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Industrial

Determination of chlorine and bromine in rubber products using hydropyrolytic combustion ion chromatography

Authors

Yukiko Kawahara, Terri Christison, Manali Aggrawal, and Jeffrey Rohrer

Thermo Fisher Scientific
Sunnyvale, CA, USA

Keywords

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Goal

To demonstrate the determination of total chlorine and bromine in rubber and synthetic rubber samples according to ISO 7725:2020(E) Method A, a tubular furnace combustion method, using a Nittoseiko Automated Combustion Furnace (AQF) model AQF-2100H/ICS-6000 Combustion IC system

Introduction

The International Organization for Standardization (ISO) recently updated its standard for the determination of chlorine and bromine content in rubber and rubber products.[1] This revised standard, ISO 7725:2020(E), now includes combustion ion chromatography (CIC) as Method A and can be applied to any rubber that contains these two halogens.

Combustion ion chromatography is an effective technique for determining the halogen contents of solid samples that can be combusted in an oxygen/argon environment.[2,3] In this application note, several rubber products commonly found in a laboratory were selected and analyzed for total chlorine and bromine in the forms of chloride and bromide combining tubular furnace combustion followed by ion chromatography (IC), as specified in the ISO method.

Solid samples are introduced to pyrolysis with a stream of oxygen-containing gas at about 1,000 °C. The resulting hydrogen halides (HX) or elemental halogens (X_2) are sparged through the absorbing solution to form anions (X^-). Once the solution is diluted to volume, it is directly injected into the IC system, and the anions are separated on the high-performance anion-exchange column and then detected by suppressed conductivity.

The ease of sample preparation via an AQF-2100H combustion unit combined with the sensitivity and accuracy of a Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system are brought together by Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, making the operation automatic, seamless, and convenient. Figure 1 shows a diagram of the CIC system.

For the CIC system with a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, the detailed configuration can be found in Thermo Scientific Technical Note 000767.[4]

Experimental

Equipment*

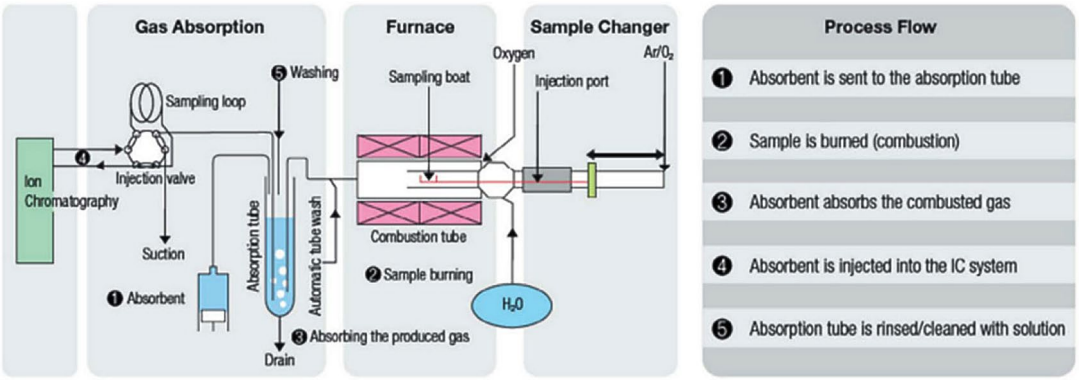
Dionex ICS-6000 HPIC system including:

- DP dual pump module with degas option
- EG eluent generator module
- DC detector/chromatography module with conductivity detector

Nittoseiko Analytech (previously Mitsubishi Analytech) AQF-2100H system, comprising:

- Horizontal Electric furnace, HF-210
- Gas absorption unit, GA-211
- External solution selector, ES-210
- Automatic boat controller, ABC-210
- Automatic sample changer, ASC-270 LS, for liquid and solid samples
- Combustion monitor, CM-210

* This application can be run on a Thermo Scientific™ Dionex™ Integrion™ RFIC system.



