Determination of Halogens and Sulphur in Complex Matrices

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This article presents a method that combines combustion digestion and ion chromatography into a single analysis (combustion ion chromatography [CIC]) making it possible to detect halogens and sulphur in complex matrices. The method is suitable for use in a wide range of application areas.

There are a number of different methods available to determine fluorine, chlorine, bromine, iodine, and sulphur in flammable substances. The majority of these are based on independent analysis steps, beginning with sample digestion using high-temperature combustion followed by halogen and sulphur analysis. As an alternative, combustion digestion coupled with ion chromatography (CIC) combines sample digestion and analysis in one step. CIC can be performed on a wide range of sample types regardless of whether solid, liquid, or gas. The only condition is that the sample has to be flammable. In addition to the halogen and sulphur analysis processes discussed in this article, which are used in the plastics, power generation, petroleum, and fuel industries, CIC is also suitable for samples from the pharmaceutical, environmental, and food sector. It is for these advantages that many international standards refer to CIC when determining the presence of halogens and sulphur in complex matrices (Table 1).

CIC Method Principles

Combustion: Combustion takes place in the presence of steam, which ensures that the gaseous halogen and sulphur compounds (HX, X_2, SO_x) are quantitatively collected by the absorption solution. Adding hydrogen peroxide to the absorption solution (for example, 90 mg/L) ensures that all sulphur compounds are present in the form of sulphate, which is necessary for ion chromatographic detection. However, when hydrogen peroxide is added as an oxidizing agent it can result in various interference peaks that overlay the fluoride peak. With in-line matrix elimination, these interferences disappear and the fluoride peak can be evaluated again (Figure 1).

An optical sensor in the pyrolysis oven indicates the progression of the combustion and regulates the feed of the sample boat. This ensures complete combustion by similarly reducing the sample's oven dwell time.

Figure 1: Effect of 90 mg/L hydrogen peroxide in the absorption solution. Red: once with in-line matrix elimination; Black: once without.

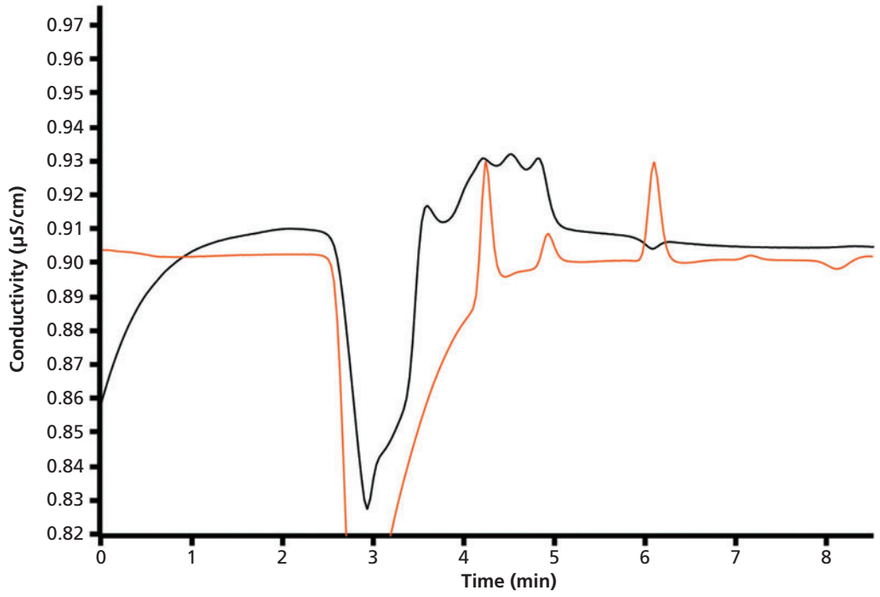

Table 1: A selection of international standards that recommend combustion ion chromatography as a means of determining the halogen and sulphur content in flammable samples.

Combustion IC in international standards	
ASTM D 7359-08	Standard test method for total fluorine, chlorine and sulphur in aromatic hydrocarbons and their mixtures by oxidative pyrohydrolytic combustion followed by ion chromatography detection (combustion ion chromatography-CIC).
UOP 991-11	Chloride, fluoride, and bromide in liquid organics by combustion ion chromatography (CIC).
ASTM D 5987-96	Standard test method for total fluorine in coal and coke by pyrohydrolytic extraction.
DIN EN 62321-3-2	Screening of total bromine in electric and electronic products by combustion ion chromatography.
DIN 51727	Testing of solid fuels — Determination of chlorine content.

