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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

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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.

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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.

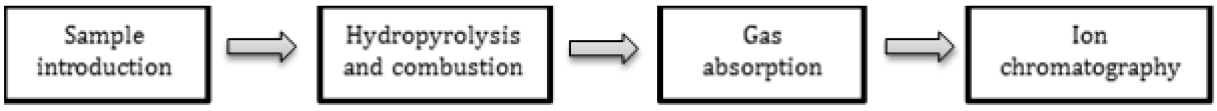

Figure 1 — Basic configuration of a C-IC system

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.