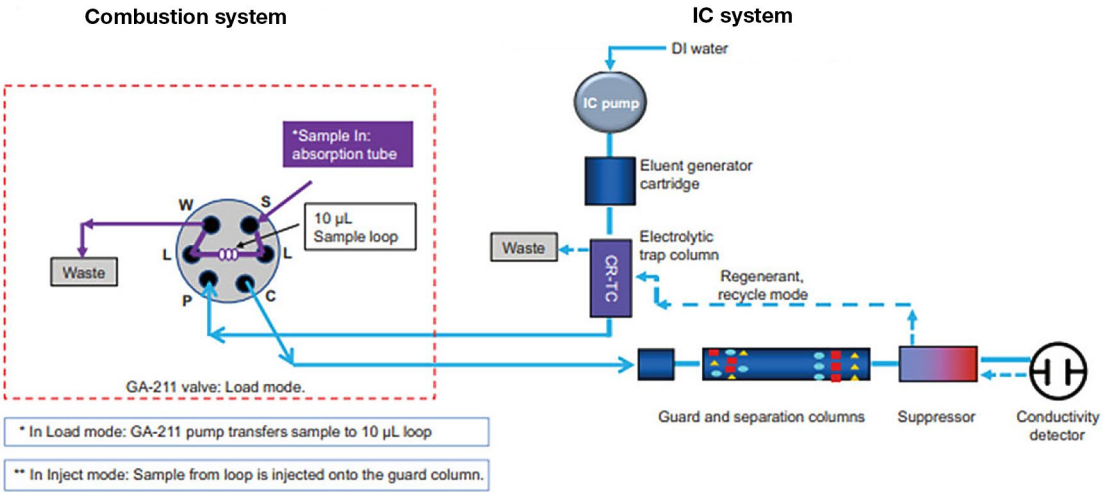


Figure 1. Diagram of combustion IC

Software

Chromeleon CDS 7.3.1 with Nittoseiko Analytech AQF2100 driver

Consumables

- Thermo Scientific™ Dionex™ ADRS™ 600 anion dynamically regenerated suppressor (P/N 088667) in recycle mode
- Thermo Scientific™ Dionex™ IonPac™ AG18 Fast-4µm guard column (2 × 30 mm) (P/N 076037)
- Thermo Scientific™ Dionex™ IonPac™ AS18 Fast-4µm analytical column (2 × 150 mm) (P/N 076036)
- Thermo Scientific™ Dionex™ EGC 500 KOH potassium hydroxide eluent generator cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 continuously regenerated anion trap column (P/N 088662)

Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistance or better
- Hydrogen peroxide, Merck (P/N 107298)*
- Sodium chloride, Sigma-Aldrich (P/N 746398)
- Potassium bromide, J.T. Baker (P/N 2998-01)
- 4-chlorobenzoic acid, Thermo Scientific™ (P/N 159250250)
- 4-bromobenzoic acid, Aldrich (P/N 128384)
- Methanol, Fisher Chemical™ (P/N A456)
- Oxygen (gas), UHP grade, 99.999%
- Argon (gas), UHP grade, 99.999%

* Hydrogen peroxide is required if total sulfur content (as sulfate) is to be measured at the same time. 6% hydrogen peroxide was used in this experiment, but it can be substituted with DI water if the halides are the only anions of interest.

Instrument method parameters

Combustion unit parameters	
AQF-2100H system	
Sample size (mg)	~70–100 (cut into small pieces)
Sample boat	Ceramic
Pyrolysis tube	Quartz tube / Quartz wool
Absorption solution	H_2O_2 aqueous solution (0.06%)
Mode	Constant volume
HF210	
Furnace inlet temp (°C)	900
Furnace outlet temp. (°C)	1,000
Argon flow (Carrier) (mL/min)	200
Oxygen flow (Combustion agent) (mL/min)	400
GA-211	
Absorption tube (mL)	10
Sample loop (µL)	10
Constant volume factor	10.18
Absorption solution vol. (mL)	5
Water supply scale	2
Argon flow for humidification (mL/min)	100
Washing parameter	
Water injection time (s)	12
Drain time (s)	17
Gas line washing times	3
Sample absorption time (s)	10
Ar time (s)	10
O_2 time (s)	600
Ar replace time (s)	30

