

Determination of halogens in polymers and electronics using a combustion ion chromatography system

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Keywords

IEC 62321-3-2, Dionex IonPac
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Goal

Develop a test method to quantify halogens (fluorine, chlorine, bromine, and iodine) in polymers and electronics using combustion ion chromatography (CIC) that includes a Mitsubishi® Automatic Combustion Unit Model AQF-2100H system and a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system.

Introduction

The widespread use of electronic products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adaptation of regulations affecting wastes, substances, and energy use of electronic products (e.g. JS709B and Restriction of Hazardous Substances (RoHS)). The use of certain substances, such as lead (Pb), cadmium (Cd), and polybrominated diphenyl ethers (PBDEs), in electronic products is a source of concern in current and proposed regional legislation. According to the U.S. Environmental Protection Agency, the amount of consumer electronic waste in the U.S. has nearly doubled since 2000. Given the widespread and growing use of electronic products, the amount of waste can only be expected to increase, thus raising concern about the potential effects on the environment and human health. While hazardous metals such as mercury and

lead are routinely accounted for when considering the environmental impact of electronic waste, the traditional use of halogens in the polymer components of consumer products is also important.

IEC 62321-3-2 specifies the screening analysis of halogens (fluorine, chlorine, bromine, and iodine) in homogeneous materials found in polymers and electronics by combustion ion chromatography (CIC).¹ CIC provides a fast and reliable method for measuring the halogen content of various consumer products and the associated waste streams.

Combustion methods have been developed that ensure complete decomposition of solid and semi-solid samples and concomitant release of halogens. These methods include the use of the Wickbold apparatus, combustion (oxygen) bombs, Schöniger flask, microwave-induced combustion, and automated furnace combustion systems such as the one described here.²

CIC uses the thermochemical decomposition of organic matter in the presence of oxygen (oxidative pyrolysis) to convert the analytes of interest to gases. The combustion by-product gases, including HX and SO₂/SO₃, are passed through an aqueous absorbing solution and directly injected into the IC instrument, thereby eliminating the sample matrix and any associated interferences (Figure 1). The absorbing solution used is dependent on the anions of interest. Typically, deionized water

is used for halides or an aqueous hydrogen peroxide solution if halides and sulfur are being determined. The hydrogen peroxide is required to ensure all the sulfur anions are oxidized to sulfate prior to injection into the ion chromatography (IC) system. The fully automated process of CIC saves time and labor, increases reproducibility, and eliminates the need to dispose of hazardous chemicals used in acid digestions or back extractions.

This application note describes a simple CIC method to determine halogens in polymers for electrotechnical products and electronics. Polymer and electronic samples were homogenized by cryogenic grinding, combusted in the Mitsubishi AQF-2100H system, and then directly injected into a Dionex Integriion HPIC system with a Thermo Scientific™ Dionex™ IonPac™ AS17-C column set.

Experimental Equipment

- Mitsubishi Automatic Quick Furnace AQF-2100H system including:
 - Solid Auto Sampler ASC-240S
 - Horizontal Furnace HF-210
 - AQF-2100H Mullite Pyrolysis Set (P/N AQ3QM5)
 - Gas Absorption Unit GA-210
 - External Solution Selector ES-210

