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

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National foreword

This British Standard is the UK implementation of EN 14582:2016. It supersedes BS EN 14582:2007 which is withdrawn.

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

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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of an identical text or by endorsement, at the latest by February 2017, and conflicting national standards shall be withdrawn at the latest by February 2017.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.

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

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.

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 $NaHCO_3$ and sodium carbonate Na_2CO_3.

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

7.1.6 Hydrazine hydrate ($H_2N\text{-}NH_2\cdot H_2O$), reagent grade about 50 % – 60 %.

7.1.7 Ascorbic acid ($C_6H_8O_6$).

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, Al_2O_3, neutral, particle size < 200 µm, 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

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 0,25g 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.

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 $NaHCO_3$ and 2,54 g sodium carbonate Na_2CO_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 µl of hydrogen peroxide solution at 3 % (dilute 5 ml H_2O_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.

Table 2 — Suitable combinations of absorption solution and determination technique for halogens and sulfur

Absorption solution	Analytical techniques for halogens and sulfur content determination									
	Fluorine		Chlorine		Bromine		Iodine		Sulfur	
	IC	Ion selective electrode	IC	Potentiometry	IC	Potentiometry	IC	Potentiometry	IC	Gravimetry
1	X	X	X	X	X	X			X	X
2	X	X	X	X	X	X			X	X
3	X	X	X	X	X				X	
4	X		X		X				X	
5	X	X	X		X		X	X	X	
6	X	X	X	X	X	X	X	X	X	

NOTE 2 The ascorbic acid and large amount of nitrate may interfere with early eluting halogens (fluoride, chloride and bromide) if detected by ion chromatography.

The determination of recoveries of halogen and sulfur from control mixtures mentioned in Table 1 is presented in Annex C, in order to show the possible use and combination between absorption solutions and different analytical methods.

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 the chosen absorption solution (see 10.2), wetting the sides of the bomb (9.1).

The sample cup should not be in contact with the absorption solution. Depending on the bomb design and/or the expected concentration range of the analytes of interest, it may be necessary to adapt the amount 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 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 (7.1.9). Liquid samples may be weighed in a capsule (7.1.11). 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 (7.1.10)) or soaked with combustion enhancer (7.1.9), depending of their calorific value. Powdery samples with low density and that burn very readily may be pressed into a pellet before combustion, to avoid material to be flung out of the crucible.

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 sulfur 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 (7.1.8) 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. After the combustion is complete, 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 sulfur (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 used in 10.3 and release the pressure at a slow, uniform rate so that only small bubbles are observed in the absorption tube.

When relatively low levels of halogens and sulfur are expected, less volume could be used inside the bomb and the combustion gas shall be also collected in an external absorption solution (the same as used in 10.3); less volume (e.g. 10 ml) could be used in the collection flask in order to limit the dilution effect on halides and sulphate.

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

NOTE 1 The volume of the absorption solution depends on the type and volume of the absorption flask.

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 the same absorption solution used for the preparation of the bomb in 10.3.

NOTE 2 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 with the same absorption solution used in 10.3). 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 or CEN standards for analysing water and waste water are applicable to analysing the absorption solutions obtained (see Table 3). 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 sulfur and chlorine, atomic emission spectrometry for chlorine and iodine, capillary electrophoresis for all the elements) but shall be validated compared with the recommended standardized methods.

Table 3 — Applicable methods (usually standardized at international levels) for analysing halogens and sulfur

	F	Cl	Br	I	S
Ion chromatography	X	X	X	X	X
ICP-OES				X	X
ICP-MS			X	X	X
Potentiometry (Ion selective electrode)	X				
Potentiometry ($AgNO_3$ titration)		X	X	X	
Gravimetry with $BaCl_2$					X

12 Control measurements

A blank test shall be carried out for each series of determinations under the same conditions as the samples: absorption solution, combustion enhancer, capsule, reactants, oxygen purges, etc.

If the value of this blank test is significant, discard the analytical batch and check each reagent.

To check the reliability of the whole procedure, a control test should be carried out for each series of determinations, using a control mixture (7.2). A triplicate analysis of one point in the middle of the working range is sufficient. For each element, the mean recovery has to be between 90 % and 110 % with a coefficient of variation less than 10 %.

If available, it is recommended to use certified reference materials. It is also recommended that quality control charts are used for control mixtures.

13 Evaluation

Calculate the halogen or sulfur content in g/kg of waste using Formula (1):

$$X_{\mathrm{i}} = (C_{\mathrm{i}} \times V) / 1\ 000\, m \qquad (1)$$

where

X_{i} is the element content (“i” = S, Cl, Br, I or F) in the test sample in grams per kilogram (g/kg);

C_{i} is the concentration expressed in milligram per litre (mg/l) of this element, “i” in the absorption solution;

V is the final volume of the absorption solution, expressed in millilitres (ml);

m is the mass of the test portion, expressed in grams (g).

If the sample contains inert materials e.g. aluminium oxide, which have been added during sample preparation the ratio of this addition should be incorporated into the calculation.

The element content resulting from Formula (1) is calculated on a dry matter basis according to Formula (2):

$$X_{\mathrm{id}} = X_{\mathrm{i}} \times 100 / w_{\mathrm{dm}} \qquad (2)$$

where

X_{id} is the element content ("i" = S, Cl, Br, I or F) calculated on dry matter in grams per kilogram (g/kg);

w_{dm} is the dry matter of the test sample, according to Clause 8, as mass fraction in percent (%).

