SLOVENSKI STANDARD
SIST-TP CEN/TR 17345:2019

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Odpadki - Dokument o stanju tehnike - Določevanje halogenov in žvepla z ionsko kromatografijo po pirohidrolitskem sežigu

Waste - State-of-the-art document - Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection

Abfall - Dokument zum Stand der Technik - Bestimmung von Halogenen und Schwefel mittels oxidativer pyro-hydrolytischer Verbrennung mit Ionenchromatographie Detektion

Caractérisation des déchets - État de l'art - Halogènes et soufre par combustion pyrohydrolytique oxydative suivie d'une détection par chromatographie ionique

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Waste - State-of-the-art document - Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection

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Ref. No. CEN/TR 17345:2019 E

Contents

Page

European foreword

This document (CEN/TR 17345:2019) has been prepared by Technical Committee CEN/TC 444 “Test methods for environmental characterization of solid matrices”, the secretariat of which is held by NEN.

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Introduction

The content of sulfur, chlorine, fluorine and/or bromine has to be determined in various waste streams such as refuse derived fuel, rubber granulates, post-shredder residue and plastics from wastes of electrical and electronic equipment (WEEE).

At the moment the determination of these elements is performed according to EN 14582. This European 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. Because the combustion has to be conducted for each sample separately and no automation is possible, this method is time-consuming and labour- intensive compared to combustion ion chromatography (C-IC).

The use of the combustion ion chromatography (C-IC) instrument would allow in one single run the combustion of the material and the simultaneous determination of fluorine, chlorine, bromine, and sulfur by ion chromatography. Moreover, the combustion module enables the sample digestion of different type of samples under pyrolysis and oxidation conditions. The instrument may also be equipped with automatic sample introduction modules for solids and liquids, which will benefit the automation and reduce significantly the labour-intensive process. The system is already offered commercially by different manufacturers.

Many laboratories are using none coupled customized hydropyrolysis systems for different kind of applications. Offline systems can be used as sample preparation systems for IC measurement, too. Coupling is no requirement for using the C-IC technique.

This document provides a technical description of the C-IC technique, an overview of available commercial instruments, the strengths and limitations of this technique, and analytical results for halogens and sulfur obtained on waste samples.

1 Scope

In the framework of EU Directive 99/31/EC [1] and EU Directive 2000/76/EC [2] halogens and sulfur need to be determined on waste samples. The implementation of the combustion-IC technique would allow in one single run the combustion of the sample followed by the determination of the halogens and sulfur with ion chromatography. Moreover, this instrument may be provided with a sample carrousel for both solids and liquids, allowing an automation of these type of analyses.

Recent developments of the C-IC technology have made this technique interesting for the determination of halogens and sulfur in waste samples. Therefore, a document on the current progress of the C-IC technology was prepared, including the evaluation of the performance of different commercially available systems and the presentation of analytical results obtained on certified reference materials and waste samples.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Description of the combustion-IC technique

4.1 Principle

Samples are introduced in the combustion tube using an automatic boat control device. First samples are thermally combusted under argon atmosphere, followed by a combustion at 800 °C to 1 100 °C with oxygen under pyrohydrolytic conditions. Sulfur in the samples converts to SO_x and halogens to hydrogen halide. These volatile compounds are trapped in an aqueous absorbing solution and subsequently injected for ion chromatographic analysis. The basic equipment configuration is shown in Figure 1.

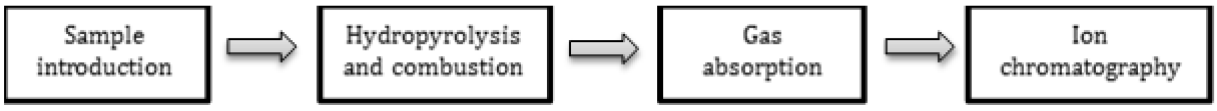

Figure 1 — Basic configuration of a C-IC system

4.2 Configuration of the system

4.2.1 Sample introduction

All the systems have the ability to measure both solids and liquids. Automation is available for boat trays as well as liquids in vials. Solid analysis is performed by weighing the sample into a sample boat. Alternative to sampling liquids from vials, they can also be injected into sample boats placed on the boat tray. In this case there should be no volatile compounds present due to possible losses by evaporation.

The intake will depend on the sample type, density and concentration. Upper limits are approximately 100 mg for solids and 100 µl for liquids. The sample shall be homogeneous with respect to sample amount.

