SLOVENSKI STANDARD
SIST EN 14582:2007

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Karakterizacija odpadkov - Vsebnost halogena in ǵvepla - Seģig s kisikom v zaprtem sistemu in metode za doloļ evanje

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 halogenes et en soufre - Combustion sous oxygene en systemes fermés et méthodes de dosage

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

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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 système fermé et méthodes de dosage

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Foreword

This document (EN 14582:2006) 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of an identical text or by endorsement, at the latest by September 2007, and conflicting national standards shall be withdrawn at the latest by September 2007.

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 pressurise sealed bottles. 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.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

Sulphur 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 sulphur 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.

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

1 Scope

This standard specifies a combustion method for the determination of halogen and sulphur 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 sulphur content. The limit of detection depends on the element, the matrix and the determination technique used.

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

2 Normative references

The following referenced documents are indispensable for the application of this document. 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 3696:1987)*

3 Terms and definitions

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

3.1
sulphur content
sum of sulphur 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

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

4 Principle

The sample is oxidized by combustion in a closed system (a bomb containing oxygen under pressure). Halogenated and sulphur 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.

In general this method is applicable for concentrations over 0,025 g/kg depending on the element, matrix and the determination technique. It may be used for aqueous samples or 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 original sample or produced during the combustion step are not completely determined by these methods.

6 Hazards

Hydrogen peroxide is very caustic, 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 sulphur and halogens.

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

7.1.3 Hydrogen peroxide (about 30 %) (H_2O_2).

7.1.4 Absorption solution 1, for the determination of fluorine, chlorine, bromine and sulphur, the nature and concentration of which may depend on the end-determination technique and on the expected content of halogens and sulphur. For example:

- water (7.1.2.); or
- 0,3 mol/l potassium or sodium hydroxide solution: dissolve 16,8 g of KOH or 12,0 g of NaOH pellets in water (7.1.2.) and dilute to 1 l; or
- carbonate/bicarbonate solution: dissolve 2,52 g sodium bicarbonate $NaHCO_3$ and 2,54 g sodium carbonate Na_2CO_3 in water (7.1.2.) and dilute to 1 l.

7.1.5 Absorption solution 2 for the determination of iodine

Ascorbic acid-solution, ($C_6H_8O_3$), w = 1 %.

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

7.1.7 Combustion enhancer (e. g. paraffin).

7.1.8 Aluminium oxide, Al_2O_3, neutral, particle size < 200 µm, pre-heated to 600 °C.

7.1.9 Gelatine or aceto-butyrate capsules.

7.2 Control mixtures

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

To create an appropriate control mixture, choose the control substances in combination so all elements that shall be determined in the samples are represented. The amount of halogen and sulphur 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 pebble mill.

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

An example of a mixture of control substances for the determination of fluorine, chlorine, and sulphur is:

Mix 0,50 g 4-fluoro-benzoic acid; 2,0 g 4-chloro-benzoic acid; 2,0 g sulfanilic acid and 55,5 g cellulose.

An example of a mixture of control substances for the determination of bromine and iodine is:

Mix 0,25 g 4-bromo-benzoic acid; 0,25 g 4-iodo-benzoic acid and 59,5 g cellulose. Homogenize the mixtures, e. g. in a pebble mill.

This first mixture of fluorine, chlorine, and sulphur contains 1,130 g/kg fluorine; 7,547 g/kg chlorine and 6,170 g/kg sulphur. The second mixture of iodine and bromine contains 1,656 g/kg bromine and 2,132 g/kg iodine.

8 Sample conservation and pre-treatment of test portion

Biological active laboratory samples should be stored at 4 °C and the analyses of halogen and sulphur 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 sulphur 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 homogenisation purposes if the sample, according to the accuracy of the method, contains only negligible amounts of halogen and sulphur 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).

NOTE Heterogeneous moist or paste like samples may be mixed with aluminium oxide (7.1.8) 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 sulphur 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.

NOTE 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.

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 oxygen 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 powers 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 have to be carried out on a control mixture (7.2), according to clause 12.

Alternately running samples high and low in halogen or sulphur 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 sulphur 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.

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.

NOTE 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 sulphur are expected (usually, less than 10 g/kg). Alkaline solution should be used for high contents of halogens and sulphur, to ensure neutralisation of the acid compounds produced.

When ion chromatography is used for the determination of halides and sulphate, the absorption may be the mobile phase, e. g. the carbonate/bicarbonate solution described in 7.1.4.

It is recommended to add 0,5 ml of hydrogen peroxide solution (7.1.3) to the absorption solution before combustion to improve the oxidation of sulphur. However, hydrogen peroxide may oxidize iodide leading to an underestimation. When sulphur 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 (7.1.5) as an absorption solution to improve the reduction to iodide. It is recommended, if the absorption solution is inside the bomb during combustion, to ensure the reduction of iodine to iodide before opening of the bomb.