These results may be also calculated and reported in milligram per kilogram (mg/kg) or in % (m/m).

Halogen and sulfur contents are usually determined on an undried sample but are always reported on dry matter.

14 Test report

The test report shall contain at least the following information:

a) reference to this European Standard;

b) reference to the analytical standard used for the determination for each element;

c) all necessary information on the full identification of the waste;

d) analytical results, referring to Clause 13;

e) details of all procedural steps which deviate from this standard together with all circumstances that may have influenced the result.

Annex A
(informative)

Performance characteristics

The method performance characteristics given in Table A.1, Table A.2, Table A.3, Table A.4 and Table A.5 have been established in a European inter-comparison study on six typical waste samples and a control mixture, carried out in 2005.

Table A.1 — Performance characteristics for the determination of fluorine

Sample	**O** **%**	**p**	**N**	**x** **% m/m**	**s_R**	**CV_R** **%**	**s_r**	**CV_r** **%**
Control mixture	0	21	63	0,381	0,082	21,43	0,046	11,95
Solid waste	4	24	70	0,597	0,236	39,48	0,081	13,51
Mixed liquid waste	0	24	71	1,230	0,244	19,85	0,100	8,13
Waste solvent	0	24	68	0,595	0,165	27,80	0,085	14,26

p Number of laboratories
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
s_r Estimate of the repeatability standard deviation
CV_R Estimate of the relative reproducibility standard deviation expressed in percent
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Table A.2 — Performance characteristics for the determination of chlorine

Sample	**O** **%**	**p**	**N**	**x** **% m/m**	**s_R**	**CV_R** **%**	**s_r**	**CV_r** **%**
Control mixture	4	27	79	0,589	0,133	22,63	0,040	6,81
Waste wood	0	28	81	1,656	0,217	13,10	0,088	5,34
Solid recovered fuel	0	28	83	2,128	0,280	13,14	0,145	6,83
Solid waste	4	28	83	0,984	0,225	22,92	0,095	9,68
Mixed liquid waste	0	28	83	1,002	0,306	30,55	0,123	12,30
Waste solvent	15	28	81	11,328	1,469	12,97	0,478	4,22
Liquid recovered fuel	0	28	83	0,799	0,140	17,54	0,077	9,68

p Number of laboratories
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
s_r Estimate of the repeatability standard deviation
CV_R Estimate of the relative reproducibility standard deviation expressed in percent
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Table A.3 — Performance characteristics for the determination of bromine

Sample	**O** **%**	***p***	***N***	***x*** **% *m/m***	**s_R**	**CV_R** **%**	**s_r**	**CV_r** **%**
Control mixture	14	22	64	0,499	0,108	21,61	0,036	7,28
Solid waste	4	23	71	0,601	0,146	24,31	0,041	6,88
Mixed liquid waste	8	23	71	0,664	0,165	24,81	0,053	8,01
Waste solvent	0	23	70	0,928	0,344	37,00	0,118	12,70

p Number of laboratories
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
s_r Estimate of the repeatability standard deviation
CV_R Estimate of the relative reproducibility standard deviation expressed in percent
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Table A.4 — Performance characteristics for the determination of iodine

Sample	**O %**	**p**	**N**	**x % m/m**	**s_R**	**CV_R %**	**s_r**	**CV_r %**
Control mixture	13	16	46	0,291	0,103	35,54	0,039	13,43
Solid waste	0	17	53	0,554	0,177	31,94	0,045	8,20
Mixed liquid waste	5	18	56	2,667	0,709	26,59	0,179	6,70
Waste solvent	0	16	52	0,574	0,172	29,94	0,059	10,32

p Number of laboratories
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
s_r Estimate of the repeatability standard deviation
CV_R Estimate of the relative reproducibility standard deviation expressed in percent
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Table A.5 — Performance characteristics for the determination of sulfur

Sample	**O %**	**p**	**N**	**x % m/m**	**s_R**	**CV_R %**	**s_r**	**CV_r %**
Control mixture	5	20	60	0,453	0,115	25,32	0,037	8,24
Waste wood	5	20	60	0,897	0,147	16,42	0,065	7,29
Solid recovered fuel	5	21	62	1,293	0,284	21,96	0,068	5,24
Solid waste	0	21	62	3,236	1,037	32,03	0,270	8,34
Mixed liquid waste	5	21	62	0,675	0,172	25,45	0,051	7,60
Waste solvent	5	21	60	0,797	0,214	26,87	0,093	11,71
Liquid recovered fuel	0	21	62	0,649	0,097	14,93	0,057	8,72

p Number of laboratories
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
s_r Estimate of the repeatability standard deviation
CV_R Estimate of the relative reproducibility standard deviation expressed in percent
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Annex B
(informative)

Oxygen flask combustion by Schoeniger

B.1 General

This informative Annex specifies a combustion method for the determination of halogen and sulfur contents in materials by combustion in a closed system containing oxygen [oxygen flask combustion (Schoeniger flask)], and the subsequent analysis of the combustion product using different analytical techniques.

