## European foreword

This document (EN 14582:2016) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, 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of an identical text or by endorsement, at the latest by February 2017, and conflicting national standards shall be withdrawn at the latest by February 2017.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 14582:2007.

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## Introduction

Sulfur and halogens (fluorine, chlorine, bromine and iodine) may be found in materials in various forms. During the combustion of these materials, corrosive and harmful compounds may be released. The determination of sulfur and halogens by oxygen combustion may be used to assess the suitability of waste for incineration.

The determination of the resultant halides and sulphate can be achieved by many different techniques, e.g. using atomic emission spectrometry, titrimetry or ion chromatography.

Validation data of these different techniques are given in Annex A (informative).

Another method, oxygen flask combustion by Schoeniger, did not pass the method validation due to lack of participants. This method is described in Annex B (informative).

Anyone dealing with waste and sludge analysis should be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous (e.g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction. Consequently these samples should be handled with special care. Gases which may be produced by microbiological or chemical activity are potentially flammable and will pressurize sealed containers. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

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**EN 14582:2016 (E)****1 Scope**

This standard specifies a combustion method for the determination of halogen and sulfur contents in materials by combustion in a closed system containing oxygen (calorimetric bomb), and the subsequent analysis of the combustion product using different analytical techniques.

This method is applicable to solid, pasty and liquid samples containing more than 0,025 g/kg of halogen and/or 0,025 g/kg of sulfur content. The limit of detection depends on the element, the matrix and the determination technique used.

Insoluble halides and sulphate present in the sample or produced during the combustion step are not completely determined by these methods.

**2 Normative references**

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 14346, *Characterization of waste - Calculation of dry matter by determination of dry residue or water content*

EN 15002, *Characterization of waste - Preparation of test portions from the laboratory sample*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

**3 Terms and definitions**

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

NOTE Be aware that the above definitions are valid for this empirical EN only and do not comply with scientific definitions of sulfur and halogen content.

**3.1 sulfur content**  
sum of sulfur contained as organic and inorganic compounds that can be converted to sulphate by combustion and then absorbed or dissolved in an aqueous solution

**3.2 halogen content**  
sum of halogens contained as organic and inorganic compounds that can be converted to halides (fluoride, chloride, bromide, iodide) by combustion and then absorbed or dissolved in an aqueous solution

**4 Principle**

The sample is oxidized by combustion in a closed system (a bomb containing oxygen under pressure). Halogenated and sulfur containing compounds are converted to fluoride, chloride, bromide, iodide and sulphate, which are absorbed and/or dissolved in an absorption solution.

Several methods may be used for the determination of halides and sulphate concentrations in the absorption solution.

The method may be used for samples that burn with difficulty, which involves the use of a combustion enhancer.



## 5 Interferences

There are no interferences in the combustion step described in this standard but interferences may occur during the subsequent determination of sulphate and halides (see corresponding standards).

Insoluble halides and sulphate present in the sample or produced during the combustion step are not completely determined by these methods.

The choice of absorption solutions may introduce interferences depending on the analytical technique used.

## 6 Hazards

Hydrogen peroxide is very caustic; potassium and sodium hydroxide are corrosive and hydrazine hydrate is harmful, toxic and carcinogenic. Thus the operator shall wear goggles and gloves and shall work under a fume hood when handling this reagent. As this method uses a gas (oxygen) at a high temperature and a high pressure, precautions shall be taken by the operator.

## 7 Reagents and control mixtures

### 7.1 Reagents

#### 7.1.1 General

All reagents shall be at least of analytical grade and suitable for their specific purposes. Particularly, they shall be free of sulfur and halogens.

The reagents correspond to the chemical compounds used for the preparation of the absorption solutions; they are not all necessary depending on the choice of the solutions made by the laboratory for the determination of halides and sulfur (see Annex C).

**7.1.2 Water of grade 1** as specified in EN ISO 3696.

**7.1.3 Sodium hydroxide (NaOH) or potassium hydroxide (KOH) pellets.**

**7.1.4 Sodium bicarbonate  $\text{NaHCO}_3$  and sodium carbonate  $\text{Na}_2\text{CO}_3$ .**

**7.1.5 Hydrogen peroxide** (about 30 %) ( $\text{H}_2\text{O}_2$ ).

**7.1.6 Hydrazine hydrate ( $\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$ )**, reagent grade about 50 % – 60 %.

