Combustion Ion Chromatography

Sulfur and Halogen Determination

This article looks at a fully automated combustion ion chromatography (CIC) system that combines ion chromatography (IC) with a combustion unit. CIC allows the simultaneous trace analysis of halogens (F, Cl, Br, and I) and sulfur in any combustible sample matrix.

The assets of the method are demonstrated by presenting the determination of halogens and sulfur in a certified polymer standard, an S-Benzyl thiouoronium chloride sample, a PVC-containing power cable insulation material, and several fuel samples.

Introduction

The determination of the halogen and sulfur content in complex matrices is a challenge. Particularly the sample preparation is demanding, highly time-consuming, and error-prone.

The most prominent techniques for halogen determination in these materials include the determination of absorbable/total organic halogens (AOX/TOX), inductively coupled plasma mass spectrometry (ICP-MS), ion-selective electrodes (ISE) and ion chromatography (IC). However, either results are unspeciated sum parameters, or samples are difficult to bring into solution. These drawbacks can be overcome by using combustion IC (CIC).

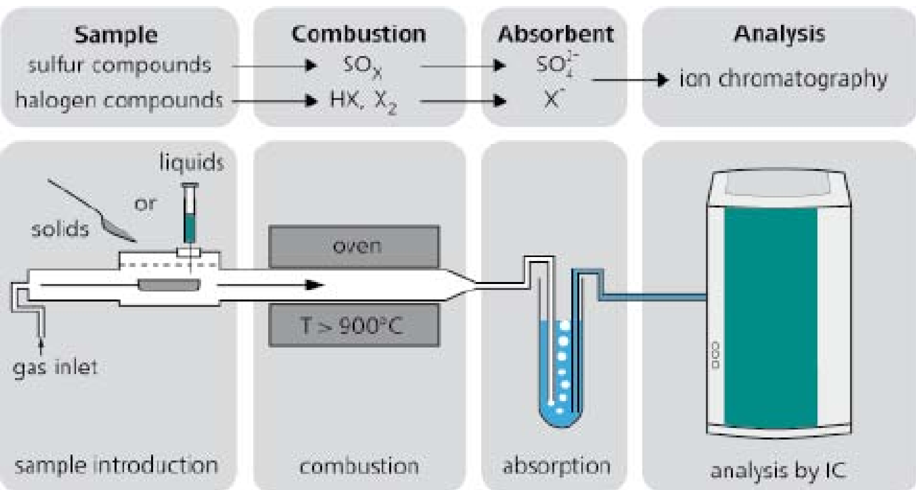

Fig. 1: Schematic illustration of the CIC system with sample introduction, combustion unit, gas absorption, and IC system

Experimental

Instrumentation

The sample introduction device automatically transfers the samples into the combustion unit, where pyrolysis takes place. The absorption solution assimilates the gaseous combustion products and is subsequently fed into the loop of the IC.

Principle

As shown in figure 1, pyrolysis takes place in the combustion system at temperatures above 900 °C. Sulfur-containing compounds are oxidized to sulfur dioxide (SO_2) and halogen-containing substances are transformed into hydrogen halides (X^-) or elemental halogens (X_2). These gaseous combustion products are fed into an oxidizing absorption solution and are subsequently detected as sulfate and halogenide by way of the ion chromatography that follows. While one chromatogram is being recorded, pyrolysis of the next sample is already under way. The MagIC Net software reliably controls the analysis and automatically calculates the sulfur and mass fractions for each sample.

Halogen and Sulfur Content

(a) in a Certified Polymer Standard

The certified polymer reference material is a low-density polyethylene granulate spiked with known amounts of chloride, bromide, and sulfur (table 1). It aims at testing the recovery and thus the accuracy and precision of the CIC method.

The results obtained by CIC for chloride, bromide, and sulfur are well within the known concentrations of the ERM-EC681k reference material. Recoveries between 96 and 103% demonstrate complete matrix destruction during combustion and the quantitative capture of gaseous halogen- and sulfur-containing compounds by the absorption solution.

(b) in S-Benzyl Thiouronium Chloride

A known amount of S-benzyl thiouronium chloride was automatically combusted and analyzed for its chlorine and sulfur content. Here too, recoveries between 97 and 101% demonstrate the applicability of the pyrolysis procedure for this organic compound class (table 2).

(c) in PVC-containing Cable Insulations

After metals, polymers form the most prevalent material fraction in electrical and electronic

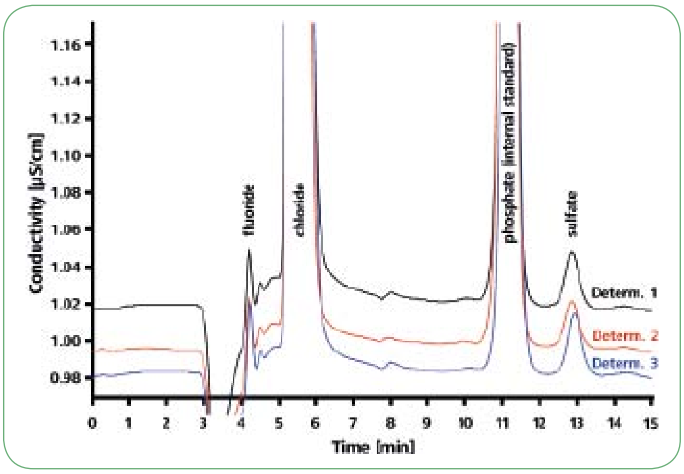

Fig. 2: Halogen and sulfur determination in three PVC-containing cable insulation materials