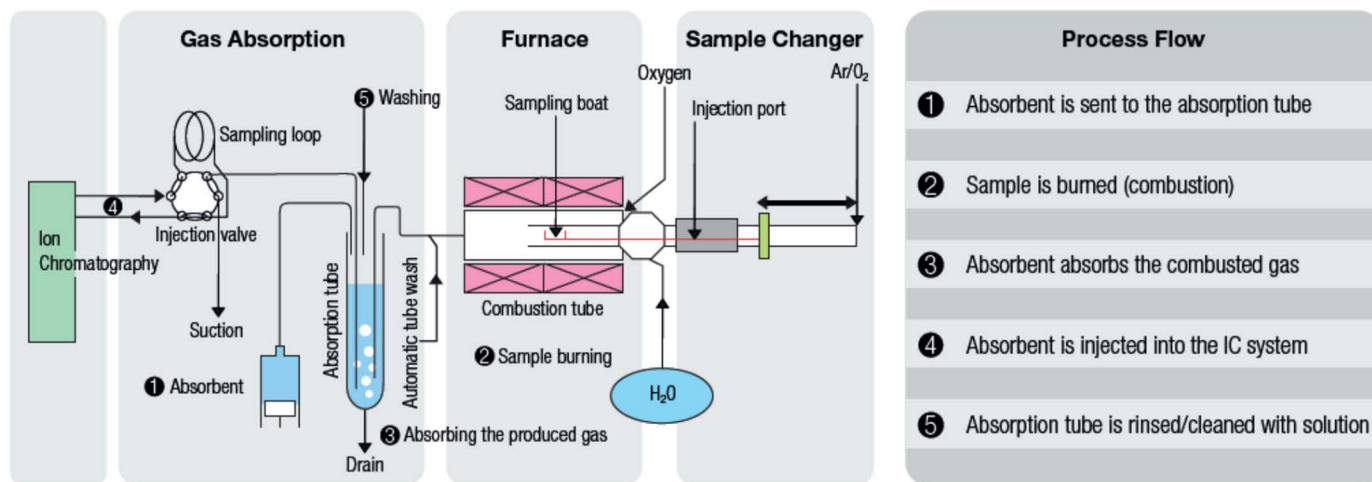


Figure 1. Diagram of a CIC system.

- Dionex Integriion HPIC system including:
 - Eluent Generator
 - Pump
 - Degasser
 - Conductivity Detector
 - Column Oven Temperature Control
 - Detector-Suppressor Compartment Temperature Control
 - Tablet Control
- SPEX SamplePrep 6770 Freezer/Mill® Cryogenic Grinder

HPIC consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)
- Thermo Scientific™ Dionex™ IC PEEK™ Viper™ Fitting Tubing Assembly Kits (P/N 088798)

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System software version 7.2 SR4
- Mitsubishi NSX-2100 software, version 2.1.6.0

Reagents and standards

Reagents

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistivity or better filtered through a 0.2 μm filter immediately before use.

Standards

- Thermo Scientific™ Dionex™ Combined Seven Anion Standard I, 50 mL (P/N 056933)
- Sodium bromide, (Granular/Certified ACS), Fisher Chemical™ (Fisher Scientific™ P/N S255-500)
- Sodium chloride, (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N S271-500)
- Sodium fluoride, (Powder/Certified ACS), Fisher Chemical (Fisher Scientific P/N S299-500)
- Sodium iodide, (Crystalline/Certified), Fisher Chemical (Fisher Scientific P/N S324-500)
- Hydrogen peroxide, 50% (Stabilized/Certified), Fisher Chemical (Fisher Scientific P/N H341-500)
- European Reference Material (ERM®) - EC680k Polyethylene (Trace Elements Low Level), ~100 g, ARMI/LGC Standards
- Oxygen, ultrahigh purity, GR 4.4
- Argon, ultrahigh purity, GR 5.0

Samples

- Four polymer samples were provided without specific identification, but we know they include an acrylonitrile butadiene styrene (ABS), an epoxy molding compound (EMS), and a polyethylene (PE).
 - Polymer Sample 1
 - Polymer Sample 2
 - Polymer Sample 3
 - Polymer Sample 4
- One printed circuit board (PCB) sample from scrap at Thermo Fisher Scientific in California

IC Conditions

Columns:	Dionex IonPac AG17-C Guard, 4 × 50 mm (P/N 066295) Dionex IonPac AS17-C Analytical, 4 × 250 mm (P/N 066294)
Eluent Source:	Dionex EGC 500 KOH Eluent Generator Cartridge with CR-ATC 600 trap column and high pressure EG degasser
Eluent:	1 mM KOH 0–3 min, 10 mM 3–10 min, 35 mM 10–18 min, 1 mM 18.1–20 min
Flow Rate:	1.0 mL/min
Column Temp.:	30 °C
Detector Compartment Temp.:	25 °C
Conductivity Cell Temp.:	35 °C
Injection Volume:	100 µL (Full Loop)
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500 Electrolytically Regenerated Suppressor (4 mm), recycle mode, 87 mA
System Backpressure:	~2300 psi
Background Conductance:	~ 0.3 µS
Run Time:	20 min

Combustion Conditions

Mass Combusted:	15–50 mg for Polymer Samples 1–4 1–10 mg for Sample PCB
Furnace Inlet Temp:	900 °C
Furnace Outlet Temp:	1000 °C
Argon Flow (Carrier):	200 mL/min
Oxygen Flow (Combustion Agent):	400 mL/min
Humidified Argon Flow (Water Supply):	100 mL/min
Humidified Argon Pump Setting (Water Supply Scale):	2
Pyrolysis Tube:	Quartz tube with ceramic insert and quartz wool
Sample Boat:	Ceramic
Absorption Solution:	H ₂ O ₂ 900 mg/kg
Absorption Tube Volume:	10 mL
Absorption Solution Volume:	3.5 mL
AQF Mode:	Constant Volume
Burning Aids:	Tungsten oxide (WO ₃ , 40 mg) only for Sample IIS3-D04
Automatic Boat Controller Program:	Table 1 for Polymer Samples 1–4 Table 2 for PCB Sample

Table 1. ABC210 program for Polymer Samples 1–4.

