Combustion Ion Chromatography

Fast and reliable determination of halogens and sulfur using pyrohydrolysis

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Ω Metrohm

Combustion digestion and ion chromatography combined in one system

Combustion Ion Chromatography (CIC) extends the range of ion chromatography to all types of combustible samples. The focus is primarily on the simultaneous determination of the various halogens and sulfur in widely differing matrices.
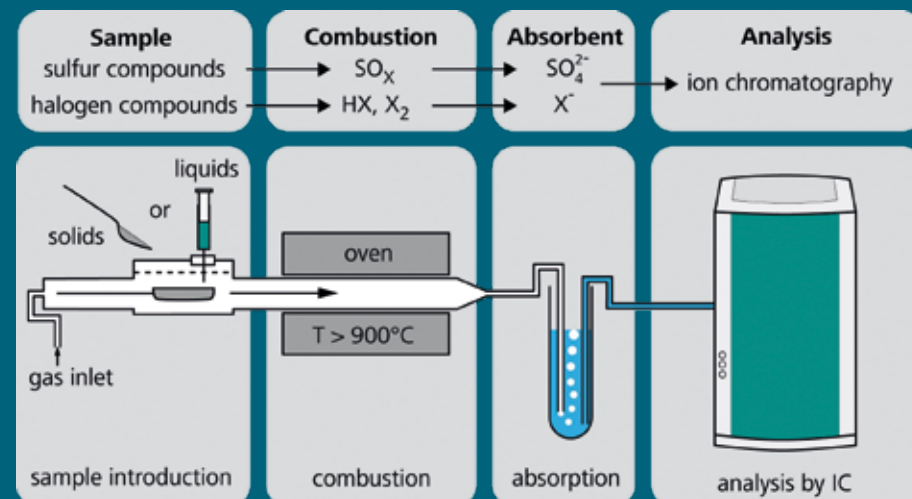
The Metrohm CIC System, including sample preparation, is completely automated. CIC is superior to offline digestion methods with regard to sample throughput on the one hand and precision and correctness of the results on the other. With CIC, unlike with alternative methods, the concentrations of the different halogens can each be determined separately.

How does CIC work?
In CIC the samples are pyrolized with oxygen and water (pyrohydrolysis) in an argon atmosphere. The resulting gaseous compounds are transferred into the 920 Absorber Module where they are collected in an absorption solution. This solution is injected into the IC system for subsequent analysis.

The CIC solution from Metrohm combines a combustion module from Analytik Jena (AJ) with an absorption module and an IC system from Metrohm. In the combustion module, sample matrices such as e.g. polymers or gasoline are digested by combustion in a special tube made of quartz glass.

Sample	Combustion	Absorbent	Analysis
sulfur compounds	SO_X	SO_4^{2-}	ion chromatography
halogen compounds	HX, X_2	X^-	

sample introduction — liquids or solids — gas inlet — oven — T > 900°C — combustion — absorption — analysis by IC

THE ADVANTAGES OF CIC AT A GLANCE

- Extends the range of IC to include all kinds of combustible samples (solid, liquid, gaseous)
- Simultaneous determination of sulfur and halogens
- Quantification of the concentration for each halogen
- Ideal for checking the latest analytical standards with regard to halogen-free products (RoHS, WEEE …)
- High sample throughput, precision, and accuracy
- MagIC Net ion chromatography software for control and data management – all information in one sample table or report

- Flame sensor ensures optimum combustion time with an universal method
- Compliance with FDA and GLP standards
- Calibration with just one standard thanks to Metrohm intelligent Partial Loop Injection Technique (MiPT)
- Fully automated sample preparation for solid and liquid samples with just one modular sample changer

APPLICATIONS

CIC is ideal for routine analysis in a variety of fields, as neither details about the nature of the sample matrix need to be known nor complicated method development is necessary. Not only is CIC recommended for quality control of raw materials, intermediates and finished products, but the method is also suitable for straigthforward and exact monitoring of compliance with the relevant laws, standards and regulatory requirements in the environmental field (e.g. DIN EN 228, IEC 60502-1, RoHS, WEEE, …).

