Total Chlorine, Bromine and Sulfur in Low-Density Polyethylene (LDPE)

Low-density polyethylene (LDPE) is a thermoplastic made from the monomer ethylene. LDPE is used for the manufacturing of various packaging materials (e.g. plastic bags, packaging foam), containers (e.g. dispensing bottles, wash bottles) and plastic films. Additives may be used to improve the physical properties of LDPE. Halogenated sulfur-containing compounds are often added as plasticizers, flame retardants, and heat stabilizers. The halogen and sulfur content need to be monitored due to the high usage of LDPE and its impact on the environment. Most governments around the world implemented legislation to monitor these elements and limit its quantities in various products.

Combustion IC enables the determination of speciated halides and sulfur compounds by a single analysis. TE Instruments developed a fully automated, extremely compact sample preparation system covering the oxidative pyrohydrolytic combustion, fraction collection, and sample injection towards the IC. In this application note, the LDPE European reference standard 'ERM-EC680K' is analyzed to demonstrate the well-functioning of the XPREP C-IC.

Solution

XPREP C-IC with NEWTON Autosampler

NEWTON Autosampler with Boat Inlet

Summary

The XPREP C-IC has been used to perform automated sample preparation for Combustion IC analysis. The XPREP C-IC covers the pyrohydrolitic combustion, fraction collection, and IC injection of samples. Good recoveries of the ERM-EC680K standard containing targeted ions (Cl, Br, S), were obtained with the boat introduction module for combustion and subsequent analysis by the IC.

Sample information

Sample Type	Low-density polyethylene (ERM-EC680k)
Component	Chlorine, Bromine and Sulfur
Concentration	80 – 184 mg/kg
Method Applicable	-

Results – Conventional Boat Inlet System

Sample	Sample amount mg	Cl mg/kg	Br mg/kg	S mg/kg
1	79.0	90.2	192.7	87.5
2	80.5	83.8	187.4	83.7
3	78.7	83.6	180.0	80.1
4	78.6	82.1	185.8	84.4
5	85.8	77.3	176.0	78.3
6	87.0	83.9	190.8	85.0
7	80.9	77.9	177.0	82.7
8	82.1	82.4	187.6	85.2
9	80.7	82.3	181.6	76.9
10	81.4	82.0	184.9	78.4
Average	-	82.6	184.0	82.2
RSD (%)	-	4.3	3.0	4.3
Certified value	-	84	181.0	86.0
% Recovery	-	98.3	101.9	95.6

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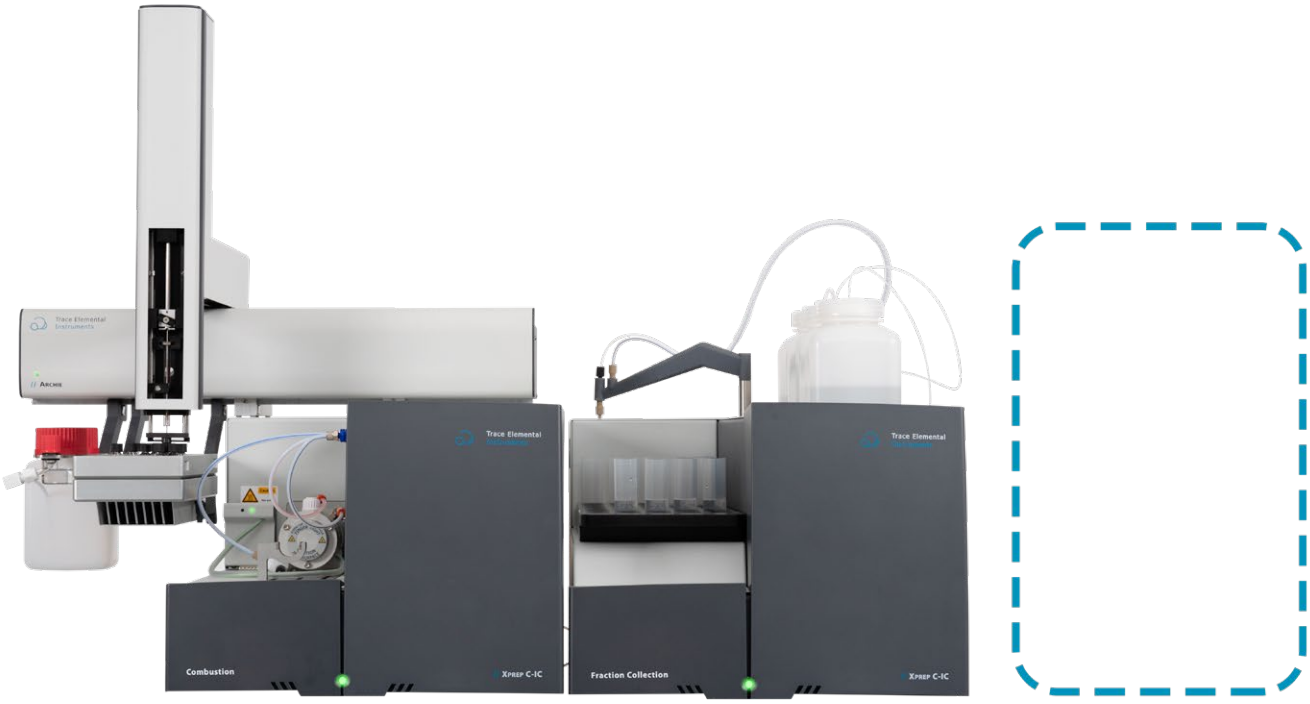
System Description