The method is applicable to solid, pasty and liquid samples containing more than 0,25 g/kg of halogen and/or 0,25 g/kg of sulfur content. The limit of detection depends on the element, matrix and determination technique used.

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

B.2 Principle

The sample is oxidized by combustion in a closed system (heavy walled glass flask - Schoeniger apparatus - filled with oxygen). 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 the halides and sulphate concentrations in the absorption solution.

The method described in this Annex is faster and easier to perform as the standardized method. It uses a smaller amount of sample and therefore needs more attention on the homogenization. In general, it is applicable for concentrations over 0,25 g/kg, depending on the element, matrix and determination technique.

B.3 Interferences and hazards

For interferences and hazards see Clause 5 and Clause 6.

B.4 Reagents and control mixtures

B.4.1 Filter paper wrappers, e.g. 3 cm x 3 cm with a 3,5 cm x 1 cm extension (see Figure B.1).

B.4.2 All other reagents and control mixtures are mentioned in Clause 7.

B.5 Equipment

B.5.1 Combustion flask: chemically resistant heavy-walled, 500 ml to 1 000 ml Erlenmeyer flask equipped with a slightly enlarged well-neck, fitted with a standard-taper ground-glass stopper.

B.5.2 A platinum wire sample carrier of heavy-gauge platinum wire and welded platinum gauze sealed into another standard taper ground glass stopper (see Figure B.1).

B.5.3 Usual laboratory equipment: homogenization devices (e.g. mixers, stirrers, grinders, mills), analytical balance (accurate at least to 0,1 mg), etc.

B.6 Safety precautions

The flask shall not contain any residue or vapours of organic solvents used for rinsing and drying. If these materials are present, a violent explosion may take place when the burning filter paper is introduced.

After inserting the flaming paper into the flask, the stopper shall be held securely. A slight pressure inside the flask during the initial stage of burning normally happens, while a slight vacuum is formed after complete absorption of the combustion products.

Combustion shall be carried out under a fume hood and the operator shall wear safety goggles and gloves.

B.7 Procedure

B.7.1 General

Before each series of determinations, a blank and a 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 the 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 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 to report the mean result from all determinations.

B.7.2 Choice of the absorption solution

Water is generally used when low concentrations of halogen and sulfur are expected (usually less than 1 g/kg). Alkaline solution should be used for high contents of halogen and sulfur to ensure neutralization of any acidic compounds produced.

When ion chromatography is used for the determination of halides and sulphate, the absorption solution 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 (7.1.5) to the absorption solution before combustion to improve the oxidation of sulfur. However, hydrogen peroxide may oxidize iodine into iodate and lead to an underestimate of iodine content.

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 (7.1.7) as 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. For this reason, ascorbic acid is used to reduce all iodine compounds to iodide.

B.7.3 Sample preparation

B.7.3.1 General

Between 10 mg and 50 mg of homogeneous (or homogenized) sample are weighed to the nearest 0,1 mg. The weighed sample shall contain not more than 10 mg to 20 mg of halogen and sulfur each.

B.7.3.2 Solid and paste like samples

Fold the filter paper (B.4.1) used for wrapping the sample to form a boat as shown in Figure B.1. Wait several minutes before weighing to allow the filter paper to equilibrate to the conditions of humidity of the room and record the tare weight to 0,1 mg.

Using a small spatula, place the estimated amount of sample on the tarred paper and reweigh to 0,1 mg. Then, using the spatula, fold the filter paper as shown in Figure B.1. Squeeze the packed filter with clean tweezers. Place the sample in the platinum sample carrier (B.5.2).

B.7.3.3 Liquid samples

Placing small-size drops on the paper, introduce the estimated amount of sample into a tarred capsule (7.1.11) containing a small piece of folded filter paper. Immediately reweigh the capsule to 0,1 mg. Wrap the capsule in the filter paper (B.4.1) as in the case of solid samples and insert in the platinum sample carrier (B.5.2).

B.7.4 Combustion

Add 10 ml of absorption solution (7.1.4 and/or 7.1.3 or 7.1.5) into the combustion flask (B.5.1). Flush the flask with oxygen for 1 min, keeping the gas delivery tube near the bottom of the flask to displace the air. Stopper the flask with the regular standard stopper.

While observing safety precautions, ignite the filter paper packet containing the sample, remove the regular stopper, and quickly replace it by inserting the stopper (B.5.2) with the burning paper into the flask. Immediately invert the stoppered flask so that the absorbing liquid forms a tight seal around the stopper.

Systems with electrical remote ignition are also applicable.

As shown in Figure B.1, the flask shall be held so that the open part of the platinum sample carrier faces upward so that the sample cannot fall out during combustion.

After the combustion is complete, allow the inverted flask to cool for 1 min, then vigorously shake it for 3 min to absorb the combustion products. Allow to stand for 5 min in the normal position.

Carefully pipette 10 ml of the absorption solution (7.1.5) into the neck-well of the flask. Lift the stopper slightly to allow the liquid to be sucked into the flask. Then let the stoppered flask gently cool for 15 min.

Transfer the contents of the flask 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 expected concentration of the solution and on the method of analysis.

B.8 Determination methods; control measurements; data evaluation and test report

Information on determination methods, control measurements, data evaluation and test report are given in the normative part of this European standard.