Examples of areas and products where analyses are possible with CIC:
- environmentally relevant substances (oil, plastic waste, glass, activated carbon, …)
- electronic components (printed circuit boards, resin, cables, insulation, …)
- fuels (gasoline, kerosene, crude oil, heating oil, coal, butane, propane, natural gas, catalysts, …)
- plastics (polymers such as polyethylene, …)
- coloring agents (pigments, paints, …)
- pharmaceutical products
- foods (oils, spices, flavorings and fragrances, …)

COMBUSTION DIGESTION

Metrohm's CIC consists of a Combustion Module (Oven + ABD) from Analytik Jena and an absorption and IC part from Metrohm. In the Combustion Module the sample digestion can be controlled automatically: An optical fiber transfers the light emitted during combustion from the pyrolysis oven to an optical sensor which controls the feed rate of the sample boat into the oven. The duration of the combustion is optimized so that combustion is always complete (no soot formation), and there is no need for waiting times as a safety buffer.

Thanks to the automated control of sample digestion, method development for combustion is not needed. Different samples as well as different sample quantities can be subjected to one and the same universal «method». If norms have to be followed which define combustion for a specific time at a specific temperature, the sample inlet into the oven can also be programmed manually.

A flame sensor measures the intensity of light in the Combustion Module and controls the combustion digestion automatically.
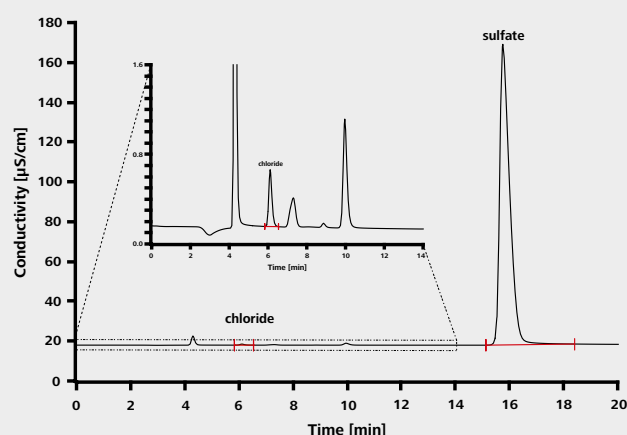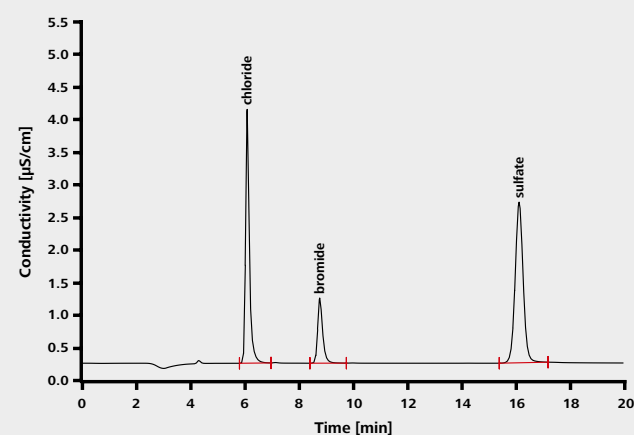
Chromatogram (left): Determination of halogens and sulfur in certified polyethylene pellets ERM-EC681k: chloride: 102.4%, bromide 95.4%, sulfur 100.3%. Injection volume 20 µL

Chromatogram (right): Determination of halogens and sulfur in coal reference material NIST 2682b: chloride: 103.4%, sulfur 96.8%. Injection volume 100 µL

Conditions (both analyses): Metrosep A Supp 5 - 150/4.0; eluent: 3.2 mmol/L Na_2CO_3, 1.0 mmol/L $NaHCO_3$, 0.7 mL/min; column temperature 30 °C; oven temperature 1050 °C; absorption solution: 100 mg/L H_2O_2

METROHM CIC COMPLIES WITH INTERNATIONAL NORMS AND STANDARDS LIKE FOR EXAMPLE …

- **ASTM D7359-18** Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)
- **UOP991-19** Chloride, Fluoride, and Bromide in Liquid Organics by Combustion Ion Chromatography (CIC)
- **ASTM D8247** Standard Test Method for Determination of Total Fluorine and Total Chlorine in Coal by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection
- **ASTM D7994-17** Standard Test Method for Total Fluorine, Chlorine, and Sulfur in Liquid Petroleum Gas (LPG) by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)

CIC AUTOMATION

The MMS 5000 Autosampler ensures fully automatic introduction of solid and liquid samples. With the appropriate kit for liquid or solid samples, respectively, this multi-matrix sampler can be converted in minutes without much effort. The combustion system is unaffected and can therefore be brought back into operation within a few minutes.

CIC automation. Solid or liquid samples – the MMS 5000 Autosampler can work with both.