NOTE 1 The ascorbic acid and large amount of nitrate may interfere with early eluting halogens (fluoride, chloride and bromide) if detected by ion chromatography.

NOTE 2 It is important that iodine is in a defined oxidation step after combustion as ascorbic acid is used to reduce all iodine compounds to iodide.

10.3 Preparation of the bomb

The bomb is prepared according to the manufacturer's instructions and the free ends of the firing wire (9.3) attached to the electric terminals of the ignition circuit (9.4). If using an absorption solution inside the bomb, add 10 ml of this absorption solution (7.1.4 with or without 7.1.3 or 7.1.5), wetting the sides of the bomb (9.1).

NOTE The sample cup should not be in contact with the absorption solution. Depending on the bomb design, it may be necessary to add less than 10 ml of the absorption solution or trap the combustion gases in an external absorption flask (see 9.5.).

10.4 Combustion

0,05 g to 1 g of sample, depending on its calorific value, the amount of element present and on the end-determination method, is weighed (to the nearest 0,1 mg) into the sample cup (9.2). Samples that burn with difficulty (e. g. mineral samples or samples with high water content), may require the addition of a combustion enhancer (7.1.7). Liquid samples may be weighed in a capsule (7.1.9). To avoid swirling up of the sample when filling the bomb with oxygen, powdery samples may be covered with inert material (e. g. aluminium oxide (7.1.8)) or soaked with combustion enhancer (7.1.7), depending of their calorific value.

Depending on the type of the bomb, the total sample mass plus enhancer should not exceed 1 g to 1,5 g to avoid dangerous high pressure and possible rupturing the bomb.

NOTE 1 The combined energy from sample and enhancer is not important to recover halogens and sulphur from the sample compounds. Hence it may be necessary to optimize the enhancer/sample amount ratio.

Place the sample cup in position and arrange the firing wire (9.3) so that it will be just in contact with the sample but not touching the sample cup (9.2).

NOTE 2 Some operators use nylon thread or cotton wick and loop it around the wire so that its ends immerse directly in the liquid sample or are in contact with the solid sample.

Assemble the bomb and tighten the cover securely. Admit oxygen (7.1.6) carefully (to avoid blowing the sample from the cup) to a pressure below the safety pressure specified by the manufacturer.

In case nitrates produced during the oxidation of the nitrogen of the air contained in the bomb interfere during the analytical determination, this ambient air should be eliminated by vacuum depletion or by flushing the bomb with oxygen.

Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Let the bomb cool to ambient temperature, e. g. in a water bath.

10.5 Collection of the halides and sulphate

When relatively high levels of halogens and sulphur (e. g. over 20 g/kg) are expected, and/or when there is no absorption solution inside the bomb, connect the exit of the bomb to an absorption flask (9.5) filled with 20 ml of the same absorption solution (7.1.4 and/or 7.1.3 or 7.1.5) used in 10.3 and release the pressure at a slow, uniform rate so that only small bubbles are observed in the absorption tube.

NOTE 1 If high levels of halogen and sulphur are expected, it is highly recommended to measure a blank value between the samples.

NOTE 2 The volume of the absorption solution depends on the type and volume of the absorption flask.

In the other cases, this collection of combustion gases in the absorption flask is not necessary and it is possible to release the pressure quickly.

Open the bomb and examine the content:

— If traces of sooty deposits are found, discard the determination and repeat again with combustion enhancer and/or with a smaller test portion.

— If pink vapours are seen, discard the determination and repeat using precautions to trap all the iodine (e. g. smaller test portion, addition of ascorbic acid).

Rinse the interior of the bomb, terminals, inner surface of the bomb cover and the sample cup thoroughly with solution from the absorption flask or 20 ml of absorption solution (see 10.2).

NOTE 3 Some calorimetric bombs are connected to a demineralized water supply, which enables automatic rinsing of the bomb interior before opening. In this case the rinsing water is pushed by weak overpressure out of the bomb and combined with the absorption solution. Transfer the solution into a volumetric flask. Dilute to the mark with water (7.1.2) or absorption solution (7.1.5). The choice of the final volume depends on the concentration of the halides and sulphate, as well as on the final method used for analysis.

10.6 Cleaning procedure

If necessary, remove any residual fuse wire from the terminals and the cup.

Using hot water, rinse the interior of the bomb, sample cup, terminals, and the inner surface of the bomb cover. Thoroughly rinse the bomb, cover and cup with demineralized water (7.1.2).

11 Recommended methods of determination

ISO/CEN Standards for analysing water and waste water are applicable to analysing the absorption solutions obtained. Since the analysis of such absorption solutions is not in the scope of these standards, it is necessary to check their applicability.

The methods referenced in the Bibliography are international standards and can be used.

Other methods may be used (e. g. photometry, nephelometry or turbidimetry for sulphur and chlorine, atomic emission spectrometry for chlorine and iodine, capillary electrophoresis for all the elements) but shall be validated compared with the recommended standardised methods.