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APPLICATION UPDATE 72588

Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion IC with a carbonate/bicarbonate eluent

Authors
Manali Aggrawal and Jeffrey Rohrer
Thermo Fisher Scientific,
Sunnyvale, CA, USA

Keywords
Combustion Ion Chromatography (CIC), Dionex IonPac AS23 column, suppressed conductivity detection, polymer, Dionex Aquion IC

Goal

To develop a CIC method for the determination of Cl, Br, and S in all forms of plastic materials

Introduction

Polyethylene (PE) is a thermo-plastic created from the polymerization of ethylene, a process that produces long straight chains of hydrocarbon monomers. By adjusting the polymerization process, different kinds of polyethylene with varying degrees of branching in their molecular structures can be made. PE compounds are classified by their molecular weight, density, and branching into major categories; the most common are linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and ultrahigh molecular weight polyethylene (UHMWPE). Different polymer materials are used for different purposes. Polyethylene is widely used in packaging (plastic bags, plastic films, containers including bottles, etc.). Plastic materials consist not only of plastic polymers, as many additives are used to improve different properties of the plastic.[1]

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Some additives prevent degradation of the polymer during processing (typical for polyvinyl chloride (PVC)), while others improve resistance to fire or prevent degradation by environmental factors (e.g., UV, temperature, humidity, microorganisms). Halogen and sulfur-containing compounds are often added as plasticizers, flame retardants, and heat stabilizers. Due to the widespread use of plastic/polymers and their subsequent impact on the environment, it is important to know the content of the halogens and sulfur when polyethylene materials are disposed or recycled. Many countries are adapting to regulate these substances.[2]

Plastic samples can be very difficult to analyze as sample preparation is required to extract analytes or remove interfering matrices, and these sample preparation techniques can be labor intensive. Combustion ion chromatography (CIC) has been demonstrated for the determination of halogens and sulfur in a variety of difficult samples including coal.[3]

In Application Note 72349, a Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4µm anion-exchange column was combined with a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, which used an electrolytically generated potassium hydroxide (KOH) eluent and suppressed conductivity detection, to determine halogens and sulfur in plastic materials.[4] This application update reports an alternative method using carbonate/bicarbonate eluent with a Thermo Scientific™ Dionex™ Aquion™ IC system. The Dionex Aquion IC system is a simple, inexpensive, and compact platform with straightforward operation for basic ion analysis. The Thermo Scientific™ Dionex™ IonPac™ AS23 carbonate eluent anion-exchange column is used for this application. Here we demonstrate that a Mitsubishi™ AQF-2100H combustion system combined with Dionex Aquion IC system can be used for automated qualitative and quantitative analysis of halogens and sulfur in plastic samples. Four plastic samples were analyzed for their chlorine (Cl), bromine (Br), and sulfur (S) content. Method accuracy was evaluated using a polymer certified reference material (ERM EC680K) for Cl, Br, and S and spike recovery experiments for each analyte.

Experimental

Equipment

Thermo Scientific Dionex Aquion IC system including:

- Dual Piston Pump
- Column Oven Temperature Control
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2 SR5

Mitsubishi™ AQF-2100H system, comprised of:

- Electric Furnace, HF-210
- Gas Absorption Unit, GA-210
- External Solution Selector, ES-210
- Automatic Boat Controller, ABC-210

Consumables

- Thermo Scientific™ Dionex™ AS23 Eluent Concentrate; Sodium Carbonate/Bicarbonate Concentrate (100×); P/N 0641611
- Dionex IonPac AS23 Analytical, (2 × 250 mm); P/N 064145
- Dionex IonPac AG23 Guard, (2 × 50 mm); P/N 064143
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor (2 mm); P/N 082541