Reliable operation under high pressure: LPG/GSS Module and LPG Module

The LPG/GSS Module makes it possible to analyze both liquefied gases (LPG) and gaseous samples (GSS) – such as natural gas – using Combustion IC. The LPG Module on the other hand allows only the analysis of liquefied gases, which however, may be subject to a higher primary pressure. The Dosing volume for all types of samples can be varied, something which even allows calibration of a wide concentration range without the need for an additional calibration gas standard. Moreover the separate flow paths for LPG and GSS in the LPG/GSS Module eliminate any risk of contamination.

MagIC Net controls the Gas Modules fully automatically. A special dosing valve that uses Peltier cooling is used for dosing liquefied gases, which prevents the sample from being released prematurely. Following the sampling process, the liquefied gas is vaporized in a heated chamber. This enables even components that are less easily volatilized to be brought into a gaseous state. The sample is fully transferred to the combustion system, a process that is also supported by a permanent flow of argon carrier gas. This prevents memory effects.

2.136.0720 LPG/GSS Module for analyzing gases in liquefied and gaseous states

2.136.0740 LPG Module for the analysis of LPG

KEY PARAMETERS FOR GAS ANALYSIS USING COMBUSTION IC

	LPG/GSS Module		LPG Module
Sample cylinder pressure	Max. 18 bar (260 psi)	Max. 250 bar (3625 psi)	Max. 31 bar (450 psi)
Pressure at sample valve	Determined by sample cylinder	0.7–1.7 bar, typically at 1 bar	Determined by sample cylinder
Sample volume	1–250 µL in 1 µL steps	1–65 mL in 250 µL steps	1–250 µL in 1 µL steps
Temperature of decompression chamber	85 °C	–	85 °C

Wide scope
of applications

RELIABLE

CIC is superior to offline digestion methods, not only with respect to sample throughput, but also in terms of precision and trueness of the results. Check standards for calibration and reference materials for the samples also increase the reliability of CIC.

FLAME SENSOR TECHNOLOGY

Whether solid or liquid samples are analyzed, or the amount of sample varies, the flame sensor optimizes the combustion process. This ensures fast, soot-free combustion.

STRAIGHTFORWARD OPERATION

Once the sample table has been created, the Combustion IC system operates entirely automatically. All parameters are controlled by MagIC Net software. The system is automatically switched off after a determination series, which saves costs in cases where for example expensive gases are being used.

HIGHLY FLEXIBLE

The MMS 5000 Autosampler makes the system highly flexible. The autosampler can be retrofitted to handle liquid samples instead of solid samples within a few minutes – meaning that just one autosampler is required. Moreover, there is no need to readjust the gas line when changing between different types of samples, saving valuable time.

STRAIGHTFORWARD CALIBRATION

Thanks to the Metrohm intelligent Partial Loop Injection Technique (MiPT), calibration can be performed rapidly, reliably, and – above all – automatically, using a single multi-ion standard. This saves time and is less prone to error.

NO INTERNAL STANDARD REQUIRED

MagIC Net documents all liquids that are dosed to the absorption solution. As a result, there is no need for an internal standard in the absorption solution. This prevents any undesirable dilution effects and also any interference between the internal standard and the analytes in the chromatogram.

930 Compact IC Flex

920 Absorber Module

Combustion Module (Oven + ABD) with MMS 5000 Autosampler

Perfect liquid handling – the 920 Absorber Module

In the Metrohm CIC System the combustion module and ion chromatograph are linked together by the 920 Absorber Module. The 920 Absorber Module ensures that the gaseous compounds of the analytes are brought into solution. The professional liquid handling also includes the input of water for combustion, matrix elimination of the hydrogen peroxide (oxidizing agent), and rinsing procedures.

Moreover, a single multi-ion standard may be used for an automated calibration of the system by means of the Metrohm intelligent Partial Loop Injection Technique (MiPT). Because MiPT allows flexible injection volumes (4–200 μL), a large concentration range can be covered.

The following items are available for the entire liquid handling: a 10-port valve, a 6-port injection valve and two patented Metrohm 800 Dosino Dosing Units.