B.9 Performance characteristics

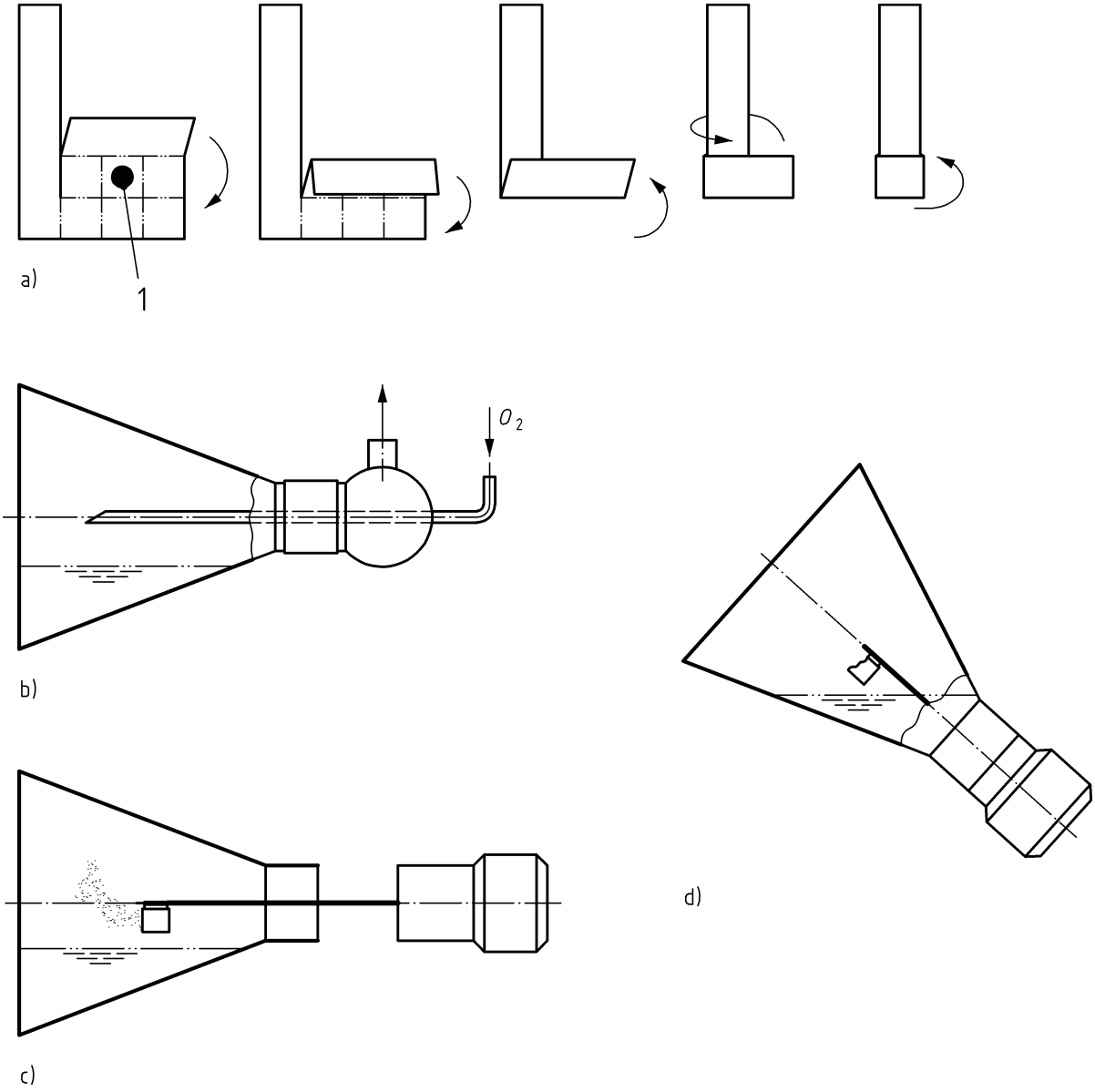
The method performance characteristics given in Table B.1 have been established in a European inter-comparison study on six typical waste samples and a control mixture, carried out in 2005. Due to a lack of participants, this method did not pass the validation criteria.

Table B.1 — Performance characteristics for the determination halogens and sulfur