4.2.2 Combustion system

The furnace is provided with a quartz or ceramic pyrolysis tube. Alkali metals such as sodium, calcium and magnesium have a tendency to react with SiO_2. Same effect can be seen when measuring silicium bearing samples. The reactions cause devitrification of the quartz pyrolysis tube, which will result in cracking of the tube. This can be overcome by working with a ceramic tube. Using a combustion improver (e.g. WO_4, Fe_3O_4), which binds with calcium and magnesium [4] will increase lifetime of glass parts. Analogously the sample boat consists of quartz or ceramic material.

To achieve complete combustion of the sample and full recovery of analytes, choosing suitable combustion temperatures, timings of boat movement, addition of water to the combustion gases (hydropoyrolysis) and possibly addition of combustion improver is required. Special attention is needed if organic matrices are analysed to prevent soot formation.

Combustion process

The sample boat is introduced under inert gas atmosphere. Samples are pyrolysed following the temperature gradient at the inlet of the furnace. To prevent soot formation, this pyrolysis shall be controlled by suitable means to ensure complete transformation of organic matter to CO_2. After complete pyrolysis, the inner tube is flushed with oxygen to mobilize remaining analytes.

Hydropyrolysis

To ensure complete mobilization of fluorine during pyrolysis, addition of water to the inert gas is required. The amount added depends on sample type and analyte concentrations.

4.2.3 Gas absorption unit

The combustion gases are fed into an absorption vessel and passed through an aqueous absorption solution. Hydrogen halides absorbed as halide anions, SO_x is converted to sulfite and sulfate. To unify analytes for quantification, H_2O_2 (or a suitable oxidant) is added to the absorption solution to oxidize all species to SO_4. H_2O_2 also acts as reducing agent if halogens, especially bromine, are combusted to halogen gas (Br_2).

The absorption unit is equipped with measures to quantify total absorption solution volume after combustion, accounting for water addition by hydropyrolysis. Such measures can be automatic or manual adjustment to a known volume, calculation of volume changes or addition of an internal standard.

Sample transfer and loading to ion chromatography sample loop can be fully automatic or manual.

4.2.4 Ion chromatography system

The ion chromatography system uses chromatographic columns based on ion exchange materials to achieve separation of anionic analytes. To achieve good signal to noise ratio, peak separation and peak resolution, different setups may be used.

Elution from the column may be performed by isocratic or gradient elution. As H_2O_2 is creating an interference with fluoride detection, additional measures are necessary if very low contents of fluorine are analysed. Suitable measures may be gradient elution to achieve better separation or physical separation of H_2O_2 by a matrix elimination/preconcentration column.

5 Available standard methods

A range of standard methods are available describing the determination of halogens and sulfur in a variety of matrices. In Table 1 a non-limited list is given of relevant standard methods containing a particular section on C-IC. For each standard method information on the analysed matrix, the element determined and the measuring range, if available, is presented. Table 2 shows a non-limited list of relevant standard methods allowing analysis by C-IC without a particular section on this technique.

Table 1 — Non-limited list of standard methods containing a particular section on C-IC

Standard method	Matrix	Elements and measuring range mg/kg				Ref.
		Fluorine	Chlorine	Bromine	Sulfur	
EN 62321-3-2	Polymers and electronics	-	-	96 to 976	-	11
ASTM D 7359–14	Aromatics hydrocarbons	0,1 to 10	0,1 –10	-	0,1 –10	12
ASTM D 7994–17	Liquified petroleum gases	1 to 300	5 to 300	-	1 - 300	13
ASTM D 8150	Crude oil (naphta fraction)	-	1 to 50	-	-	14
ASTM UOP 991-13	Liquid organics	0,1 to 100	0,1 to 100	0.2 to 100	-	15
ASTM UOP 1001-14	Liquified petroleum gases	1 to 1 500	1 to 1 500	-	-	16
JIS K 7392	Waste plastic	-	-	100 to 20 000	-	17
JEITA ET-7304A	Halogen free soldering material	< 1 000	< 1 000	< 1 000	-	18
KS M01080-2009	Electronic equipment	X	X	X	-	19

Table 2 — Non-limited list of standard methods allowing analysis by C-IC without a particular section on C-IC

Standard method	Matrix	Elements and measuring range mg/kg				Ref.
		Fluorine	Chlorine	Bromine	Sulfur	
EN ISO 16994	Solid biofuels	-	60 to 2 000	-	90 to 1 200	20
ISO 11724	Coal, cole and fly ash	X	-	-	-	21

