

Determination of adsorbable organic halogen in wastewater using a combustion ion chromatography system

Authors

Jingli Hu and Jeffrey Rohrer

Thermo Fisher Scientific,
Sunnyvale, CA

Keywords

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Goal

To combine automated combustion with ion chromatography to quantify adsorbable organic halogens in wastewater

Introduction

Organohalogenes are toxic and persistent compounds that are often given high priority in the monitoring and control of environmental pollution. Two of the most frequently used sum parameters for organohalogenes—adsorbable organic halogens (AOX) and extractable organic halogens (EOX)—are general indicators of industrial pollution of water, sediment, and soil. AOX represents the equivalent amount of fluorine, chlorine, and bromine contained in organic compounds, expressed as chloride substances that can be adsorbed from water onto activated carbon. The main sources of AOX are the chlorine chemicals used to bleach fibers in the paper and pulp industry. Smaller amounts are also formed during the routine chlorination (disinfection) of drinking water, swimming pools, and industrial effluents.

Organic halogen compounds cannot be directly analyzed by ion chromatography (IC). Automated combustion ion chromatography (CIC) is often used to determine these organic halogen contaminants. In CIC, the samples including halogen-containing compounds are first combusted and the resultant gases are released into an absorption solution, which is directly injected into an IC.

As shown in Figure 1, pyrolysis takes place in the combustion system at temperatures above 900 °C. Sulfur-containing compounds are oxidized to sulfur dioxide (SO₂) and halogen-containing substances are transformed into hydrogen halides (HX) or elemental halogens (X₂). These gaseous combustion products are fed into an oxidizing absorption solution and are subsequently detected as sulfate and halide (e.g., chloride) by the IC that follows. While one chromatogram is being recorded, pyrolysis of the next sample is already underway. In contrast to the AOX method where only the sum of organic halogens is measured by amperometric titration, the CIC method provides halogen speciation and additional information about the adsorbable organic

fluorine. A DIN standard using CIC is under development.¹ The fully automated sample processing capabilities from sample introduction into the furnace to data analysis by the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software has found numerous applications.^{2,3}

The method described here is the determination of AOX associated with the EPA Clean Water Act, the EPA Resource Conservation and Recovery Act, and the Environmental Protection Law of the China. This method can be considered a combination of several existing methods for organic halide measurement.⁴⁻⁶ CIC is achieved by interfacing a Thermo Scientific™ Dionex™ Integriion™ HPIC™ system to an AQF-2100H (Auto Quick Furnace) with with a COSA-Mitsubishi™ GA-210 (Gas Adsorption Unit). AOX in wastewater is determined by adsorption onto granular activated carbon (GAC), washing the adsorbed sample and GAC to remove inorganic halides, combustion of the sample and GAC to form the hydrogen halides, absorption of hydrogen halides to form halides, and determination of halides with a Dionex IonPac AS18-4µm column set.