ABC210/ASC-270LS: Boat controller settings (ABC program default: 003_Solid2_Polymers0.1g)

Position (mm)	*Wait time (s)*	*Speed (mm/s)*
130	90	20.00
160	90	0.12
End	100	20.00
Cool	60	40.00
Home	90	40.00

IC parameters	
System	Dionex ICS-6000 HPIC system
Columns	Dionex IonPac AS18 Fast-4µm, Analytical, 2 × 150 mm Dionex IonPac AG18 Fast-4µm, Guard, 2 × 30 mm
Eluent source	EGC 500 KOH
Eluent	15 mM KOH
Flow rate	0.25 mL/min
Column temp.	30 °C
Injection vol.	10 µL
Detection	Suppressed conductivity with Dionex ADRS 600 Dynamically Regenerated Suppressor, recycle mode
Suppresser current	10 mA
System backpressure	~2,700 psi (18.6 MPa)
Background conductance	<1 µS/cm
Noise	<1 nS/cm
Run time	18 min

Preparation of solutions and reagents

Calibration standard solution

52.0 mg NaCl were dissolved in 487.0 g DI water to make 64.8 mg/L chloride stock solution. 45.2 mg KBr were dissolved in 495.7 g DI water to make 61.2 mg/L bromide stock solution. Each stock solution was diluted in DI water to an appropriate concentration and immediately used as calibration standard solution.

4-chlorobenzoic acid solution for recovery test

43.9 mg of 4-chlorobenzoic acid were dissolved in 78.7 g methanol to make 99.5 mg/L chloride solution.

4-bromobenzoic acid solution for recovery test

26.1 mg of 4-bromobenzoic acid were dissolved in 78.6 g methanol to make 103.9 mg/L bromide solution.

Sample preparation

Several rubber laboratory items, including stoppers and a pipette bulb, were collected and cut into small pieces less than 2 mm in length with scissors. The sample was weighed (0.06–1 g), and placed in a ceramic sample boat. Each boat was then covered with a small amount of quartz wool to secure the samples.

Sample preparation for recovery test

50 µL of chloride and bromide recovery test solutions were each added to a prepared sample boat immediately prior to combustion.

Calculation of Constant Volume Factor

Constant Volume Factor is the final volume of the liquid at the end of the combustion process and needs to be determined experimentally. Phosphate is a good choice for this experiment because it is not detected in a combusted sample.

To determine Constant Volume Factor, a phosphate solution of known concentration was externally injected, and its peak area calculated (A_1). Second, the same phosphate solution was used in place of the absorption solution in normal absorption injection mode, and its peak area calculated (A_2). The Constant Volume Factor was calculated as follows and later used to calculate the amount ratio of total chlorine and bromine in the sample.

$$V = \frac{A_1}{A_2} \times \text{absorption solution volume (mL)}$$

V: Constant Volume Factor (mL)
A_1: Area of phosphate standard externally injected
A_2: Area of phosphate standard used as absorption solution

Calculation of halogen content

Below is the formula used to calculate the content of total chlorine/bromine in sample (%, w/w)

$$w = \frac{c \times V}{W \times 1{,}000{,}000} \times 100$$

w: Halogen content (%, w/w)
c: Ion concentration of halogen (chloride or bromide) (mg/L)
V: Constant Volume Factor (mL)
W: Weight of solid sample (g)

*In the ISO method, the ion concentration of the blank solution is subtracted from the calculated ion concentration. We could omit this step as the blank solution did not contain bromide, and the chloride amount was less than 0.1% of what was found in the samples.

Results and discussion

The AQF2100 combustion system includes several default programs for the Automatic Boat Controller. After testing several manually created combustion programs, the default program for 0.1 g polymer was determined to be adequate for this application.

For IC separation, the Dionex IonPac AS18-Fast-4µm column with its guard column was selected for its speed and resolution. The analysis is simplified (e.g., no eluent or suppressor regenerant preparation), precise, and sensitive by using a Reagent-Free IC system.