	Sample	**O** %	***p***	***N***	***x*** % *m/m*	s_R	CV_R %	s_r	CV_r %
Fluorine	Control mixture	0	6	18	0,499	0,068	13,72	0,024	4,74
	Solid waste	17	6	18	0,771	0,269	34,81	0,059	7,70
	Mixed liquid waste	0	4	12	1,393	0,156	11,23	0,118	8,46
	Waste solvent	0	4	12	0,802	0,116	14,46	0,046	5,73
Chlorine	Control mixture	14	7	21	0,608	0,072	11,82	0,020	3,21
	Waste wood	0	7	21	0,933	0,048	5,17	0,044	4,76
	Solid recovered fuel	14	7	21	2,504	0,575	22,98	0,166	6,63
	Solid waste	0	7	21	1,154	0,245	21,28	0,156	13,52
	Mixed liquid waste	0	4	12	0,911	0,353	38,80	0,120	13,19
	Waste solvent	0	5	15	8,574	5,036	58,73	0,521	6,08
	Liquid recovered fuel	0	5	15	0,578	0,425	73,55	0,128	22,18
Bromine	Control mixture	14	7	21	0,553	0,033	5,93	0,012	2,09
	Solid waste	14	7	21	0,737	0,056	7,62	0,032	4,38
	Mixed liquid waste	0	5	15	0,846	0,405	47,87	0,056	6,58
	Waste solvent	20	5	15	0,977	0,082	8,36	0,088	9,01
Iodine	Control mixture	0	5	15	0,434	0,067	15,53	0,045	10,41
	Solid waste	0	5	15	0,878	0,305	34,72	0,032	3,66
	Mixed liquid waste	0	3	9	3,183	1,095	34,40	0,434	13,62
	Waste solvent	0	3	9	0,658	0,217	32,99	0,099	14,99
Sulfur	Control mixture	0	6	18	0,502	0,059	11,84	0,027	5,33
	Waste wood	0	4	12	0,933	0,048	5,17	0,044	4,46
	Solid recovered fuel	0	6	18	1,378	0,121	8,78	0,111	8,07
	Solid waste	17	6	18	1,805	0,704	39,00	0,349	19,34
	Mixed liquid waste	0	4	12	0,762	0,069	9,03	0,028	3,66
	Waste solvent	0	4	12	1,119	0,301	26,92	0,050	4,45
	Liquid recovered fuel	25	4	12	0,737	0,075	10,22	0,082	11,10

p Number of laboratories
N Number of observed values
O Percentage of outliers

	Sample	**O** %	***p***	***N***	***x*** % *m/m*	s_R	CV_R %	s_r	CV_r %
x	Mean value								
s_R	Estimate of the reproducibility standard deviation								
s_r	Estimate of the repeatability standard deviation								
CV_R	Estimate of the relative reproducibility standard deviation expressed in percent								
CV_r	Estimate of the relative repeatability standard deviation expressed in percent								



Key

a) sample (1) is wrapped into a piece of filter paper
b) erlenmeyer flask is filled with oxygen
c) burning/glowing filter paper which contains the adsorption solution is introduced into the Erlenmeyer flask
d) flask is immediately turned to seal the stopper with the adsorption solution

Figure B.1 — Procedure of Schoeniger flask combustion

Annex C
(informative)

Recovery yields obtained for control mixtures with different absorption solutions and analytical techniques

A comparative study of different absorption solutions combined with adequate analytical techniques is presented in this Annex. The sample analysed were control mixtures prepared according to the recommendations of the EN 14582 standard (7.2).

Each mixture has been homogenized and milled using a disk mill. The sample fractions were dispatched in different glass flasks with polytetrafluoroethylene (PTFE) caps and then put in a freezer in order to avoid the loss of volatile halogenated and sulfur compounds and to limit biodegradation. Two mixtures have been used (see Table C.1).

Table C.1 — Composition of the both mixtures used for the study

Mixture A		**Mixture B**	
Organic compound	Concentration of element	Organic compound	Concentration of element
4-chloro-benzoic acid	7,547 g/kg Cl	4-bromo-benzoic acid	1,656 g/kg Br
4-fluoro-benzoic acid	1,130 g/kg F	4-iodo-benzoic acid	2,132 g/kg I
Sulfanilic acid	6,170 g/kg S	cellulose	-
cellulose	-		

These mixtures have been analysed at least in triplicate (in 1 to 3 laboratories) by combustion and collected using different absorption solutions. The results obtained have been compared in terms of performance of halogens and sulfur recovery (see Table C.2 below). Recovery rates of halogens and sulfur were calculated regarding the concentration of the elements prepared in the control mixtures.

Table C.2 — Recovery yields obtained for each element as function of the absorption solutions and analytical techniques used

		CHLORINE				BROMINE			
		Mixture A				*Mixture B*			
	Theorical values %	**0,75**				**0,17**			
	Absorption solutions	Ion Chromatography		Potentiometry		Ion Chromatography		Potentiometry	
		Recovery rate	Standard deviation	Recovery rate	Standard deviation	Recovery rate	Standard deviation	Recovery rate	Standard deviation
Mobile phase for the ion chromatography	$Na_2CO_3/NaHCO_3$ in water	90%	0.7%	91%	2.9%	63%	6%	97%	36.7%
	$Na_2CO_3/NaHCO_3$ in water + collection of gas in NaOH (0.3mol/L)	87%	7.9%	91%	6.6%	67%	9%	80%	17%
Solutions with Ascorbic Acid	Ascorbic Acid 1% (1g of sample)	99%	4.3%	94%	2.7%	67%	11%	84%	3%
	Ascorbic Acid 1% (1g of sample) + collection of gas in NaOH (0.3mol/L)	87%	1.7%	92%	1.7%	75%	0.8%	131%	6.4%
	Ascorbic Acid 1% (0.3g of sample)	104%	nd	95%	3.1%	66%	nd	82%	nd
	Ascorbic Acid 1% (0.3g of sample) + collection of gas in NaOH (0.3 mol/L)	85%	nd	91%	3.3%	87%	nd	156%	nd
	Ascorbic Acid 5% (0.3g of sample) + collection of gas in NaOH (0.3mol/L)	183%	nd	91%	1.4%	93%	nd	162%	nd
	Acide Ascorbique 5% with correction of recovery by calculation	Not analyzed	nd	98%	nd	Not analyzed	nd	102%	nd
Solutions with Hydrazine Hydrate	Hydrazine Hydrate 5%	88%	0.2%	94%	1.5%	74%	2.5%	117%	5.6%
	NaOH (0.25mol/L) / 0.5ml Hydrazine Hydrate 50%	94%	nd	97%	3.5%	96%	nd	162%	5%
	NaOH (0.25mol/L) / 0.5ml Hydrazine Hydrate 50% + collection of gas in NaOH (0.3mol/L)	Not analyzed	nd	Not analyzed	nd	107%	nd	Not analyzed	nd
Solution with NaOH and H_2O_2	NaOH (0.25 mol/L) / 50 µL H_2O_2 (3%) + collection of gas in NaOH (0.3mol/L)	93%	nd	Not analyzed	nd	Not analyzed	nd	Not analyzed	nd