Instrument setup and installation

Configuring the modules in the Chromeleon CDS software

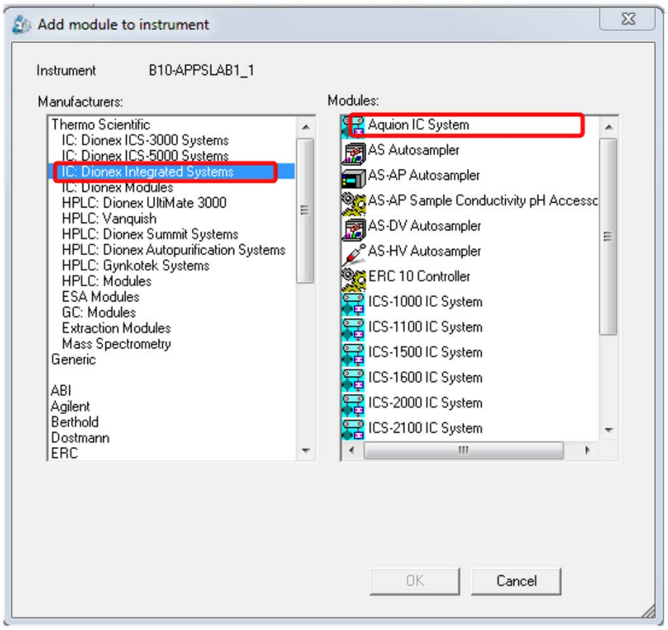
To configure the IC system:

1. Start the Chromeleon Instrument Controller program.
2. Select the link, Configure Instruments, to open the Chromeleon Instrument Configuration Manager.
3. Right-click on the local computer name.
4. Select Add an Instrument.
5. Enter an appropriate name (for example: AquionCIC).
6. Add the following modules to this instrument configuration: Aquion IC system and Remote Inject, as detailed below.

Adding Dionex Aquion IC system module

1. Select Add a Module, Aquion IC System (Figure 1). A window with multiple tabs will automatically open up.
2. Select the Model Serial No. on the General tab. (Figure 2)

The Mitsubishi AQF-2100H system communicates with the Dionex Aquion IC system using TTL signals.



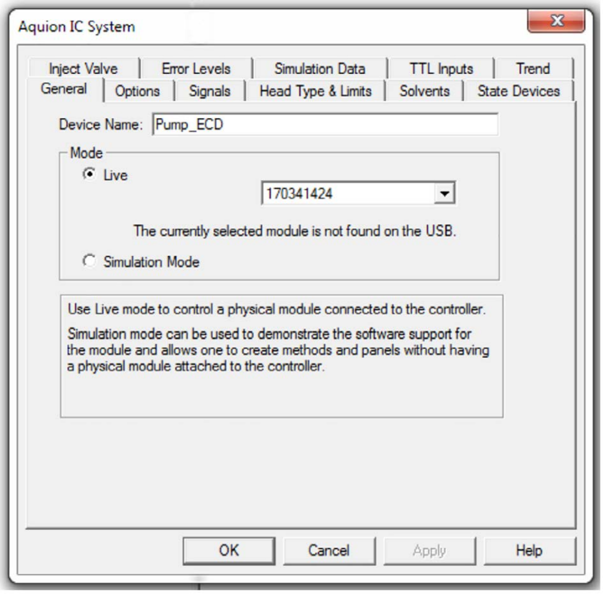
Add module to instrument

Instrument B10-APPSLAB1_1

Manufacturers: IC: Dionex Integrated Systems

Modules: Aquion IC System

Figure 1. Creating a configuration.



Aquion IC System

Device Name: Pump_ECD

Mode

● Live 170341424

The currently selected module is not found on the USB.

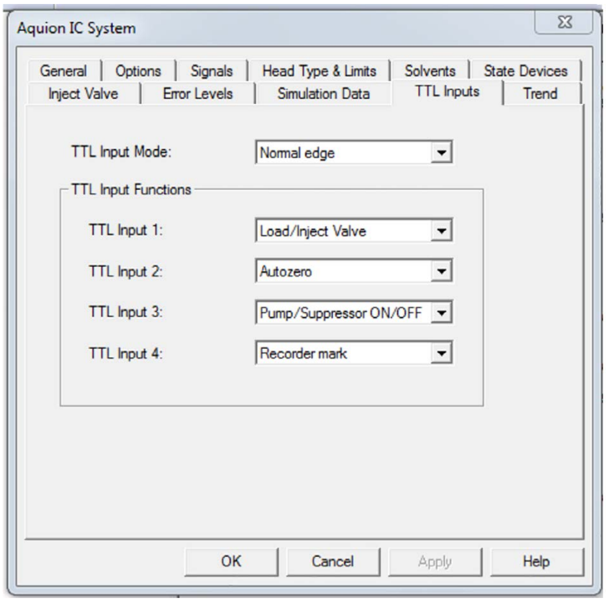
○ Simulation Mode

Use Live mode to control a physical module connected to the controller.