Position (mm)	Wait Time (s)	Speed (mm/s)
50	30	5
95	60	1
120	60	0.06
160	30	5
END	300	5
Cool	60	40
Home	200	20

Ar time 0 (s); O₂ time 300 (s)

Table 2. ABC210 program for Sample PCB.

Position (mm)	Wait Time (s)	Speed (mm/s)
85	30	10
135	30	10
END	360	10
COOL	60	10
Home	120	20

Ar time 0 (s); O₂ time 600 (s)

Preparation of standards

Stock solution

To prepare the 1000 mg/L stock solution, accurately weigh the amounts of standard compounds listed in Table 3, transfer to a 100 mL volumetric flask, and fill to the mark with DI water. Mix thoroughly and store at 4 °C.

Table 3. Amounts of compounds used to prepare 100 mL of 1000 mg/L stock solutions.

Anion	Compound	Mass (mg)
Bromide	Sodium Bromide	128.8
Chloride	Sodium Chloride	164.9
Fluoride	Sodium Fluoride	221.0
Iodide	Sodium Iodide	118.1

Working standard solutions

Prepare the highest concentration working standard solutions (8 mg/L) by pipetting the appropriate amount of 1000 mg/L stock into a 100 mL volumetric flask and diluting to the mark with DI water. Prepare the 0.005,

0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 8.0 mg/L (Cl) and 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 8.0 mg/L (F, Br, I) standard solution mixes by diluting the highest concentration working standards with DI water. When the standard solutions are not in use, store at 4 °C.

Preparation of hydrogen peroxide solution

Add 1.8 mL of H₂O₂ (w = 50%) to 998.2 mL of degassed DI water to prepare 1 L of 900 mg/kg H₂O₂.

Sample preparation

The test sample is homogenized by the cryogenic grinder with a magnetically driven impactor. The impactor is inserted into the vial along with the sample to be ground, and this assembly is then placed into the coil assembly within the mill, which is lowered into the liquid nitrogen bath. Grinding is accomplished by alternating the magnetic field in the coil assembly forcing the impactor into the end caps. The most important aspect for a successful grinding procedure is the sufficient cooling of the milling material to ensure brittleness of the sample. To this end, the filled vial is inserted into the opening of the coil assembly and immersed into a liquid nitrogen bath. For brittleness the sample was left in the nitrogen bath for approximately 12 min. Subsequently, the sample was ground for three minutes. After waiting for one minute to ensure brittleness, the sample was ground again. Three of these cycles were performed, which corresponds to a grinding time of nine minutes. For this grinding program, approximately eight grams of starting material were used.

System preparation and configuration

Dionex Integrion HPIC system

Install, hydrate, and condition the Dionex EGC 500 KOH eluent generator cartridge, the Dionex CR-ATC 600 trap column, and the Dionex AERS 500 suppressor. Finish the system setup according to the product manuals and the Dionex Integrion HPIC system Operator's Manual.^{3,4} Install and condition the guard and separation columns for 30 min prior to installing the column in line with the suppressor.

Combustion system

This application requires the use of a ceramic (mullite) pyro-tube insert. Refer to the Mitsubishi AQF-2100H instruction manual for complete system setup.⁵

Constant volume determination

Make a 2–5 mg/L phosphate standard and compare the peak area counts of the peak via direct injection to that from dilution into the adsorption tube of the gas adsorption unit (GA-210). Multiply this peak area ratio by the dispense volume of the adsorption solution (set as 8 mL in the GA parameter) to get the final volume of the absorption solution before injection into the IC. (See Equation 1).

Recovery Study

In this study, chloride was selected for the recovery study. To be certain that our measurement is accurate, the homogenous samples were spiked with ERM pellets.

Results and Discussion

Separation

Standard halide solutions were prepared in DI water and directly injected into the IC system to obtain the required calibration curves. Figure 2 shows the separation of calibration standards. Fluoride, chloride, bromide, and iodide were well resolved within 20 min.