		FLUORINE				IODINE		SULFUR	
		Mixture A				*Mixture B*		*Mixture A*	
	Theorical values %	**0,11**				**0,22**		**0,62**	
	Absorption solutions	Ion Chromatography		Ion Selective Electrode		Ion Chromatography		Ion Chromatography	
		Recovery rate	Standard deviation	Recovery rate	Standard deviation	Recovery rate	Standard deviation	Recovery rate	Standard deviation
Mobile phase for the ion chromatography	$Na_2CO_3/NaHCO_3$ in water	92%	2.7%	91%	3.9%	18%	2.1%	82%	1.9%
	$Na_2CO_3/NaHCO_3$ in water + collection of gas in NaOH (0.3mol/L)	79%	9.6%	72%	3.5%	27%	17.4%	79%	0.6%
Solutions with Ascorbic Acid	Ascorbic Acid 1% (1g of sample)	108%	1.4%	80%	2.6%	63%	3.3%	83%	2.5%
	Ascorbic Acid 1% (1g of sample) + collection of gas in NaOH (0.3mol/L)	152%	15.4%	77%	2.8%	70%	3.5%	80%	5%
	Ascorbic Acid 1% (0.3g of sample)	102%	nd	55%	nd	63%	nd	98%	nd
	Ascorbic Acid 1% (0.3g of sample) + collection of gas in NaOH (0.3 mol/L)	135%	nd	76%	0.5%	80%	nd	80%	nd
	Ascorbic Acid 5% (0.3g of sample) + collection of gas in NaOH (0.3mol/L)	150%	nd	69%	3.1%	79%	nd	86%	nd
	Acide Ascorbique 5% with correction of recovery by calculation	Not analyzed	nd	97%	nd	Not analyzed	nd	82%	nd
Solutions with Hydrazine Hydrate	Hydrazine Hydrate 5%	91%	0.5%	80%	5.3%	79%	1.9%	79%	1.5%
	NaOH (0.25mol/L) / 0.5ml Hydrazine Hydrate 50%	96%	nd	106%	nd	88%	nd	96%	nd
	NaOH (0.25mol/L) / 0.5ml Hydrazine Hydrate 50% + collection of gas in NaOH (0.3mol/L)	Not analyzed	nd	Not analyzed	nd	102%	nd	Not analyzed	nd
Solution with NaOH and H_2O_2	NaOH (0.25 mol/L) / 50 µL H_2O_2 (3%) + collection of gas in NaOH (0.3mol/L)	103%	nd	Not analyzed	nd	Not analyzed	nd	100%	nd

Annex D
(informative)

Examples of possible control substances

Table D.1 lists possible control substances for the determination of halides and sulfur.

Table D.1 — Example of possible control substances

Compound	**Formula**	**Element content** %				
		S	**F**	**Cl**	**Br**	**I**
L-cystein	$C_3H_7HO_2S$	26,47				
4-aminobenzensulfonic acid (sufanilic acid)	$C_6H_6NO_3S$	18,51				
1-(2-thiazolylazo)-2-naphtol	$C_{13}H_9N_3OS$	12,56				
Thiourea	CH_4N_2S	42,13				
Taurine	$C_2H_7NO_3S$	25,62				
Sulfanilide	$C_6H_8N_2O_2S$	18,62				
Potassiumxanthogenate (potassium-O-ethyldithiocarbonate)	$C_3H_5KOS_2$	40,04				
Vitamin B1	$C_{12}H_{17}ClN_4OS$ x HCl	9,51		21,03		
S-benzyl thiouronium chloride	$C_8H_{11}ClN_2S$	15,82		17,49		
2,2,2-trifluoroacetamide	$C_2H_2F_3NO$		50,42			
4-fluoro-benzoic acid	$C_7H_5FO_2$		13,56			
4-chloro-benzoic acid	$C_7H_5ClO_2$			22,64		
Chloronitrobenzene	$C_6H_4ClNO_2$			22,50		
4-chloro 3,5-dinitrobenzoic acid	$C_7H_3ClN_2O_6$			14,40		
Bromothymol blue	$C_{27}H_{28}Br_2O_5S$	5,14			25,59	
Bromocresol purple	$C_{21}H_{16}Br_2O_5S$	5,94			29,58	
Bromo-4-acetanilide	C_8H_8BrNO				37,32	
Tetraheptylammonium bromide	$C_{28}H_{60}BrN$				16,30	
4-bromo-benzoic acid	$C_7H_5BrO_2$				39,75	
4-iodo-benzoic acid	$C_7H_5IO_2$					51,17
Tetrahexylammonium iodide	$C_{24}H_{52}IN$					26,40
O-iodo-hippuric acid	$C_9H_8INO_3$					41,6