Simulation mode can be used to demonstrate the software support for the module and allows one to create methods and panels without having a physical module attached to the controller.

Figure 2. Selecting model serial number.

3. Open the TTL inputs and make the selections shown in Figure 3.



TTL Input Mode: Normal edge

TTL Input 1: Load/Inject Valve

TTL Input 2: Autozero

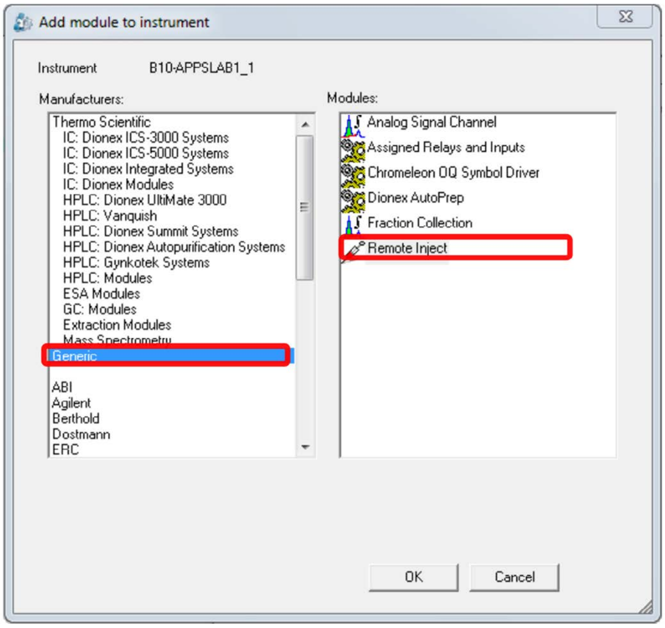
TTL Input 3: Pump/Suppressor ON/OFF

TTL Input 4: Recorder mark

Figure 3. Dionex Aquion TTL inputs.

Adding Remote Inject Module

Select Add a Module, Generic, and Remote Inject (Figure 4). The default device name is InjectValve and needs to be renamed (for example: InjectValve_CIC). Select Remote Start on Inject Port (Figure 5).



Instrument B10-APPSLAB1_1

Manufacturers:

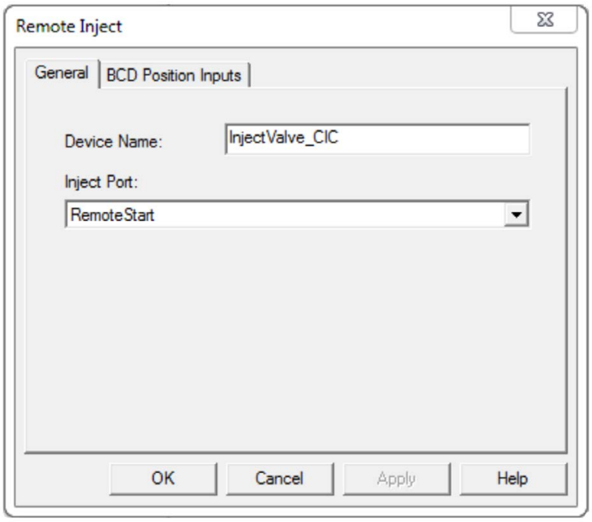
Thermo Scientific
  IC: Dionex ICS-3000 Systems
  IC: Dionex ICS-5000 Systems
  IC: Dionex Integrated Systems
  IC: Dionex Modules
  HPLC: Dionex UltiMate 3000
  HPLC: Vanquish
  HPLC: Dionex Summit Systems
  HPLC: Dionex Autopurification Systems
  HPLC: Gynkotek Systems
  HPLC: Modules
  ESA Modules
  GC: Modules
  Extraction Modules
  Mass Spectrometry
Generic

ABI
Agilent
Berthold
Dostmann
ERC

Modules:

Analog Signal Channel
Assigned Relays and Inputs
Chromeleon OQ Symbol Driver
Dionex AutoPrep
Fraction Collection
Remote Inject

Figure 4. Adding the Remote Inject Module to the instrument.



Device Name: InjectValve_CIC

Inject Port: RemoteStart

Figure 5. Configuring the Remote Inject Module.

Physical TTL connections

With a pair of twisted wires, make the connections in Table 1 (Figures 6 and 7).