Introduction - The NEWTON solids auto sampler automatically introduces the quartz cups carrying the weighed-in solid sample into the boat introduction module. Once analyzed and cooled down, clean sample cups are retrievable from the clean cup collection point and ready to be re-used again.

Combustion - The Combustion Unit is fitted with a dual-zone furnace. Every sample is completely oxidized by pyrohydrolitic combustion in an oxygen-rich environment at high temperature. The specially developed pyrohydrolitic combustion tube includes a single-stage capturing and collision flow technique. The single stage capturing filter protects the downstream flow path against soot deposition. The capturing filter is "self-cleaning", as it continuously regenerates itself by the high temperatures and presence of oxygen flow.

Collection - After combustion, absorber solution is added automatically to the output gas stream to guarantee a complete absorption of the analytes in the fraction collection unit. In this process the H-X, X_2 and SO_x are converted to F^-, Cl^-, Br^-, I^- and SO_4^{2-}. All these negatively charged ions will be separated in the IC column. Up to 65 combusted samples can be absorbed and stored in the individual absorption vials. The collected samples can be transferred to the IC immediately or stored for analysis at a later stage.

IC-Injection - Once sample preparation has been finalized, the absorbent containing the analytes is automatically transferred from the fraction collection unit towards any renowned IC. The internal syringe pumps of the collection unit load and rinse the IC sample loop. A six-way-valve and 100 µL sample loop are by default integrated at the front of the fraction collection unit. This sample loop may be used to fill the pre-concentrator when present in the IC.



Combustion **Fraction Collection** **IC System**

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System Settings

	Boat Inlet
Oxygen flow	300 mL/min
Argon flow	100 mL/min
Oxygen collision flow	100 mL/min
Furnace temperature I	750 °C
Furnace temperature II	1000 °C
Introduction module	Quartz Boat Module
Sample amount Combustion unit	~ 80 mg
Absorption solution	10 mg/L hydrogen peroxide
Absorption tubes	23 mL
Typical volume absorption tubes	10 mL
Sample loop IC	100 µL