**7.1.7 Ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ).**

**7.1.8 Oxygen, free of combustible material**, available at a pressure of 3 MPa to 4 MPa (30 atm to 40 atm) (e.g. medical grade).

**7.1.9 Combustion enhancer** (e.g. paraffin).

**7.1.10 Aluminium oxide**,  $\text{Al}_2\text{O}_3$ , neutral, particle size < 200  $\mu\text{m}$ , pre-heated to 600 °C.

**7.1.11 Gelatine or aceto-butyrate capsules.**

### 7.2 Control mixtures

Select a certified reference material (CRM) or create an appropriate control mixture by choosing the control substances in combination so all elements that shall be determined in the samples are

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represented. The amount of halogen and sulfur contents shall be in the same range of the element contents of the samples and approximately in the middle of the working range of the determination techniques. If necessary, dilute with cellulose or aluminium oxide to get a suitable element content. The mixture of the control substances and the cellulose or aluminium oxide needs to be homogenized, e.g. using a pestle with mortar or ball mill.

Table D.1 lists examples of control substances that give complete (90 % to 110 %) recoveries of halogen and sulfur.

NOTE Combined combustion of iodine and sulfur may interact to improve the reduction of iodine to iodide and the oxidation of sulfur to sulphate. If the actual samples only contain one of the elements, a combined control mixture may give false assurance of the method capacity.

Examples of composition for a control mixture to determine fluorine, chlorine and sulfur (control mixture 1) and another control mixture for bromine and iodine (control mixture 2) are detailed in Table 1.

**Table 1 — Examples of control mixture to test the recoveries of halogens and sulfur with a defined analytical method**

	Control mixture 1	Control mixture 2
Amount of control substances	0,50 g of 4-fluoro-benzoic acid 2,0 g of 4-chloro-benzoic acid 2,0 g sulfanilic acid 55,0 g cellulose	0,25 g 4-bromo-benzoic acid 0,25 g 4-iodo-benzoic acid 59,5 g cellulose
Content of halogens and sulfur	1,130 g/kg fluorine 7,547 g/kg chlorine 6,170 g/kg sulfur	1,656 g/kg bromine 2,132 g/kg iodine

## 8 Sample conservation and pretreatment of test portion

Biological active laboratory samples should be stored at 4 °C and the analyses of halogen and sulfur should be carried out within seven days after sampling. If this is not possible, the samples should be further preserved by e.g. freezing, if possible, to minimize biodegradation and loss of volatile halogenated and sulfur compounds.

The test sample is prepared according to EN 15002. For solid materials, the particle size should be less than 200 µm.

During preparation of the test sample, the use of halogenated polymers, e.g. PVC gloves, should be avoided.

Drying the laboratory sample may be carried out for homogenization purposes if the sample, according to the accuracy of the method, contains only negligible amounts of halogen and sulfur compounds volatile at the temperature intended for the drying process.

Dry matter is determined according to EN 14346 on a separate sub sample (the result will be used for calculation).

Heterogeneous moist or paste like samples may be mixed with aluminium oxide (7.1.10) until granular material is obtained and then reduced to a granular powder, preferably with a particle size less than 200 µm. In this case, the ratio of aluminium oxide to sample should be incorporated into the calculation of the halogen and sulfur content and combustion enhancer should be added if necessary.

## 9 Equipment

### 9.1 Calorimetric bomb, with a capacity of not less than 200 ml and equipped with a purging system

This bomb shall not leak during testing and shall permit a quantitative recovery of the liquid. Its inner surface may be made of stainless steel or any other material that will not be affected by combustion gases.

Materials used for the bomb assembly, such as the head gasket and wire insulation, shall be heat and chemical action resistant and shall not undergo any reaction that will affect the results.

Bombs with pitted surfaces should never be used because of their tendency to retain halides and sulphate. After repeated use of the bomb, a film may build up on the inner surface. This dullness should be removed by periodically polishing the bomb according to the manufacturer's instructions.

The internal surface of some calorimetric bombs may have a ceramic coating or platinum buckets, which have better resistance to corrosion.

### 9.2 Sample cup, platinum or stainless steel or quartz.

### 9.3 Firing wire, platinum or stainless steel or nickel/chromium alloy or an equivalent.

### 9.4 Ignition circuit, capable of supplying a sufficient current to ignite the sample without melting the wire.

### 9.5 Absorption flask (e.g. a 200 ml test tube equipped with a glass frit dip-tube for bubbling the combustion gases).