Table 1. TTL connections.

	Dionex Aquion IC System	Mitsubishi AQF-2100H System
Red Wire	TTL-1 IN	1
Black Wire	TTL GND 1	2

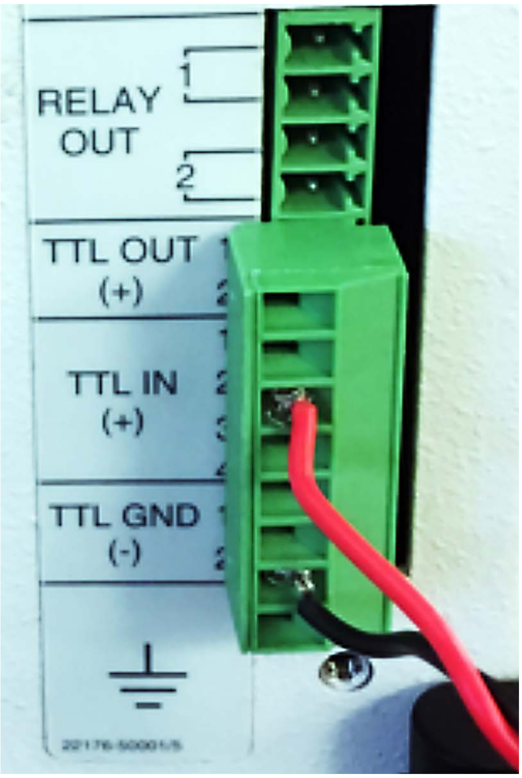


Figure 6. TTL connections at the rear panel of the Mitsubishi AQF-2100H system.

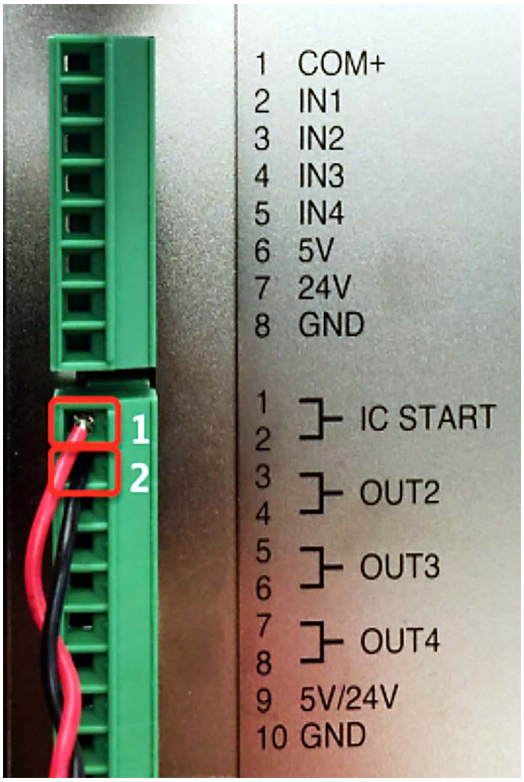


Figure 7. TTL connections at the rear panel of the Dionex Aquion IC system.

Direct injection using the injection valve in the Mitsubishi GA-210 module

This is the most common combustion IC setup. In this setup, the sample loop is installed on the Mitsubishi GA-210 injection valve. When the sample is ready for IC analysis, the Mitsubishi GA-210 module loads the sample loop. The schematic is shown in Figure 8. This setup is recommended for isocratic applications with pressures up to 3000 psi. Please see Technical Note 72211 for more details.[5]

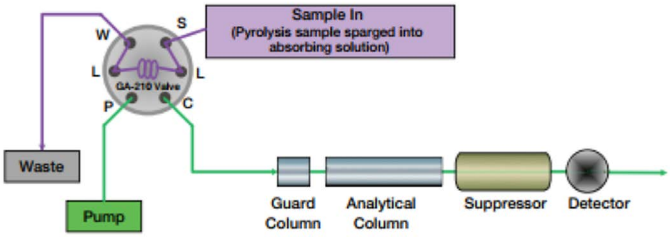


Figure 8. Direct injection using the injection valve in the Mitsubishi GA-210 module.

Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistance or better
- Thermo Scientific™ Dionex™ Combined Seven Anion Standard I, 50 mL (P/N 056933)
- Thermo Scientific™ Dionex™ Chloride Standard (1000 mg/L), 100 mL (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)
- Potassium bromide, Crystal BAKER ANALYZED® ACS Reagent (P/N 2998-01)
- European Reference Material ERM® - EC680K Polyethylene (Trace Elements Low Level), ~100 g, ARMI/LGC standards

Table 2A. Combustion parameters.

AQF-2100H	
Sample size:	~20–35 mg (2–3 pellets)
Sample boat:	Quartz
Pyrolysis tube:	Quartz tube / Quartz wool
Absorption solution:	H_2O_2 aqueous solution (30 ppm)
Mode:	Constant volume
HF-210	
Furnace inlet temp.:	900 °C
Furnace outlet temp.:	1000 °C
Argon flow (Carrier):	200 mL/min
Oxygen flow (Combustion agent:	400 mL/min
GA-210	
Absorption tube:	10 mL
Sample loop:	100 µL
Final absorption solution volume:	10 mL
Absorption solution volume*:	3.5 mL
Water supply scale:	3
Argon flow for humidification:	100 mL/min
GA-210 washing parameters	
Water injection time:	20 s
Drain time:	12 s
Washing times:	3
Gas line washing time:	0.5 s
Gas line washing interval:	3 s
Gas line washing times:	3
Washing time of sample absorption line:	5 s
Syringe washing times:	3
GA-210 gas line collection parameters	
Collection time:	0.5 s
Collection interval:	3.0 s
Times:	3

*This is the starting absorption volume. Final absorption volume is adjusted to a constant about 10 mL and is determined accurately according to the manual.[6]

Table 2B. Combustion parameters (continued).

GA-210 injection parameters		
Washing time for injection start:	0 s	
Sample purge time:	5 s	
Sample absorption time:	10 s	
ABC-210/ASC-250L		
Argon time:	10 s	
Oxygen time:	600 s	
Position (mm)	*Wait time (s)*	*Speed (mm/s)*
130	90	20
160	90	0.12
End	90	20
Cool	60	40
Home	120	40

Table 3. IC parameters.

IC parameters	
System:	Dionex Aquion IC
Columns:	Dionex IonPac AS23 Analytical, 2 × 250 mm Dionex IonPac AG23 Guard, 2 × 50 mm
Eluent:	4.5 mM Na_2CO_3/ 0.8 mM $NaHCO_3$
Flow rate:	0.36 mL/min
Column temp.:	30 ˚C
Detection:	Suppressed conductivity with Thermo Scientific™ Dionex™ ERS™ 500 Electrolytically Regenerated Suppressor, recycle mode
Suppresser current:	9 mA
System backpressure:	~2500 psi
Background conductance:	~18.5–19.5 µS
Noise:	~8.4–10 nS/min peak-to-peak
Run time:	18 min

Preparation of solutions and reagents

1000 mg/L stock chloride solution

Dionex Chloride Standard (1000 mg/L), 100 mL (P/N 037159)

1000 mg/L stock sulfate solution

Dionex Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)

1000 mg/L stock bromide solution

Weigh 0.149 g of dry potassium bromide into a 125 mL polypropylene bottle and tare the balance. Add 100 g of DI water to make a 1000 mg/L bromide stock solution. Cap the bottle and shake to completely dissolve the solid material. The standard is stable for one week when stored at 4 ˚C.

Working standard solutions

Deliver the appropriate volume of the 1000 mg/L stock solution into a 125 mL polypropylene bottle and bring to volume (by weight) with DI water. For this application, calibration standards were prepared at 0.1, 0.2, 0.4, 0.5, 0.75, and 1.25 mg/L. Aliquots were stored at –40 ˚C and thawed prior to use.