Linearity

To determine the linear calibration ranges, the peak responses to concentration were determined using triplicate injections of calibration standards. Table 4 shows the linear concentration ranges, the coefficients of determination (r^2), and retention time and peak area precisions of three replicate injections. Plotting peak area versus concentration demonstrated linearity for the concentration ranges used, as exemplified by the chloride calibration curve (Figure 3), bromide calibration

Columns: Dionex IonPac AG17-C Guard, 4 × 50 mm
 Dionex IonPac AS17-C Analytical, 4 × 250 mm
 Eluent: 1 mM KOH 0-3 min, 10 mM 3-10 min,
 35 mM 10-18 min, 1 mM 18.1-20 min
 Eluent Source: Dionex EGC 500 KOH cartridge with CR-ATC 600
 Temperature: 30 °C
 Flow Rate: 1 mL/min
 Inj. Volume: 100 µL
 Detection: Dionex AERS 500 suppressor, 4mm, recycle mode, 87 mA
 Peaks: 1. Fluoride 1 mg/L
 2. Chloride 1
 3. Bromide 1
 4. Carbonate
 5. Iodide 1

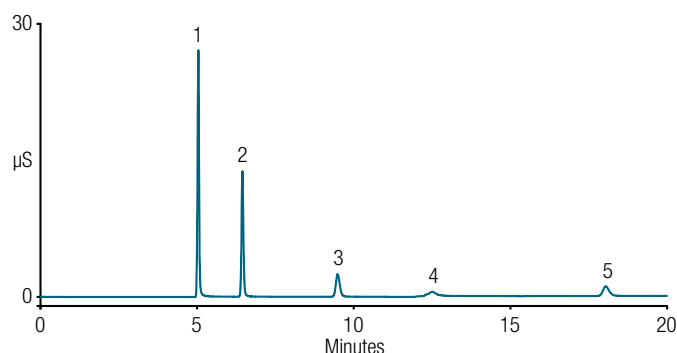


Figure 2. Separation of an anion standard mixture.

curve (Figure 4), and iodide calibration curve (Figure 5). The exception was fluoride, which exhibited a quadratic relationship to concentration (Figure 6). Coefficient of determinations (r^2) ranged from 0.9996 to 0.9999. The excellent retention time stability and peak area precision are consistent with results typically obtained when using an electrolytically generated high-purity potassium hydroxide eluent. The use of an electrolytically generated potassium hydroxide eluent further simplifies the method by eliminating the time required to manually prepare eluents.

Equation 1.

$$\text{Constant volume (mL)} = (\text{Absorption Solution Volume}) \left(\frac{\text{Area of Direct Injection}}{\text{Area of Dilute Injection}} \right) = 8 \left(\frac{\text{Area of Direct Injection}}{\text{Area of Dilute Injection}} \right)$$

Table 4. Linearity and retention time and peak area precisions (n=3).

Analyte	Range (mg/L)	Coefficient of Determination (r^2)	Cal. Type	Peak Area Precision (RSD)	Retention Time Precision (RSD)
Fluoride	0.1–8	0.9996	Quad, WithOffset	<0.5	<0.2
Chloride	0.005–8	0.9999	Lin, WithOffset	<0.5	<0.2
Bromide	0.1–8	0.9999	Lin, WithOffset	<0.5	<0.2
Iodide	0.1–8	0.9997	Lin, WithOffset	<0.5	<0.2

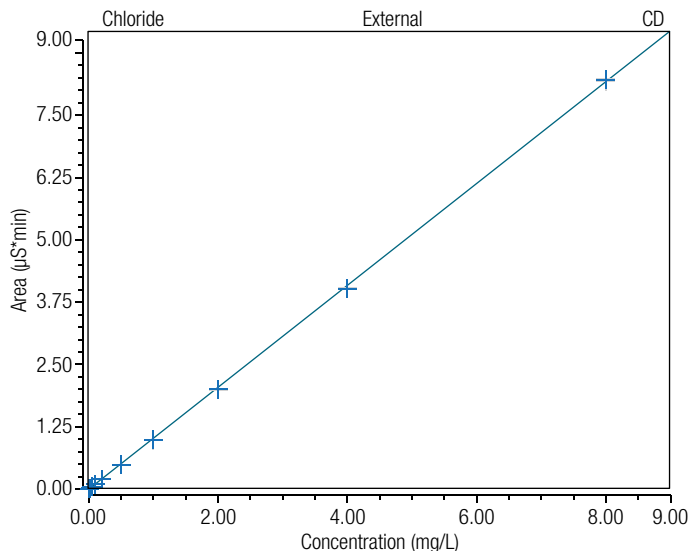


Figure 3. Chloride calibration curve.