Figure 2: Determination of halogens and sulphur in polymer standard ERM–EC680k. Column: Metrosep A Supp 5 - 150/4.0, eluent: 3.2 mmol/L sodium carbonate, 1 mmol/L sodium hydrogen carbonate, 0.7 mL/min, column temperature: 30 °C.

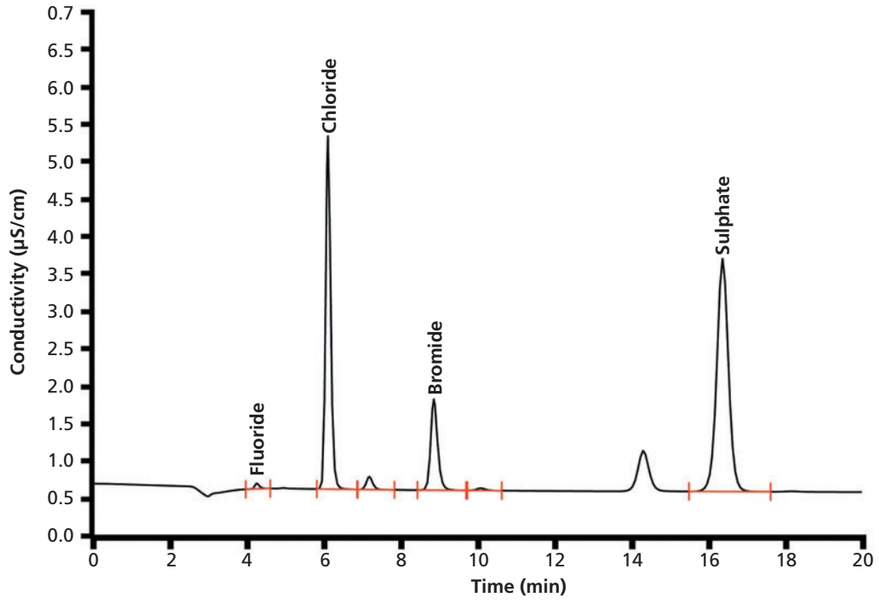

Table 2: Certified chlorine, bromine, and sulphur content of the polymer standard ERM–EC680k determined using combustion ion chromatography.

	ERM-EC680k[a] Certified content (mg/kg)	Combusion IC[b]		
		Content (mg/kg)	RSD (%)	Recovery (%)
Chlorine	102.2 ± 3.0	104.7	1.3	102.4
Bromine	96.0 ± 4.0	97.1	1.8	101.2
Sulphur	76.0 ± 4.0	75.2	3.6	99.0

[a]Certified polyethylene standard from the Institute of Reference Materials, Geel, Belgium
[b]Mean of three determinations

Instrumentation: The combustion unit is from Analytica Jena, while the liquid handling and IC are from Metrohm. The software used was MagIC Net from Metrohm.

Application Areas

The application areas described in this article illustrate the precision and accuracy of CIC. The samples analyzed were plastic and fuel samples as well as latex and vinyl gloves.

Plastic Samples: The combustion of organic materials containing halogen and sulphur produces toxic gases that are harmful to humans and materials. To guarantee that plastics are halogen- and sulphur-free, a quick and reliable analysis is required. A certified polymer standard, ERM–EC680k (Institute for Reference Materials and Measurements, Geel, Belgium), is used to check the precision and accuracy of CIC. It is a low-density polyethylene granulate containing known quantities of chlorine, bromine, and sulphur. Figure 2 illustrates the analysis of halogen and sulphur content of the reference standard by CIC. The recovery rates, ranging between 99% and 102.4% (Table 2), demonstrate that the plastic has quantitatively combusted and that the combustion gases have been completely collected by the absorption solution.

Liquid Fuels: Burning fuels that contain sulphur produces sulphur dioxide that is harmful to the environment. In addition, high sulphur content deactivates catalysts in combustion engines and affects both the storage stability and ignition behaviour of fuels. The halogen content also plays an important role, as chloride in particular accelerates corrosion in the refinery process and in engines.

The quality requirements for gasoline are defined in DIN EN 228 and DIN 51626-1.