Results and discussion

By using a CIC system consisting of an automatic quick furnace AQF-2100H and Dionex Aquion Ion Chromatography (IC) system, the concentrations of halogens and sulfur were determined in plastic materials. Combustion and IC parameters used for this application are listed in Tables 2 and 3. About 20 to 35 mg of plastic sample are weighed in a quartz sample boat and introduced into system, where the sample is thermally decomposed in argon (Ar) atmosphere, then combusted in oxygen atmosphere. Halogens in the sample are converted to hydrogen halide, and halogen gas and sulfur to sulfur oxide. These components are collected into absorbing solution and converted to halide ion and sulfate ion. For sulfur-containing samples, hydrogen peroxide is added to the absorbing solution to oxidize hydrogen sulfite, resulting from the incomplete oxidation of sulfur, which will be quantified as sulfate in aqueous solution. The resulting solution is analyzed by injecting into an IC system. The Dionex IonPac AS23 column can be used with isocratic carbonate/bicarbonate eluents and suppressed conductivity detection. Due to the higher background conductivity of the carbonate eluent, the carbonate peak does not interfere with the analysis of most of the common anions. However, achieving very low detection limits using a carbonate/bicarbonate eluent system can prove difficult. Figure 9 shows the chromatogram of the combusted plastic certified reference material (ERM-EC680K) containing the anions chloride, bromide, and sulfate separated with a Dionex IonPac AS23 column. The run time is 18 min, slightly longer than that with hydroxide eluent on the Dionex Integrion HPIC system.[4] Depending upon the need, faster run times can be achieved with other carbonate eluent anion-exchange columns such as the Dionex IonPac AS22 fast column.[7]

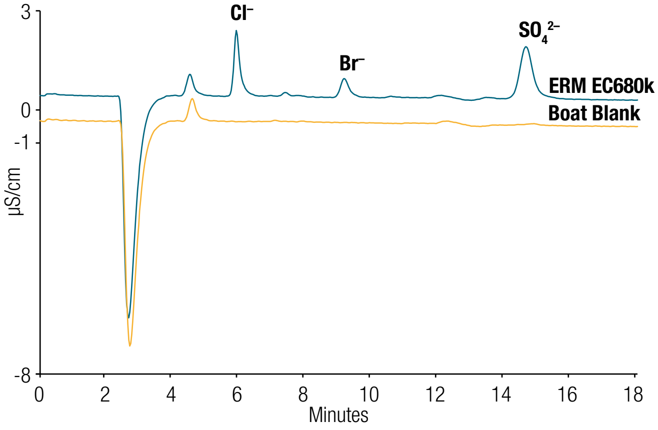


Figure 9. Chromatogram of ERM EC680K.

Calibration

There are two methods for calibration. Method 1 uses direct injection of liquid standards through the External Solution Selector ES-210. In this method, calibration standards containing the components of interest are injected and measured directly through IC. Using the calibration curve of each component, the concentration of the component in the sample is calculated using the formula below:

$$\text{Concentration (mg/L)} = \text{Cc} * \text{A} * \frac{1}{\text{s}} * 1000$$

Cc is component concentration (mg/L), A is absorption solution at constant volume (mL), and s is sample weight in mg. Absorption solution at constant volume is determined following instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual.[6] The dilution factor is approximately 10,000 when a 10 mL absorption tube is used. The weight of sample (S) and dilution factor (A*1000) are then entered into the data sequence pane of the Chromeleon CDS software console window, which automatically calculates the concentration of the component in the sample.

Method 2 uses injection of liquid standards through the Liquid Sample Changer Module ASC-250L. In this method, standard solution prepared with organic solvent is injected into the combustion unit where it is first combusted and then measured by IC. Using the calibration curve of each component, the concentration of each component in the sample is calculated:

$$\text{Concentration (mg/L)} = \text{Cc} * \frac{1}{\text{s}}$$

Because both the standards and samples are combusted in the same way, the dilution correction factor is not needed. Only the weight of each sample is entered into the data sequence pane of the Chromeleon CDS software.

Sample analysis

Four plastic materials listed in Table 4 were analyzed for their Cl, Br, and S content. Figure 10 shows chromatograms of plastic samples (1, 2, 3, and 4) containing various anions. Besides chloride and sulfate, fluoride, nitrite, and nitrate are also observed in these samples. The concentrations of anions (Cl, Br, and S) were calculated using the calibration method 1 as discussed above in calibration section. Bromide was not found in any of the four samples analyzed. This could be that because of bromide's toxicity it is no longer used as a plastics additive. Sample #2 (transfer pipette) was found to contain very little or almost no chlorine and sulfur. In the samples, sulfur was found to be in low concentration except for in Sample #3 (plastic wrap) where it was almost 60 mg/L. Plastic wrap contains mostly PVC material and PVC has high amounts of sulfur-containing organotin compounds used as heat stabilizers.

Table 4. List of plastic materials used in this study.