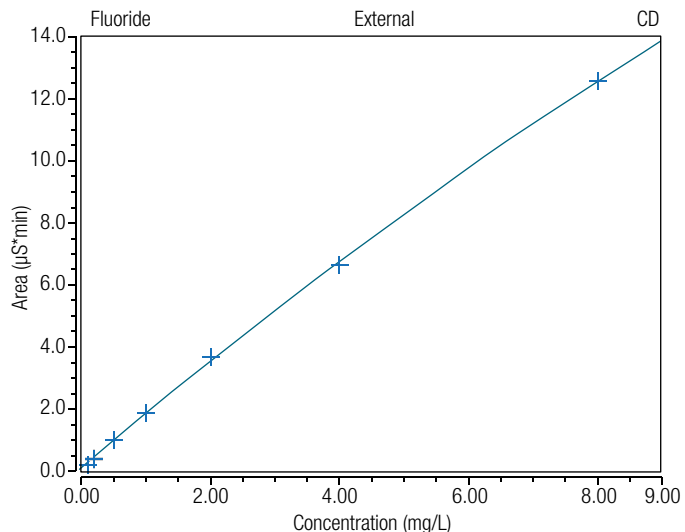


Figure 6. Fluoride calibration curve.

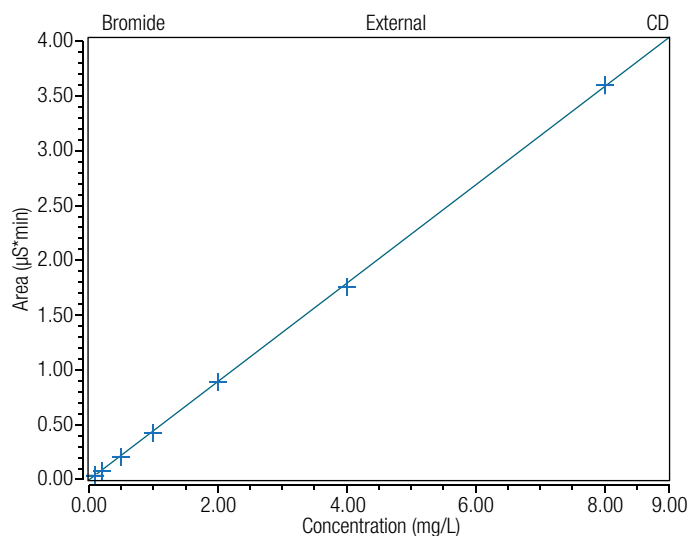


Figure 4. Bromide calibration curve.

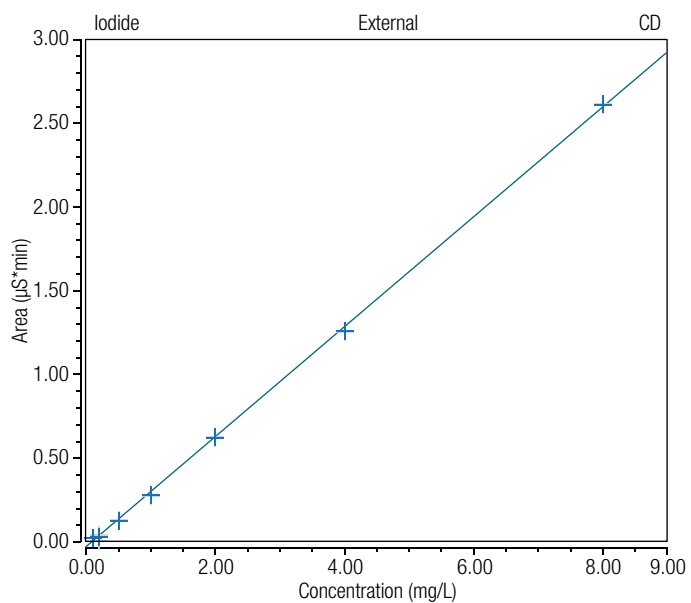


Figure 5. Iodide calibration curve.

Determination of halogens in polymers and electronics

Four polymer samples and one PCB sample were analyzed for their F, Cl, Br, and I contents in triplicate. Figure 7 shows chromatograms of the five samples. Polymer samples contained 0–512 mg/kg fluorine, 4–95 mg/kg chlorine, 0–111 mg/kg bromine, and 0–1307 mg/kg iodine, while the PCB sample contained ~1314 mg/kg fluorine, ~323 mg/kg chlorine, ~25,742 mg/kg bromine, and undetectable iodine. Iodine was detected in Polymer Sample 2, but the concentration was below the lowest level standard (0.1 mg/L). The amount of measured halogen in the samples is summarized in Table 5.