Calibration and estimated limit of detection (LOD)

Standard curves for chloride and bromide were created by injecting aqueous standards using the external liquid injection valve. Figure 2 shows the resolution of chloride and bromide in the standard mixture. The estimated LODs were calculated using 3 × S/N by injecting standards with low concentration. Because a low amount of chloride was present in blank DI water, the chloride LOD is defined as 3 × S/N above the blank water concentration (Table 1).

Columns:	Dionex IonPac AG18 FAST 4µm, 2 × 30 mm Dionex IonPac AS18 FAST 4µm, 2 × 150 mm
Eluent:	15 mM KOH via EGC 500 KOH
Flow rate:	0.25 uL/min
Injection volume:	10 µL
Column temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, legacy mode, 10 mA, recycle mode
Pyrolysis:	900 °C, 10 s, Ar, 200 mL/min
Combustion:	1,000 °C, 100 s; O_2, 400 mL/min
Absorption solution:	0.06% hydrogen peroxide*, 5 mL, diluted to 10 mL for injection**
Collection gas:	Ar carrier, 100 mL/min., DI water
Sample prep:	~0.1 g rubber sample was cut into small pieces and placed on pre-baked ceramic boat. Small amount of quartz wool was placed on top to secure the sample.

* Can be substituted with DI water if total sulfur content (as sulfate) is not the anion of interest.
** Final dilution volume (Constant Volume Factor) needs to be experimentally determined.

Peaks:	1. Chlorine	2.2 mg/L
	2. Bromine	1.0 mg/L

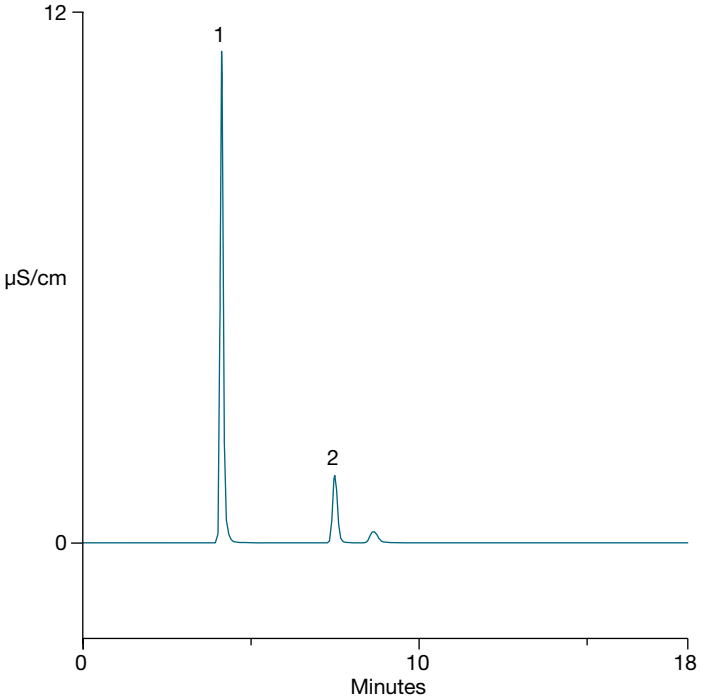


Figure 2. Chromatogram of a standard solution

Table 1. Summary of calibration results and estimated limit of detection

Anion	Calibration				Est. LOD*
	Range (mg/L)	Points	Cal. type	Coeff. Det. (r^2)	c(mg/L)
Chloride (Chlorine)	0.24–78	5	Lin, WithOffset, 1/A	1.000	0.32
Bromide (Bromine)	0.01–1.02	5	Lin, WithOffset, 1/A	0.998	0.30

*LOD = 3 × S/N for bromide. 3 × S/N above baseline water concentration for chloride

Sample analysis

Figure 3 shows the analysis results of four different rubber samples. We found that the amount of bromine was very low in all the samples.