Figure 3: Determination of sulphur and halogen content in gasoline. Column: Metrosep A Supp 5 - 150/4.0, eluent: 3.2 mmol/L sodium carbonate, 1 mmol/L sodium hydrogen carbonate, 0.7 mL/min, column temperature: 30 °C.

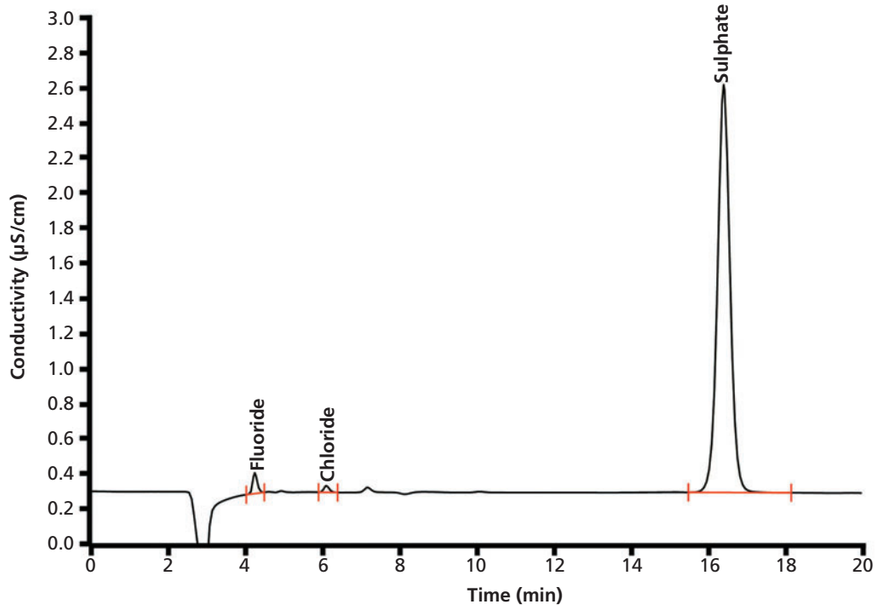

Table 3: Determination of sulphur content in gasoline.

	Content[a] (mg/kg)	RSD (%)
Fluorine	0.78	0.46
Chlorine	0.75	0.34
Sulphur	9.88	0.42

[a]Mean of three determinations

The sulphur content must not exceed a limit value of 10 mg/kg. Figure 3 shows that in the gasoline sample under investigation, the sulphur content was just below this limit value at 9.88 mg/kg.

Solid Fuels: It is also possible to analyze halogens and sulphur in solid fuels such as wood pellets and brown or black coal (Figure 4). In the case of the analyzed coal sample, the results demonstrated similar precision to those for the liquid fuel. Recovery rates in the coal sample were 96.8% for sulphur and 103.4% for chlorine. Representative and, therefore, homogeneous samples are a prerequisite for reproducible results. In the case of solid samples, however, these are something of an exception, which is why any irregularities

Figure 4: Determination of halogen and sulphur in a coal sample. Column: Metrosep A Supp 5 - 150/4.0, eluent: 3.2 mmol/L sodium carbonate, 1 mmol/L sodium hydrogen carbonate, 0.7 mL/min, column temperature: 30 °C.