Boat program

Position (mm)	Speed (mm/s)	Pause (s)
95	5	60
100	5	180
200	5	120
20	10	0

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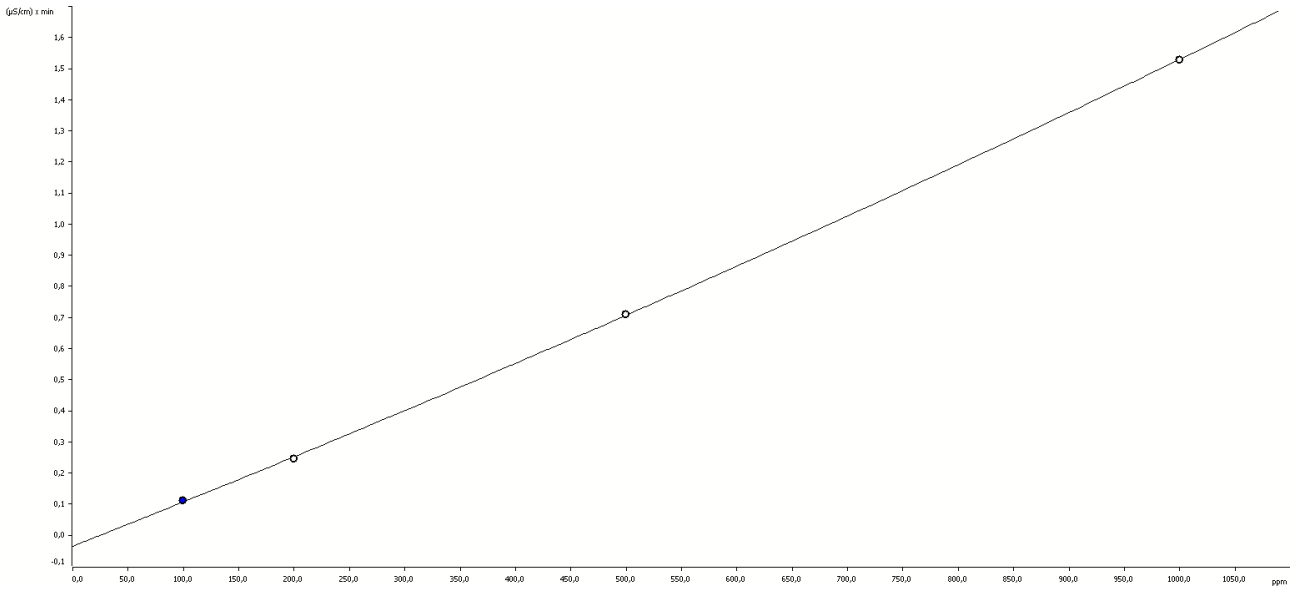
Calibration

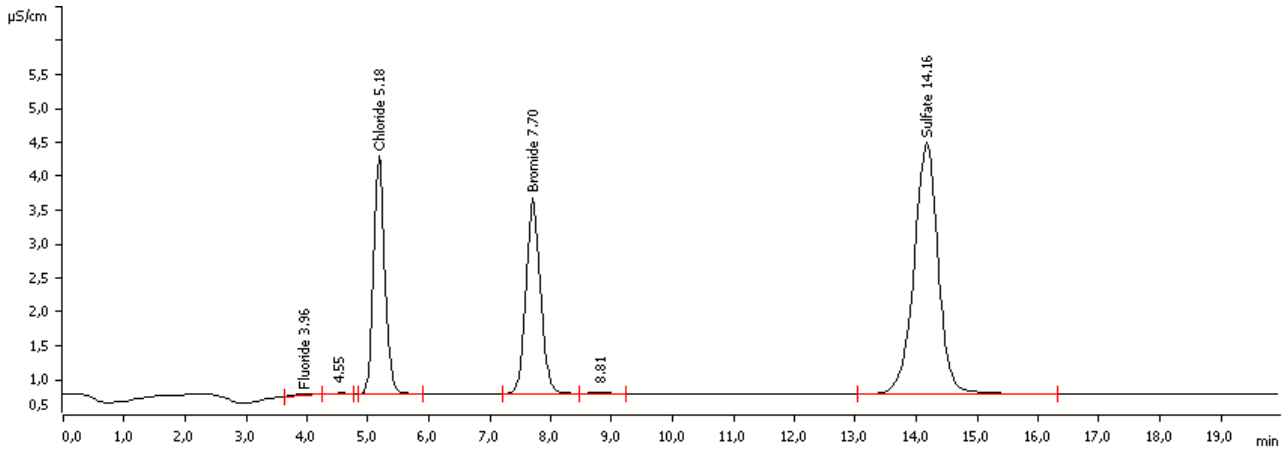
The standards used to calibrate the IC are made of Fluorobenzene (F), Chlorobenzene (Cl) and Thiophene (S) in Xylene. The IC has been calibrated in the range of 0 – 1000 mg/L (0, 100, 200, 500, 1000). The total bromine calibration curve is provided as an example below. All calibration curves used in this application note have a correlation coefficient (r^2) greater than 0.995.



Calibration line – Bromine

r^2: 0.9999

Calibration



Low-density polyethylene (ERM-EC680k)

Concentrations: 82.6 mg/kg (Cl), 184 mg/kg (Br), 82.2 mg/kg (S)

Replicates: 10

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