The 920 Absorber Module can also be used as a semi-online sampler for direct absorption of gas compounds (NH_3, HNO_2, HNO_3, HCl, SO_2) from the air. In this way, for example, volatile acids (hydrochloric acid, sulfuric acid) can be monitored in process flue gases or in the ambient air at workplaces.
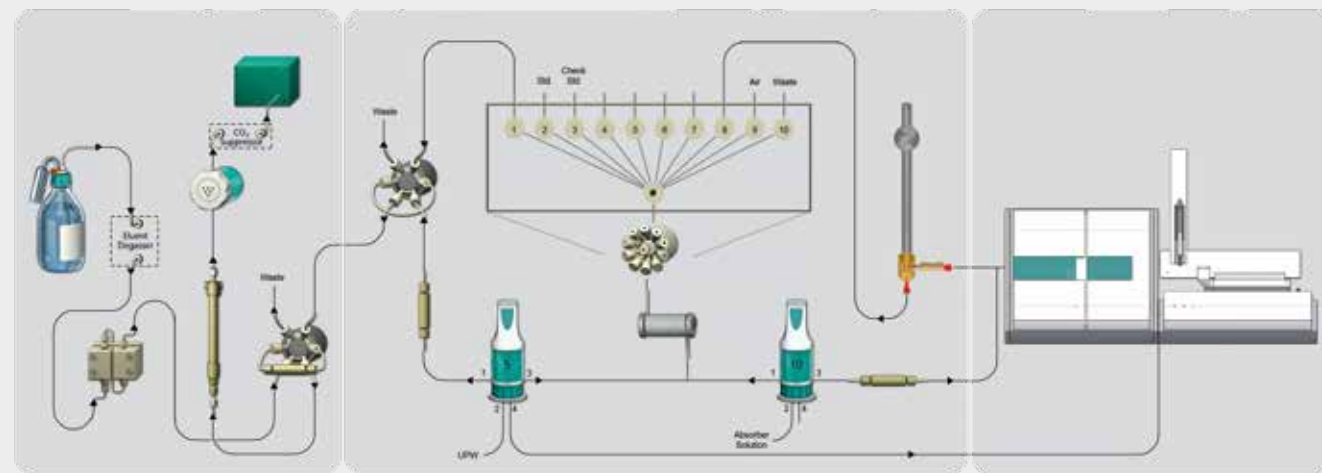
Straighforward control with MagIC Net software

The complete CIC system is controlled by MagIC Net, the proven software for ion chromatography. MagIC Net offers great flexibility with regard to configuration, layout and method programming. Several monitoring and control functions are available to the user. MagIC Net meets all FDA and GLP requirements and is also available in numerous languages. A modern data management system and a powerful report generator round off the package.

MagIC Net guarantees easy, robust, and reliable handling of the system. The user is able at all times to keep an overview of all the liquid quantities that are introduced into the absorption solution. Consequently, it is possible to work without an internal standard or other tools.

930 Compact IC Flex   920 Absorber Module   Combustion Module

ORDERING INFORMATION

Instrument		
Metrohm markets the complete system, including installation, service and training – all from the same supplier.		

Combustion IC packages		
2.930.9010	**930 Combustion IC PP (AJ). The package includes:**	
	2.930.2560	Compact IC Flex Oven/SeS/PP/Deg
	2.850.9010	IC Conductivity Detector
	2.920.0010	Absorber Module
	2.136.0700	Combustion Module (Oven + ABD, AJ)
	6.2832.000	MSM Rotor A
	6.2842.020	Adapter for Vario for MSM
	6.6059.321	MagIC Net 3.2 Compact
	6.1006.340	Metrosep A PCC 2 HC/4.0
2.930.9020	**930 Combustion IC DR (AJ). The package includes:**	
	2.930.2460	Compact IC Flex Oven/SeS/Deg
	2.850.9010	IC Conductivity Detector
	2.920.0010	Absorber Module
	2.136.0700	Combustion Module (Oven + ABD, AJ)
	6.2832.000	MSM Rotor A
	6.2842.020	Adapter for Vario for MSM
	6.6059.321	MagIC Net 3.2 Compact
	6.1006.340	Metrosep A PCC 2 HC/4.0
	2.800.0020	800 Dosino
	6.3032.120	Dosing Unit 2 mL
2.136.0700	Combustion Module (Oven + ABD, AJ)	
2.136.0710	Auto Boat Drive (AJ)	
2.136.0720	LPG/GSS Module (AJ)	
2.136.0730	Combustion Module (Oven + LPG/GSS, AJ)	
2.136.0740	LPG Module (AJ)	
2.136.0750	Combustion Oven (AJ)	
6.7304.030	Oven coupling for LPG/GSS (AJ)	

Sample changers	
2.136.0800	MMS 5000 Autosampler (AJ)
6.7302.000	Kit for solid samples for MMS 5000, 35 positions
6.7303.000	Kit for liquid samples for MMS 5000, 112 positions

Columns	
6.01032.420	Metrosep A Supp 17 - 150/4.0
6.01032.500	Metrosep A Supp 17 Guard/4.0

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