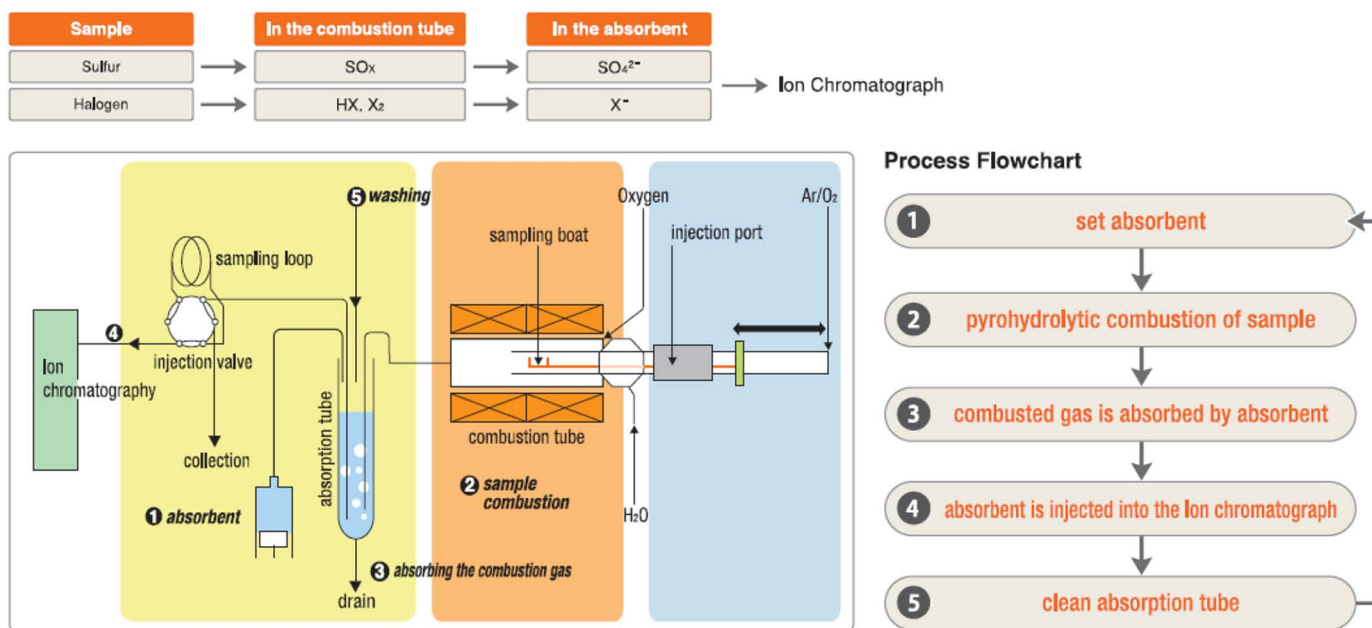


Figure 1. Diagram of a CIC system.

Experimental

Equipment and Supplies

Dionex Integrion HPIC system including:

- Eluent Generation
- Dionex Integrion HPIC System Pump
- CD Conductivity Detector
- Degasser
- Detector Compartment Temperature Control
- Column Oven Temperature Control
- Tablet Control
- Consumables Device Tracking Capability

Mitsubishi Automatic Combustion Unit Model AQF-2100H system including:

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

HPIC consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic trap column (P/N 088662)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)

Software

- Chromeleon Chromatography Data System (CDS) Software, version 7.2 SR4 MUb (8525) and above
- Mitsubishi NSX-2100 software, version 2.1.6.0

Column adsorption system

A schematic of the pressurized column adsorption system is shown in Figure 2A. Alternatively, sample or nitrate washing solution can be delivered by a Masterflex® C/L Dual-Channel Variable-Speed Tubing Pump (Figure 2B).

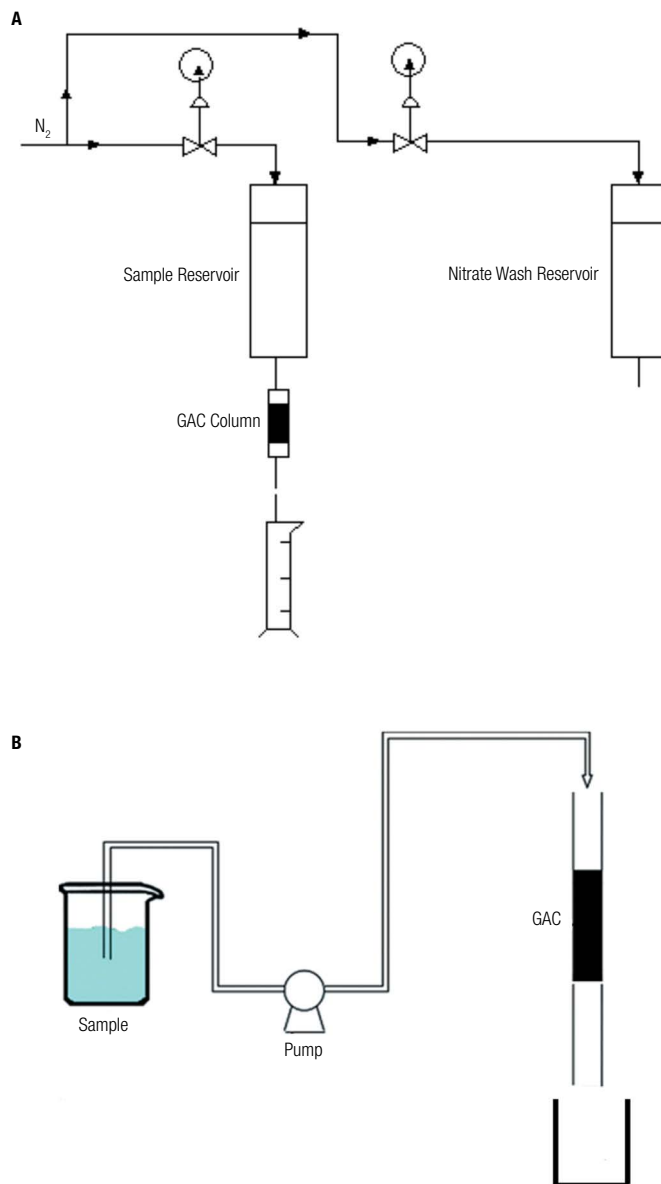


Figure 2. (A) Schematic of the column adsorption system using nitrogen gas and (B) Schematic of the column adsorption system using a pump.