Sample #	Sample	Polymer Type
1	Wash bottle	LDPE
2	Transfer pipette	LDPE
3	Plastic wrap	Mostly PVC
4	Bubble wrap	LDPE or HDPE

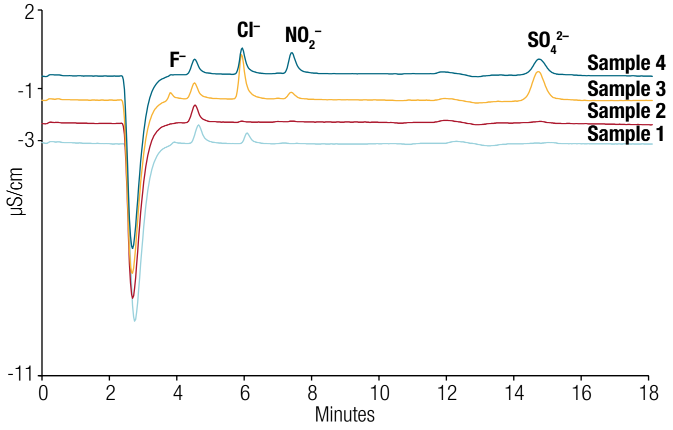


Figure 10. Chromatograms of polymer samples 1,2, 3, and 4.

Precision and accuracy

The precision and accuracy for Cl, Br, and S were evaluated using a certified reference material of low-density polyethylene (EC680k), by European Reference Materials (ERM, Belgium). Table 5 lists the amount of Cl, Br, and S along with their certified values. The percent relative standard deviation (RSD) is less than 2.0 % for all three anions indicating good precision. The recovery is in the range 98–100%.

Table 5. Amount of chlorine, bromine, and sulfur in ERM EC680K.

Sample	Chlorine (ppm)	Bromine (ppm)	Sulfur (ppm)
1	100	94.7	74.0
2	102	96.1	77.1
3	102	95.5	74.8
4	100	95.0	75.8
5	100	95.0	77.1
6	102	93.8	76.4
7	101	94.7	77.3
8	100	95.4	74.5
Average	101	95.0	75.9
Certified value	102	96	76
% Recovery	98.7	99.0	99.8

Recovery

For the recovery experiment, the plastic sample was spiked with CRM pellets and then the percentage recovery was calculated using the equations below:

$$\text{Recovery \%} = \frac{\text{C spiked sample - C unspiked sample}}{\text{C added}} * 100$$

$$\text{C spiked sample} = \text{Cc} * \text{A} * \frac{1}{\text{Weight of plastic sample}} * 1000$$

$$\text{C unspiked sample} = \text{Cc} * \text{A} * \frac{1}{\text{Weight of plastic sample}} * 1000$$

$$\text{C added} = \text{Cc} * \text{A} * \frac{1}{\text{Weight of CRM pellet}} * 1000$$

where Cc is the component concentration (ppm) obtained from the chromatogram, A is the absorption solution at constant volume (mL) determined following the instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual.[6]

Figures 11, 12, 13, and 14 are the chromatograms of the spiking experiment for samples 1, 2, 3, and 4, respectively. Table 6 contains spike recovery results for chloride and sulfate in the four plastic samples. The percent recovered ranged from a low of 87.8% to a high of 128% for chloride and 88.8% to 96.4% for sulfate.

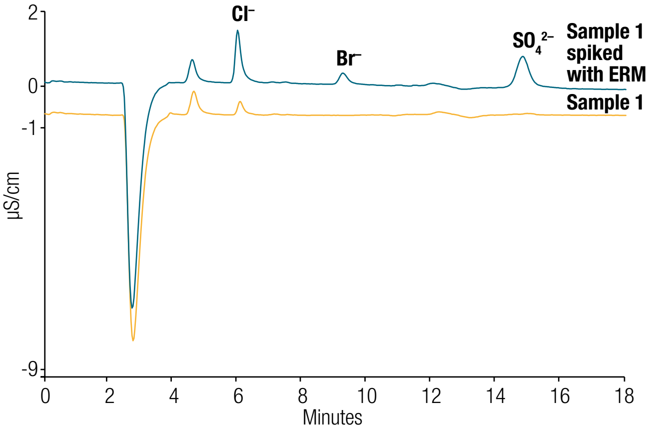


Figure 11. Chromatograms of unspiked sample 1, and sample 1 spiked with ERM pellet.