	(w)A	(w)B	(w)C	(w)D
1. Chlorine	0.011	0.025	0.073	0.790
2. Bromine	0.000	0.006	0.000	0.001

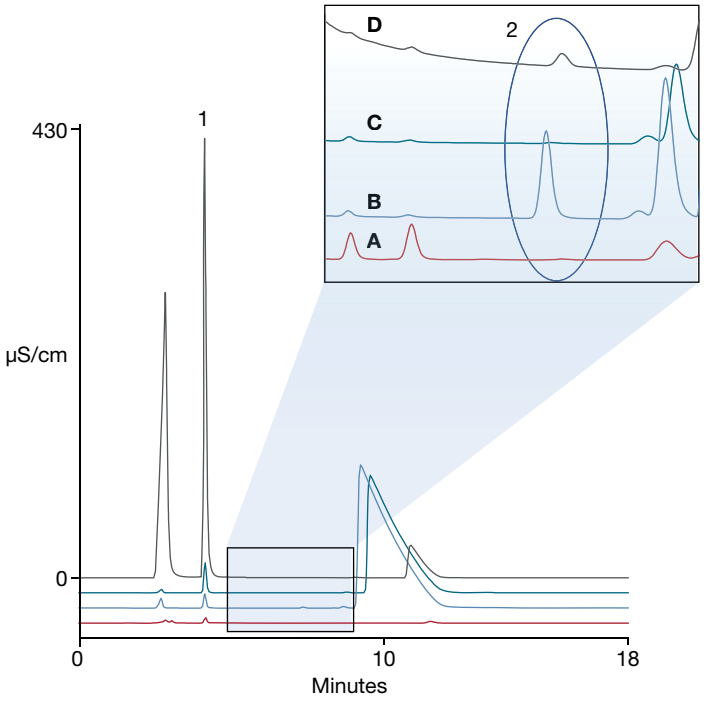


Figure 3. Chromatograms of samples: (A) rubber bulb, (B) black glassware stopper, (C) white glassware stopper, and (D) black vial stopper. Retention time of bromide peak in sample B has shifted due to column overloading of sulfate.

Repeatability

Analysis was repeated five times and repeated after ten days for each sample. Table 2 shows the average weight % and RSD of five replicates. The results were consistent when repeated after 10 days.

Recovery

To determine recovery, 50 µL of the chloride and bromide recovery test standards were added to a sample boat with prepared solid sample before combustion. Table 3 shows the average results of three tests per sample, demonstrating good accuracy.

Conclusion

Using a CIC system consisting of an AQF-2100H and a Dionex ICS-6000 HPIC system, the concentrations of chlorine and bromine were determined in rubber materials according to the ISO method with excellent reproducibility, LOD, and recovery.

References

1. ISO 7725:2020(E) Rubber and rubber products – Determination of chlorine and bromine content (2020).
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3. Thermo Fisher Scientific Application Note 73280: Determination of fluorine and chlorine in iron ore using combustion ion chromatography, 2019, https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73280-fluorine-chlorine-iron-ore-an73280-en.pdf
4. Thermo Fisher Scientific Technical Note 000767: Combustion ion chromatography with a Dionex Integrion HPIC system using Chromeleon 7 CDS software, 2022. https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-000767-ic-integrion-environmental-tn000767-na-en.pdf

Table 2. Repeatability of analysis (n=5), 10 days apart

Sample	Halogen	Repeatability (n=5)		Repeatability (n=5) after 10 days	
		Average (w)	RSD	Average (w)	RSD
A	Chlorine	0.01	9.0	0.01	10.4
	Bromine	0.00	0.0	0.00	0.0
B	Chlorine	0.03	1.4	0.02	1.3
	Bromine	0.01	15.2	0.01	6.6
C	Chlorine	0.07	1.5	0.07	2.0
	Bromine	0.00	0.0	0.00	0.0
D	Chlorine	0.78	0.8	0.77	1.0
	Bromine	0.00	0.0	0.00	0.0

Table 3. Recovery results

Sample	Chloride			Bromide		
	Expected (mg/kg)	Measured (mg/kg)	Recovery (%)	Expected (mg/kg)	Measured (mg/kg)	Recovery (%)
A	1.64×10^2	1.53×10^2	99	58.0	46.5	94
B	3.00×10^2	2.99×10^2	98	1.18×10^2	1.10×10^2	91
C	7.81×10^2	7.69×10^2	99	58.8	53.5	93
D	7.86×10^3	7.78×10^3	94	67.1	59.7	80

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