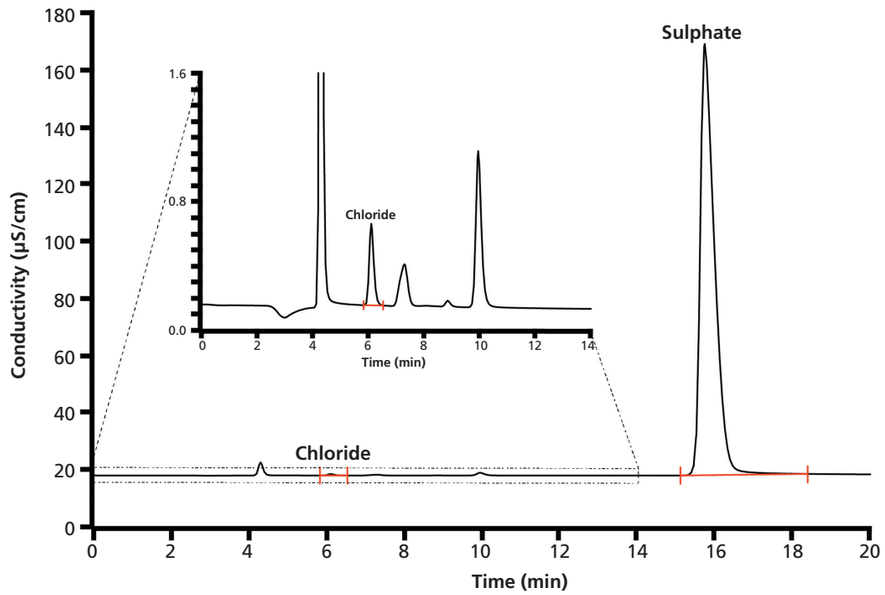

Table 4: Determination of chlorine and sulphur in solid fuels.

	Content[a] (mg/kg)	RSD (%)
Chlorine	17	5.5
Sulphur	1439	1.5

[a]Mean of three determinations

must be taken into consideration when selecting samples.

Gloves in Clean Room Environments: Gloves are used in clean room environments to hold back the ionic contamination found in perspiration from hands. Only materials with low amounts of halogen and sulphur may be used in the water-steam cycle of power plants and the primary circuit of pressurized water reactors, so that no corrosive halogenides or sulphates can get into these systems. Halogen and sulphur content is therefore a key consideration when selecting appropriate materials for use in clean room environments. In this case, vinyl gloves are the better choice because of their significantly lower halogen and sulphur content (Figure 5 and Table 5).

Figure 5: Determination of chloride and sulphate in latex gloves. Column: Metrosep A Supp 5 - 150/4.0, eluent: 3.2 mmol/L sodium carbonate, 1 mmol/L sodium hydrogen carbonate, 0.7 mL/min, column temperature: 30 °C.

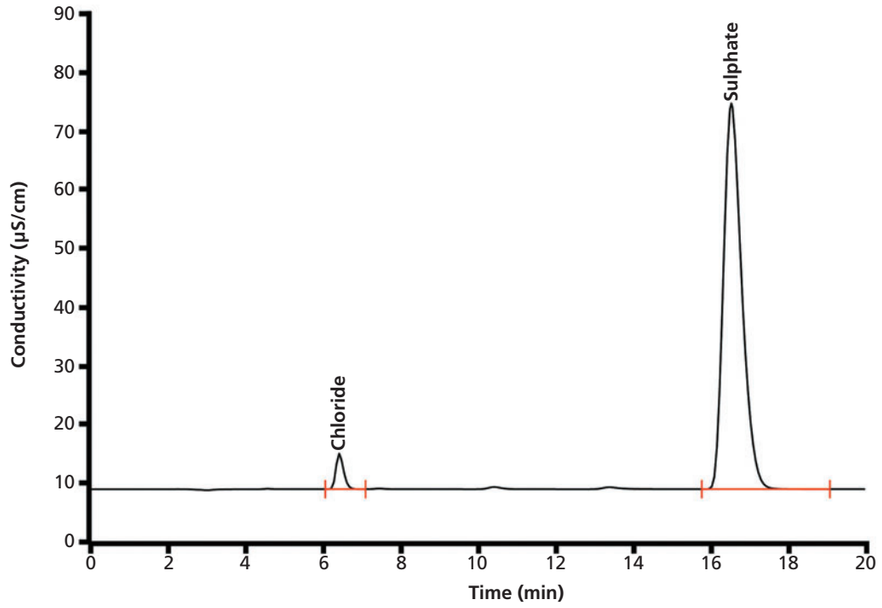

Table 5: Chlorine and sulphur content in latex and vinyl gloves.

		Latex	Vinyl
Chlorine	Content[a] (ppm) RSD (%)	638.8 4.4	35.9 3.3
Sulphur	Content[a] (ppm) RSD (%)	7263.6 4.7	363.2 2.4

[a]Mean of three determinations

Summary

The CIC technique presented here provides a fully automated method of determining individual halogens and sulphur in a multitude of organic matrices — regardless of whether they are in liquid, solid, or gaseous form. Following combustion digestion of the samples, the combustion products containing halogens and sulphur are collected in an oxidizing absorption solution and determined as halogenides and sulphate during the subsequent ion chromatography process.

By measuring the light intensity, a sensor tracks the progress of the combustion digestion and ensures that the samples combust fully. Complex samples no longer require method development because the optimum parameters for combustion digestion are selected according to the type and quantity of the sample.

References

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