

## Summary

This Combustion IC system provides a fully automated method of detecting organic halogen and sulfur compounds in combustible samples. Following complete pyrolysis of the sample matrix, the combustion products containing halogens and sulfur are collected in an oxidizing absorption solution and determined as halogenides and sulfate during the next process, namely the IC separation. Offering outstanding detection limits in the lower ppm range, almost quantitative recovery rates, and the guarantee of high sample throughput thanks to the partially synchronized pyrolysis and separation processes, Combustion IC is an indispensable part in quality control. Furthermore, it is not restricted to plastic and fossil fuel analyses of the kind explained here. Combustion IC is also perfectly at home with samples from the pharmaceutical, power generation, environmental, and foodstuffs sectors.

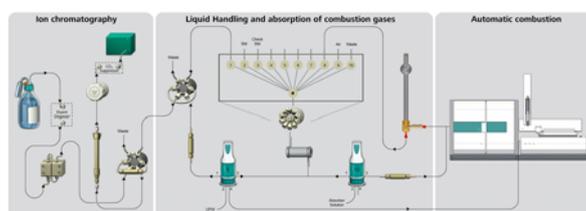
## Introduction

Determining halogen and sulfur content in complex matrices poses significant challenges for analysis processes – whether it involves checking halogen content in electrical and electronics devices (in compliance with IEC 61249-2-21, IEC 60502-1, and DIN EN 62321-3-2, for example), or determining the sulfur content of fuels to meet the requirements of DIN EN 228. Preparing samples of the components, polymers, or fuels to be analyzed is a particularly demanding task, usually requiring time-consuming, error-prone digestion processes that mostly take place offline.

The solution: an automated combination of instruments that incorporates both pyrolysis (combustion digestion) and Liquid Handling, plus the subsequent ion chromatography (IC) process, supports rapid, reliable analysis of halogen and sulfur content in all combustible samples.

## The principle: Liquid Handling at its best

The samples are first digested in an oven unit under an argon atmosphere and then burned with oxygen. During this process, small quantities of water are continually added, both in order to minimize deposits and glass corrosion in the pyrolysis oven and as a means of conveying the combustion gases into the absorption solution. The absorption solution contains H<sub>2</sub>O<sub>2</sub> so that the SO<sub>2</sub> can oxidize into sulfate. As the H<sub>2</sub>O<sub>2</sub> will disrupt the chromatography process, however, it is removed by Inline Matrix Elimination.



The sample digestion process that takes place in the Combustion Module is controlled automatically. Optical fibers guide the light generated in the pyrolysis oven during combustion to an optical sensor that measures the light intensity; this then serves as a control variable that regulates the feed of the sample boat into the oven and, as a result, optimizes the combustion process. In turn, this enables rapid, quantitative combustion without the formation of soot. Thanks to the automation behind this process of controlling sample digestion, there is no need for any time-consuming method development.

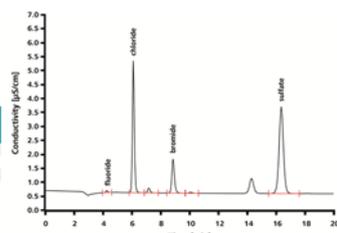
## Polymer standard ERM®-EC680k

A certified polymer standard, ERM®-EC680k (Institute for Reference Materials and Measurements, Geel, Belgium), is used to check the precision and accuracy of the Combustion IC system. This material is a low-density polyethylene granulate pre-concentrated with known quantities of chlorine, bromine, and sulfur. The recovery rates are evidence of the excellent precision and accuracy this method offers.

**Column:** Metrosep A Supp 5 - 150/4.0  
**Column temperature:** 30 °C  
**Eluent:** 3.2 mmol Na<sub>2</sub>CO<sub>3</sub>  
 1.0 mmol/L NaHCO<sub>3</sub>  
**Flow:** 0.7 mL/min

	ERM®-EC680k <sup>a</sup> certified content (mg/kg)	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
Sulfur	76.0 ± 4.0	75.2	3.6	99.0

<sup>a</sup>low-density polyethylene granulate spiked with known amounts of chlorine, bromine, and sulfur  
<sup>b</sup>mean of 3 determinations



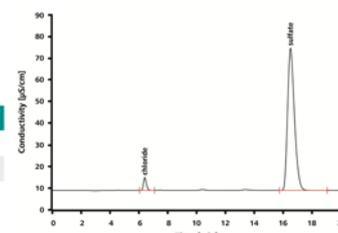
## Gloves in clean room environments

Gloves are used in clean room environments as a means of containing the ionic contamination found in perspiration from hands. Only halogen and sulfur-free materials 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 sulfates can get into these systems. Halogen and sulfur content is a key consideration when selecting the most appropriate materials for clean room environments.

**Column:** Metrosep A Supp 5 - 150/4.0  
**Column temperature:** 30 °C  
**Eluent:** 3.2 mmol Na<sub>2</sub>CO<sub>3</sub>  
 1.0 mmol/L NaHCO<sub>3</sub>  
**Flow:** 0.7 mL/min

		Latex	Veilto
Chlorine	Content [ppm]	638.8	35.9
	RSD [%]	4.4	3.3
Sulfur	Content [ppm]	2263.6	363.2
	RSD [%]	4.7	2.4

<sup>a</sup>mean of three determinations



## Standards

Standard	IC in international standards
ASTM D 7359-08	Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrolytic Combustion Followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)
VOP 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 Hydrolytic 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



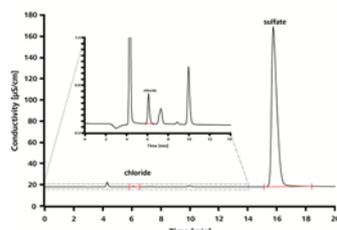
## Instruments

- 930 Compact IC Flex
- 920 Absorber Module
- Combustion Module (Analytik Jena)
- Autosampler MMS 5000 with sample rack

## Coal reference material NIST 2682b

During combustion, fossil fuels containing sulfur produce sulfur dioxide (SO<sub>2</sub>). This reacts with water and oxygen to create sulfuric acid – which, in the form of acid rain, has a harmful effect on the environment. Combustion Ion Chromatography provides a reliable means of determining sulfur and halogen content. The investigations carried out for the coal reference material NIST 2682b revealed recovery rates of 96.8% for sulfate and 103.4% for chlorine.

**Column:** Metrosep A Supp 5 - 150/4.0  
**Column temperature:** 30 °C  
**Eluent:** 3.2 mmol Na<sub>2</sub>CO<sub>3</sub>  
 1.0 mmol/L NaHCO<sub>3</sub>  
**Flow:** 0.7 mL/min



## Other applications

Combustion IC can also determine the sulfur and halogen content (absorbable/total organic halogens, AOX/TOX, even AOF) of the following products with ease:

- Substances with significance for the environment (oil, plastic waste, activated carbon)
- Electronics components (PCBs, synthetic resin, cables, insulating material)
- Fuels (gasoline, kerosene, crude oil, heating oil, coal, LPG, petroleum gas)
- Plastics (polymers such as polyethylene and polypropylene)
- Dyes (pigments, lacquers)
- Pharmaceutical products (raw substances, semifinished products, finished products)
- Foodstuffs (cooking oil, spices, scents and flavoring agents)

The 920 Absorber Module is suitable not only for Combustion IC, but also for directly absorbing gas compounds from the air. This means that it also acts as a semicontinuous online sampler for monitoring process waste gases or ambient air.