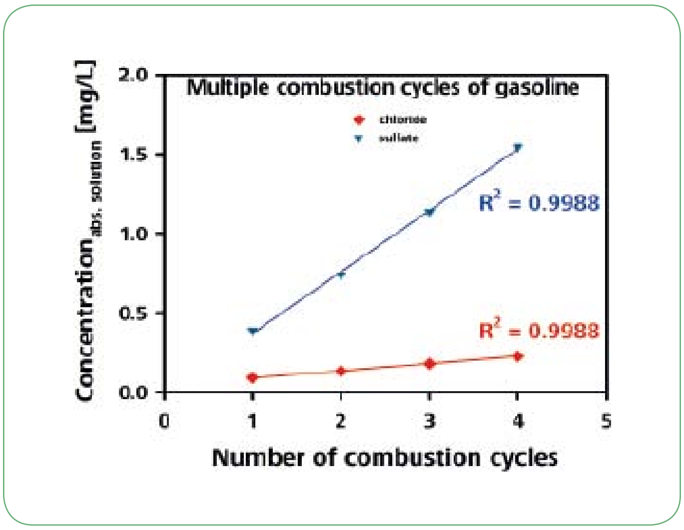

Fig. 3: Chloride and sulfate concentrations of combusted gasoline 95 against the number of combustion cycles. Chlorine and sulfur species from multiple combustion cycles of unleaded gasoline were absorbed in the very same absorption solution.

	ERM-EC681k standard known contents [mg/kg]	Experimental Content [mg/kg]	RSD [%]	Recovery [%]
Chloride	800.0 ± 50	800.3	0.6	100.0
Bromide	770.0 ± 40	742.1	0.9	96.4
Sulfur	630.0 ± 40	648.4	0.8	102.9

Table 1: Known and experimentally determined chloride, bromide, and sulfur concentrations of the certified polymer standard ERM-EC681k

	Chlorine (= 17.5%)[a]			Sulfur (= 15.8%)[a]		
	Content[b] [%]	RSD [%]	Recovery [%]	Content[b] [%]	RSD [%]	Recovery [%]
Sample 1	17.1	2.3	97.7	15.3	2.5	97.0
Sample 2	17.4	0.7	99.5	15.7	0.6	99.1
Sample 3	17.7	0.6	100.9	15.9	0.6	100.5

Table 2: Theoretical and experimentally determined chlorine and sulfur contents of S-benzyl thiouronium chloride ($C_8H_{11}SN_2Cl$; molecular weight: 202.7013 g/mol)
[a]calculated chlorine and sulfur content in S-benzyl thiouronium chloride
[b]mean of five determinations

equipment. Especially, the cheap and easy to process polyvinylchloride (PVC) is critical, because during fires PVC-coated cables release corrosive hydrochloric acid and toxic chloride-containing dioxins and furans. Therefore, halogen-free (also known as zero-halogen) electrical cables and wiring are increasingly used.

CIC is a helpful tool for determining whether the investigated materials comply with laws, standards, and requirements (IEC 60502-1, RoHS, …). In addition to a high chloride content of up to 25%, low amounts of fluoride (< 30 mg/l) and sulfate (< 75 mg/l) were determined (figure 2). Bromide, which elutes at approx. 9 min, was not detected.

(d) in Different Fuel Samples

Sulfur in fossil fuels is present in both inorganic ionic and organic-bound form. The first fraction mainly affects the motor performance in terms of precipitating salts. Organosulfur compounds, when combusted, emit detrimental sulfur dioxide with severe adverse environmental impacts. In view of these drawbacks, the sulfur content, whether in the inorganic ionic or in the chemically bound organic form, has to be controlled. Whereas the water-soluble inorganic ions can be selectively determined by IC coupled to upstream inline dialysis or extraction, the total organic sulfur content can be determined by CIC.

Chlorine concentration in all investigated fuels range between 4 and 8 mg/l (table 3). While sulfur concentrations in the unleaded gasoline and the two - mainly fossil - diesel samples are approximately 10 mg/kg, the sulfur content of the rapeseed biodiesel sample is significantly lower (3.8 mg/kg).

When multiple combustions are collected in the same absorption solution, as displayed in figure 3, there is a linear correlation between the concentration of the combustion products in the absorption solution and the number of performed combustion cycles. By collecting multiple ´burns´ into a single absorption solution, combustion IC achieves detection limits in the sub-ppm range.

Conclusions

The automated CIC system allows straightforward inline combustion and is designed to quantitatively trap the gaseous combustion products in an oxidizing absorption solution for subsequent ion chromatographic analysis. Sample preconcentration is achieved by trapping analytes from multiple combustion cycles in the same absorption solution. CIC is capable of determining sulfur and total speciated halogens down to 0.5 mg/l.

Application fields include the petroleum, coal, plastic, semi-conductor, and power generation industries as well as the environmental sector which are obliged to monitor banned toxic compounds as they are sources of corrosion or poison.

References are available from the authors.

	Unleaded gasoline 95		Diesel		Biodiesel blend B5[a]		Rapeseed biodiesel	
	Chloride	Sulfur	Chloride	Sulfur	Chloride	Sulfur	Chlorine	Sulfur
Content [mg/kg]	7.9	10.8	4.5	9.1	5.0	10.4	4.9	3.8
RSD [%]	2.3	1.0	1.3	1.1	1.2	1.1	3.1	1.5

Table 3: Chlorine and sulfur contents in different fuel types determined by CIC
[a]B5 blend consisting of 5% biodiesel and 95% fossil diesel

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