

Teknisk rapport

SIS-CEN/TR 17345:2019

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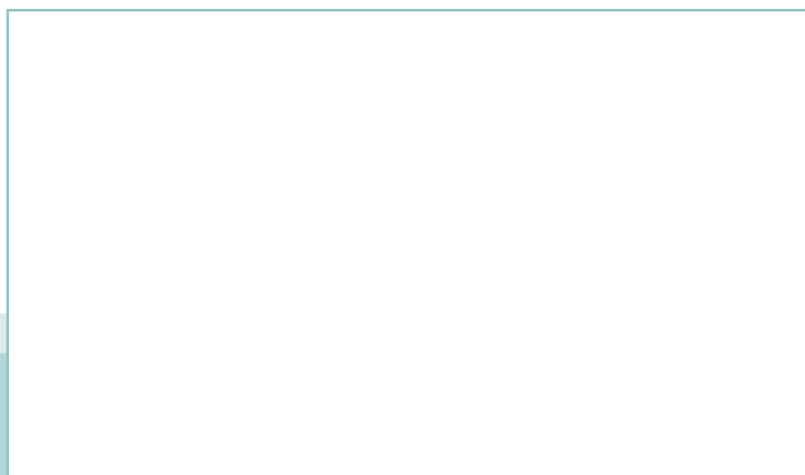
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**Avfall – Rapport om den senaste tekniska utvecklingen –
Bestämning av halogener och svavel genom oxidativ
pyrohydrolytisk förbränning följt av jonkromatografidetektion**

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



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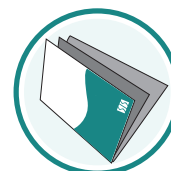
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TECHNICAL REPORT

CEN/TR 17345

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

February 2019

ICS 13.030.40

English Version

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

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

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

This Technical Report was approved by CEN on 4 February 2019. It has been drawn up by the Technical Committee CEN/TC 444.

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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.

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.

SIS-CEN/TR 17345:2019 (E)**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 hydrolysis 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 carousel 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.

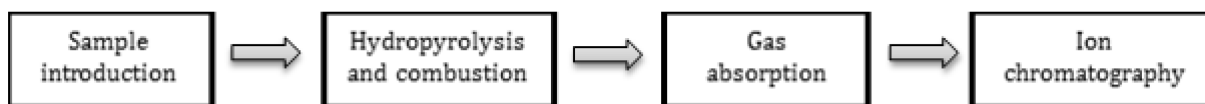


Figure 1 — Basic configuration of a C-IC system

SIS-CEN/TR 17345:2019 (E)**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 SiO₂. 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. WO₄, Fe₃O₄), 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 (hydropyrolysis) 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 CO₂. 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, H₂O₂ (or a suitable oxidant) is added to the absorption solution to oxidize all species to SO₄. H₂O₂ also acts as reducing agent if halogens, especially bromine, are combusted to halogen gas (Br₂).

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 H₂O₂ 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 H₂O₂ 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