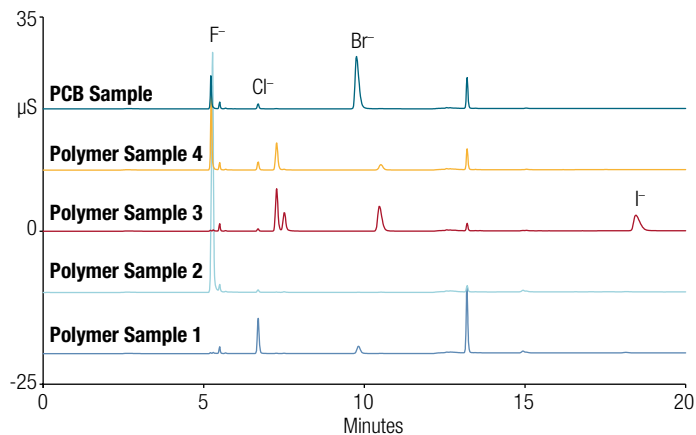


Figure 7. Chromatograms of four polymer samples and one PCB sample.

Table 5. Halogen quantification in polymers and electronics.

Sample	Fluorine (mg/kg*)	Chlorine (mg/kg*)	Bromine (mg/kg*)	Iodine (mg/kg*)
Polymer Sample 1	–	94.5	4.64	–
Polymer Sample 2	513	3.98	–	–
Polymer Sample 3	–	6.14	–	1307
Polymer Sample 4	93.5	21.5	–	–
PCB Sample	1314	323	25,742	–

*Amount present after correcting for the mass and dilution

*n=3

Precision and accuracy

The precision and accuracy for our CIC method were evaluated using a certified reference material of low density polyethylene (EC680k), by European Reference Materials (ERM, Belgium) purchased from ARMI/LGC Standards. It contains known quantities of chlorine, bromine, and sulfur. This standard was used previously to assist in the evaluation of consumer plastics (e.g. plastic wrap).⁶

Good precision was achieved as evidenced by the relative standard deviation (RSD) values of measured chlorine amounts in ERM pellets (Table 6). The RSD is 1.03% for three replicates, indicating good precision. The accuracy of our CIC method was verified by determining recoveries of chlorine in spiked polymers and PCB samples. Samples were spiked with a series of known

Table 6. Method precision.

Sample	Weight (mg)	Measured Halogen(Cl) (mg/kg)	RSD
ERM pellets 1	34.8	98.2	
ERM pellets 2	32.6	97.8	1.03
ERM pellets 3	35.0	96.3	

masses of ERM pellets. Recoveries were calculated from the difference in response between the spiked and unspiked samples. Table 7 shows the recovery for four polymer samples and one PCB sample ranged from 89.9% to 114.2%, indicating that this method can accurately determine halogens in polymer and electronic samples.

Table 7. Method accuracy.

Sample Name	Weight (mg)	Amount Spiked (mg)	Measured Halogen (Cl) (mg/kg)	Certified Value (mg/kg)	Recovery %
Polymer Sample 1	15.5	16.3	92.1	102.2	90.1
Polymer Sample 2	20.7	18.0	93.4	102.2	91.4
Polymer Sample 3	19.1	16.5	91.8	102.2	89.9
Polymer Sample 4	21.9	18.3	116.7	102.2	114
PCB Sample	4.4	15.7	95.2	102.2	93.1

Note: Recovery is calculated as follows: $[(\text{Amount in spiked sample} - \text{Amount in sample}) / \text{Amount added to sample}] \times 100\%$ where

(Amount in spiked sample – Amount in sample) = Measured halogen value

Amount added to sample = Known certified value from ERM pellets

Conclusion

This application note demonstrates that individual halogens can be precisely and accurately determined in polymers and electronics using CIC. This method allows polymer and electronic manufacturers to monitor halogen levels to ensure compliance with government regulations. The CIC technique presented here provides a fully automated method by using the Mitsubishi AQF-2100H system in combination with the Dionex Integriion HPIC Reagent-Free IC (RFIC) system equipped with a Dionex IonPac AS17-C column set. The HPIC system makes its own potassium hydroxide eluent and regenerant for suppressed conductivity detection, thereby eliminating errors and ensuring high chromatographic reproducibility.

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