### 9.6 Usual laboratory equipment, as homogenization devices (e.g. mixers, stirrers, grinders, mills), analytical balance (accurate at least to 0,1 mg), etc.

### 9.7 Safety precautions

The bomb shall not contain any organic residue (vapours of organic solvents, grease, etc.).

Respect shall be given to the manufacturer's instructions, especially to the oxygen pressure inside the bomb and the maximum allowable calorific value of the test portion.

NOTE Combustion of 1 g of hydrocarbons such as lubricating oil produces about 40 kJ (the calorific values of benzoic acid and isooctane are about 26 MJ/kg and 48 MJ/kg).

## 10 Procedure

### 10.1 General

Before each series of determinations, a blank and quality check shall be carried out on a control mixture (7.2), according to Clause 12.

Alternately running samples high and low in halogen or sulfur content should be avoided whenever possible as it is difficult to rinse the last traces of ions from the internal surfaces of the apparatus and a tendency for residual elements to carry over from sample to sample has been observed. When a sample high in halogen or sulfur content has preceded a sample low in concentration, the test on the second sample should be repeated and one or both of the low values thus obtained should be considered suspect if they do not fall within the limits of repeatability of this method. It is good practice to insert a blank between each sample, unless the series of samples being analysed has similar expected concentrations.

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When the composition or homogeneity of the sample is unknown, it is better to carry out the analysis in duplicate or triplicate and report the mean result from all determinations with the associated standard deviation.

In case of significant carry over it is recommended to collect the exhaustion gases of the sample and the following blank sample in one absorption liquid.

**10.2 Choice of the absorption solution**

The combustion gases can be collected inside and/or outside the bomb in an absorption solution. Water is generally used when low concentrations of halogens and sulfur are expected (usually, less than 10 g/kg). Alkaline solution should be used for high contents of halogens and sulfur, to ensure neutralization of the acid compounds produced.

The composition of absorption solutions depend on the determination technique and on the expected content of halogens and sulfur. Applicable examples are:

- Solution 1: Water (7.1.2);
- Solution 2: 0,3 mol/l potassium or sodium hydroxide solution: dissolve 16,8 g of KOH or 12,0 g of NaOH pellets (7.1.3) in water (7.1.2) and dilute to 1 l;
- Solution 3: Carbonate/bicarbonate solution: dissolve 2,52 g sodium bicarbonate  $\text{NaHCO}_3$  and 2,54 g sodium carbonate  $\text{Na}_2\text{CO}_3$  (7.1.4) in water (7.1.2) and dilute to 1 l;
- Solution 4: 0,25 mol/l sodium hydroxide solution (dissolve 10,0 g NaOH pellets (7.1.3) in water (7.1.2) and dilute to 1 l) + 50  $\mu\text{l}$  of hydrogen peroxide solution at 3 % (dilute 5 ml  $\text{H}_2\text{O}_2$  (7.1.5) into 50 ml);
- Solution 5: 0,25 mol/l sodium hydroxide solution (dissolve 10,0 g NaOH pellets (7.1.3) in water (7.1.2) and dilute to 1 l) + 0,5 ml of hydrazine hydrate (7.1.6);
- Solution 6: Ascorbic acid-solution at 1 % or at 5 % prepared with pure reagent (7.1.7) in water (7.1.2).

NOTE 1 More details regarding these solutions and there performances in terms of halogens and sulfur recovery are available in Annex C.

When ion chromatography is used for the determination of halides and sulphate, the absorption solution may have the composition of the mobile phase, e.g. carbonate/bicarbonate solution.

It is recommended to add 0,5 ml of hydrogen peroxide solution (7.1.5) to the absorption solution before combustion to improve the oxidation of sulfur. However, hydrogen peroxide may oxidize iodide leading to an underestimation. When sulfur and iodine are to be determined in the same sample, it is recommended to carry out two different combustion operations.

For iodine and bromine use 10 ml of 1 % ascorbic acid (solution 6) as an absorption solution to improve the reduction to iodide or bromide before opening of the bomb.

The most suitable combinations of absorption solutions with determination techniques for the expected halogens or sulfur are presented in Table 2.