Compound	**Formula**	**Element content** %				
		S	**F**	**Cl**	**Br**	**I**
N-(4-bromophenyl)-N'-(2 chloro-4 nitrophenyl) thiourea (BCR 71)	$C_{13}H_9BrClN_3O_2S$	8,30		9,17	20,65	
N-(2-chloro-4-nitrophenyl)-N`-(4-iodophenyl) thiourea (BCR 72)	$C_{13}H_9ClIN_3O_2S$	7,35		8,11		29,32
1-(1-(4-bromophenyl-methyl)-4-piperidinyl)-5-chloro-2-(trifluoromethyl) −1H-benzimidazole (BCR 73)	$C_{20}H_{18}BrClF_3N_3$		12,07	7,49	16,90	

Annex E
(informative)

Additional results of inter-laboratory tests

Inorganic compounds were analysed by five laboratories during the validation round robbin test for EN 14582:2007 using the normative bomb combustion method (4 laboratories) and the informative Schoeniger method (1 laboratory). Results see Table E.1.

Table E.1 — Recovery of inorganic compounds in %

		Bomb combustion				**Schoeniger**
Sulfur (S)						
Compound	S %	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Sodium sulphate	22,57	91	96	97	89	100
Sodium sulphide hydrate	14,5	78	80	56	74	32
Sodium sulphite	25,44	76	81	69	-	97
Potassium disulphate	25,2	54	96	80	103	95
Ammoniumthiosulphate	43,2	100	86	86	88	98
Sulfur	99 - 101	100	96	89	92	101
Chlorine (Cl)						
Compound	Cl %	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Sodium chloride	60,67	95	93	94	100	91
Sodium chlorate	33,31	89	85	96	97	90
Potassium perchlorate	25,59	95	93	102	103	86
Calciumhypochlorite	49,6	43	80	95	101	48
Iodine (I)		**Ascorbic acid method**				
Compound	I %	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Iodine-Solution **c = 0,05 mol/l**	1,27	-	-	-	88	100
Potassium iodide	76,44	98	90	-	97	-
Potassium iodate	59,30	94	84	-	83	-
Bromine (Br)						
Compound	Br %	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Sodium bromide	77,66	95	73	99	98	99
Fluorine (F)						
Compound	F %	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Sodium fluorid	45,24	68	62	98	95 93	31

In Table E.2 different ratios of paraffin to sample were analysed. The total amount of sample and enhancer shall not be higher than 1 g.

Table E.2 — Comparison of different enhancer/sample-ratio (bomb combustion)

Enhancer/sample ratio	**Recovery of chlorine from potassium perchlorate** %
1: 1	63,7
2: 1	65
3: 1	90,3
5: 1	98,5
7: 1	99,8
10: 1	99,5

Annex F
(informative)

Summary of general requirements and recommendations

The purpose of this summary is to support the organization of sampling and sample pretreatment processes. The information given should be helpful to prepare a sampling plan.

Requirements not mentioned in this document are considered as recommendations. Summary see Table F.1.

Table F.1 — Summary of general requirements and recommendations

Matrix restrictions	Waste
Typical working range	Above 0,025 g/kg
Sampling instruments	Any instrument that does not release halogen and sulfur
Container pretreatment	Clean and dry; free of solvents
Container material	Any appropriate sample container
Transport conditions	Dark and cool
Preservation	Cooling at 4 °C
Storage conditions	At 4 °C in the dark not longer than 1 week; longer storage at −18 °C
Required amount	50 g test sample
Test portion	0,05 g – 1 g of the homogenized test sample
Drying procedure	Drying only applies if samples contain negligible amounts of volatiles at the drying temperature, except water
Sieving (particle size)	Not applicable
Grinding	Particle sizes < 200 μm
Compatibility with	Sample can be used for determination of hydrocarbons (GC and gravimetric), Total organic Carbon (TOC), dry matter as well. Depending on the number of parameters the sample amount has to be increased.

Annex G
(informative)

Additional validation data

G.1 General

Except for direct validation data a validation study contains a number of additional data which may be relevant for the users of this European Standard.