Standard method	Matrix	Elements and measuring range mg/kg				Ref.
		Fluorine	Chlorine	Bromine	Sulfur	
ISO 17947	Nitride	X	X	X	X	22
ASTM D 5987–07	Coal and coke	20 to 500	-	-	-	23
DIN 51723	Solid fuels	X	-	-	-	24
DIN 51724	Coal and coke	-	-	-	X	25
JIS R 1616	Silicon carbide	X	-	-	-	26
JIS R 9301–3-11	Alumina powder	X	-	-	-	27
JIS Z 7302–6/7	Refuse derived fuel	-	X	-	X	28

6 Evaluation study of the C-IC technique

6.1 General

A study was conducted by the Flemish Institute for Technological Research (VITO, Flanders, Belgium) in commission of the Public Waste Agency of Flanders (OVAM, Belgium) to evaluate the C-IC technique for the determination of halogens and sulfur in waste samples [3]. The main results of this study are incorporated in this document.

The evaluation of the C-IC technique was performed by conducting comparative tests on C-IC systems from 2 suppliers (Mitsubishi Chemical, Japan in combination with ion chromatography from Thermo Fisher Scientific, USA and Metrohm, Belgium). These two different C-IC units were used to analyse about 9 certified reference materials, as well as 10 waste samples. The analyses on the Mitsubishi system were performed by Mitsubishi itself, while the analyses on the Metrohm C-IC system were performed by VITO in the application laboratory of Metrohm in Antwerp, Belgium.

6.2 Description of the samples

For this study, the reference samples considered were oil, clay, coal, fly ash, polymer, phosphate rock. Table 3 lists the certified values for these reference materials.

Table 3 — Overview certified values of the reference materials

Identification	Matrix	x_{ass} Fluorine mg/kg		x_{ass} Chlorine mg/kg		x_{ass} Bromine mg/kg		x_{ass} Sulfur mg/kg	
AOD 1.11	Oil	-		9 500	±50	-		6 500	±40
AOD 1.12	Oil	4 300	±40	-		9 500	±50	-	
BCR 461	Clay	568	±10	*119*	*±25*	-		-	
BCR 460	Coal	225		*59*		-		-	
BCR 182	Coal	-		3 700	±70	*36,5*		-	

Identification	Matrix	x_{ass} Fluorine mg/kg		x_{ass} Chlorine mg/kg		x_{ass} Bromine mg/kg		x_{ass} Sulfur mg/kg	
BCR 038	Fly ash	538	±13	323	±22	-		-	
N1633b	Fly ash	-		-		*2,9*		2 075	±11
BCR 681	Polymer	-		93	±2,8	98	±2,8	78	±17
BCR 032	PO_4 rock	40 400	±600	-		-		7 360	±320
Where x_{ass} is the assigned value italic: indicative values									

In consultation with OVAM, a number of waste samples were selected for analysis with C-IC as presented in Table 4. All waste samples were dried at 105 °C and fine grinded down to < 0,5 mm using an universal cutting mill.

Table 4 — Overview of analysed waste samples

Sample number	Type of sample
CIC1	Fine shredder
CIC2	SRF fraction(industrial waste)
CIC3	SRF fraction (household waste)
CIC4	Sewage sludge
CIC5	Post shredder residue (electrical equipment)-SRF
CIC6	Post shredder residue (electrical equipment)
CIC7	Post shredder residue (electrical equipment)-fluff shredder
CIC8	Rubber granulates
CIC9	Plastics from WEEE (containing bromine)
CIC10	Rubber fraction

6.3 Description of the applied C-IC systems

The C-IC unit 1 (C-IC 1) is a double furnace system which was equipped with a ceramic pyrolysis tube and ceramic boats. Furnace 1 was set at 900 °C and furnace 2 at 1 000 °C for organic samples and at 1 100 °C for both furnaces for inorganic samples and mixtures. The samples were pyrolysed under humidified inert atmosphere and combusted in oxidising atmosphere. The resultant vapors were absorbed in an aqueous solution (H_2O_2 added), gas lines were washed, the absorption volume adjusted to a defined volume by liquid level sensor and afterwards injected directly into the IC system for analysis. H_2O_2 was added into the absorbing solution to oxidize SO_2 to form SO_4^{2-}.

In some cases, especially for the determination of sulfur, a combustion improver (WO_3) was added. The IC measurements were conducted using a separation column at 35 °C and 2,7 mM Na_2CO_3 and 0,3 mM $NaHCO_3$ as eluent with a flow rate of 1 ml/min. The ion chromatograph was calibrated for fluorine, chlorine and sulfate (for this study the element bromine was not calibrated, although it is feasible). There was no need for usage of a pre-concentration column or variable injection volumes for the IC.