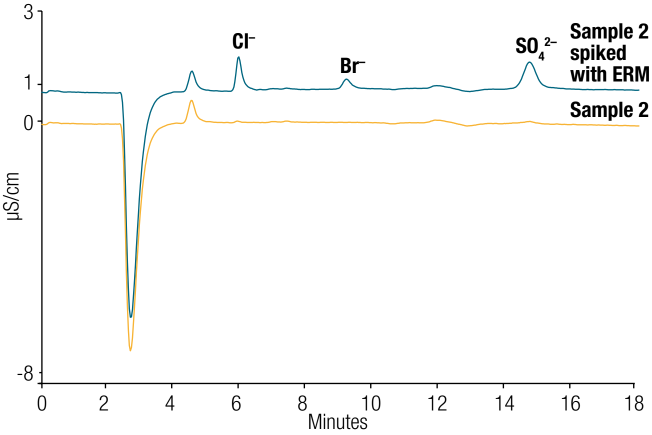


Figure 12. Chromatograms of unspiked sample 2, and sample 2 spiked with ERM pellet.

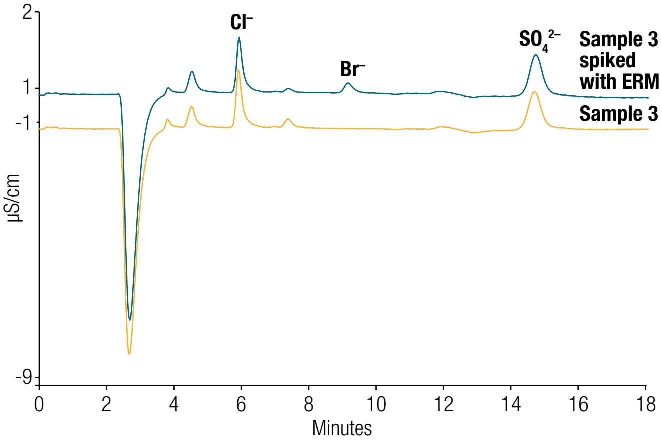


Figure 13. Chromatograms of unspiked sample 3, and sample 3 spiked with ERM pellet.

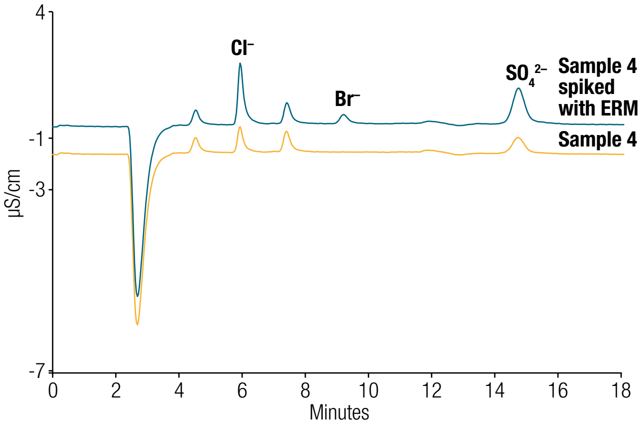


Figure 14. Chromatograms of unspiked sample 4, and sample 4 spiked with ERM pellet.

Table 6. Spike recovery for samples 1, 2, 3, and 4.

	Unspiked (ppm)	Added (ppm)	Spiked (ppm)	Recovery (%)
Sample #1				
Chlorine	20.6	98.6	135	116
Sulfur	0	82.2	76.6	93.2
Sample #2				
Chlorine	3.09	95.8	106	107
Sulfur	2.30	79.5	75.5	92.1
Sample #3				
Chlorine	90.4	97.5	176	87.8
Sulfur	62.0	76.9	130	88.8
Sample #4				
Chlorine	55.3	98.1	181	128
Sulfur	30.8	79.9	108	96.4

Conclusion

The results demonstrate that the Dionex Aquion IC system combined with the Mitsubishi AQF-2100H system can be used for both qualitative and quantitative analysis of Cl, Br, and S in plastic samples. The method was validated using certified reference material ERM EC680K with recoveries within 98 to 100%. This automated method is simple, easy to use, saves time, and produces fewer environmental contaminants than other sample preparation procedures, such as acid digestions or back extractions from organic solvents. This analysis will allow polymer manufacturers to monitor halogen/sulfur concentration levels to ensure compliance with government regulations.

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