G.2 Samples

a) Control mixture

18,819 g of cellulose powder and the following substances were mixed and homogenized using a planetary ball mill: 4-fluorobenzoic acid (3,670 4 g), 4-chlorobenzoic acid (2,9529 g), 4-bromobenzoic acid (1,4696 g), 4-iodobenzoic acid (0,896 5 g) and sulfanilic acid (2,7042 g).

b) Liquid recovered fuel

This sample was a liquid waste material (originally from a metallurgic process) used as derived fuel at a combined heat and power plant. The material consisted mainly of medium to high boiling hydrocarbons. The material was spiked with defined amounts of compounds containing chlorine and sulfur.

c) Mixed liquid waste

This sample was a liquid waste material from a chemical factory intended for incineration in a waste incineration plant. The material consisted mainly of low boiling solvents such as acetone and contained chlorine, bromine and iodine. To achieve relevant concentrations of all analytes, the material was spiked with defined amounts of compounds containing fluorine and sulfur.

d) Solid recovered fuel

This sample was a mixture of solid waste material used as derived fuel at a combined heat and power plant. To achieve relevant concentrations of the analytes, the material was spiked with defined amounts of compounds containing chlorine and sulfur. The substances used for spiking were dissolved in acetone. The resulting solution was added to the solid fuel batch. The material was dried at room temperature in a laboratory hood and homogenized.

e) Solid waste

This sample was a solid waste material from a metallurgic process intended for waste disposal in a landfill. It contained chlorine and sulfur. To achieve relevant concentrations of the analytes, the material was spiked with defined amounts of compounds containing fluorine, bromine and iodine. The substances used for spiking were dissolved in acetone. The resulting solution was added to the solid waste batch. The material was dried at room temperature in a laboratory hood and homogenized.

f) Waste wood

Waste wood pieces were collected at a municipal waste treatment site. Pieces of 3 cm x 3 cm were grinded using a cutting mill (Retsch SM-2000). To achieve relevant concentrations of the analytes, the material was spiked with defined amounts of compounds containing chlorine and sulfur. The

substances used for spiking were dissolved in acetone. The resulting solution was added to the solid fuel batch. The material was dried at room temperature in a laboratory hood and homogenized.

g) Waste solvent

A mixture of liquid organic solvents was from an industrial process. This sample was a liquid waste material from a chemical factory intended for incineration in a waste incineration plant. The material consisted mainly of low boiling solvents such as acetone, ethanol, methanol and toluene and contained chlorine, bromine and iodine. To achieve relevant concentrations of all analytes, the material was spiked with defined amounts of compounds containing fluorine and sulfur.

G.3 Homogeneity and stability

Homogeneity of samples was investigated by eight repeated analyses from different sample containers. Data from homogeneity testing are given in Table G.1.

Stability and in-bottle homogeneity of samples were tested by three to eight repeated analyses from one sample container. Additional analyses were performed during the experimental phase of the study. Results showed that all analytes were stable.

Table G.1 — Results from homogeneity testing

Sample material		**Chlorine**	**Fluorine**	**Sulfur**	**Bromine**	**Iodine**
Control mixture	mean (%)	0,812	0,580	0,438	0,510	0,396
	s_r	0,051 7	0,026 9	0,012 1	0,061 7	0,026 1
	CV_r (%)	6,4	4,6	2,8	12,1	6,6
Secondary recovered fuel	mean (%)	2,330	nd	1,369	nd	nd
	s_r	0,164 4	nd	0,036 3	nd	nd
	CV_r (%)	7,1	nd	2,6	nd	nd
Waste wood	mean (%)	1,783	nd	0,927	nd	nd
	s_r	0,061 0	nd	0,0215	nd	nd
	CV_r (%)	3,4	nd	2,3	nd	nd
Solid waste	mean (%)	1,229	0,945	3,039	0,719	0,726
	s_r	0,081 2	0,086 1	0,404 6	0,0270	0,022 0
	CV_r (%)	6,6	9,1	13,3	3,8	3,0
Liquid recovered fuel	mean (%)	0,843	nd	0,698	nd	nd
	s_r	0,0171	nd	0,0135	nd	nd
	CV_r (%)	2,0	nd	1,9	nd	nd
Waste solvent	mean (%)	13,349	0,794	0,880	0,893	0,559

Sample material		**Chlorine**	**Fluorine**	**Sulfur**	**Bromine**	**Iodine**
	s_r	0,722 6	0,058 3	0,043 0	0,046 3	0,063 6
	CV_r (%)	5,4	7,3	4,9	5,2	11,4
Mixed liquid waste	mean (%)	1,339	1,573	0,736	0,616	2,980
	s_r	0,0888	0,0551	0,0259	0,0205	0,1704
	CV_r (%)	6,6	3,5	3,5	3,3	5,7

nd not determined.
s_r Estimate of the repeatability standard deviation
CV_r Estimate of the relative repeatability standard deviation expressed in percent

Bibliography

[1] ASTM E 442:1991, *Standard Method of Test for chlorine, bromine, or iodine in organic compounds by oxygen flask combustion*

[2] ASTM E 443:1991, *Standard Method of Test for sulphur in organic compounds by oxygen flask combustion*

[3] ASTM D 808:2005, *Standard Test Method for chlorine in new and used petroleum products (bomb method)*

[4] EPA 5050, *Bomb combustion method for solid waste*

[5] EN ISO 10304-1, *Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1)*

[6] ISO 10304-2, *Water quality — Determination of dissolved anions by liquid chromatography of ions - Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulphate in waste water (ISO 10304-2)*

[7] EN ISO 10304-3, *Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate (ISO 10304-3)*

[8] EN ISO 11885, *Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885)*

[9] ISO 9297, *Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*

[10] ISO 10359-1, *Water quality — Determination of fluoride - Part 1: Electrochemical probe method for potable and lightly polluted water*

[11] L. Chireux, C. Granet, Determination of halogen and sulfur content in waste — choice of the absorption solution; CIRSEE Suez Environnement, July 2011

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