Pre-packed AC Columns (COSA P/N MC06454) or manually packed columns, prepared using empty adsorption columns (5 cm long × 6 mm O.D. × 2 mm I.D.) can be used. A funnel for filling the columns and a rod (3 mm ID × 6 mm OD × 49.5 mm) (CPI P/N 634-801) for pushing out the carbon are also required.

Reagents and standards

- Activated carbon 50–150 µm particle size (Sigma® P/N 80485-25G)
- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistivity
- 4-Fluorobenzoic acid
- 2,4,6-Trichlorophenol, 98%
- 4'-Bromoacetanilide, 98%
- Sodium fluoride, sodium chloride, and sodium bromide for the preparation of inorganic stock standard
- Sodium sulfite (0.2 M): Prepare by dissolving 2.521 g of sodium sulfite in 100 mL of DI water
- Nitric acid, HNO₃ (1 M): Prepare by adding approximately 80 mL of DI water into a 100 mL volumetric flask, slowly adding 6.33 mL of concentrated nitric acid (15.8 M) to the volumetric flask, and bringing to volume with DI water.
- Sodium nitrate stock solution, acidified, 0.2 M: Prepare by dissolving 17 g of sodium nitrate (NaNO₃) in DI water in a 1,000 mL volumetric flask, adding 25 mL of nitric acid, and making up to volume with DI water.
- Sodium nitrate washing solution (0.01 M): Prepare by diluting sodium nitrate stock solution 20-fold with DI water.
- Combined Seven Anion Standard I (P/N 056933)
- Ammonium chloride (NH₄Cl) solution (100 µg/mL of Cl⁻). Prepare by dissolving 150.9 mg NH₄Cl in 1,000 mL DI water.
- Oxygen, ultrahigh purity, GR 4.4
- Argon, ultrahigh purity, GR 5.0

IC Conditions

Columns:	Thermo Scientific™ Dionex™ IonPac™ AG18-4µm Guard Column, 4 × 30 mm (P/N 076035) Thermo Scientific™ Dionex™ IonPac™ AS18-4µm Analytical Column, 4 × 150 mm (P/N 076034)
Eluent:	30 mM KOH
Eluent Source:	Thermo Scientific™ Dionex™ 500 KOH cartridge with Dionex CR-ATC 600 trap column and high pressure EG degasser
Flow Rate:	1.00 mL/min
Column Temperature:	30 °C
Detector Compartment Temperature:	25 °C
Detector Temperature:	35 °C
Injection Volume:	100 µL, (Full loop)
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ AERS™ 500 suppressor, 4 mm, recycle mode, 75 mA
Run Time:	10 min
Background Conductance:	< 0.2 µS/cm
Typical Noise:	< 0.5 nS/cm
System Backpressure:	~ 2,800 psi

Combustion Conditions

Mass Combusted:	Contents of the GAC column (40–50 mg)
Furnace Inlet Temp:	900 °C
Furnace Outlet Temp:	1,000 °C
Argon Flow (Carrier):	200 mL/min
Oxygen Flow (Combustion Agent):	400 mL/min
Humidified Argon Flow:	100 mL/min
Water Supply Scale:	2
Pyrolysis Tube:	Quartz tube with ceramic insert and quartz wool
Sample Boat:	Ceramic
Absorption Solution:	Water
Absorption Tube Size:	10 mL
Absorption Solution Volume:	3.5 mL
AQF Mode:	Constant Volume
Automatic Boat Controller Program:	Table 1

Table 1. ABC 210 program.

Position (mm)	Wait time (s)	Speed (mm/s)
135	60	10
End	300	20
Cool	60	20
Home	200	20

Preparation of inorganic halide standards

Stock solution

To prepare the 1,000 mg/L stock solution, accurately weigh the amounts of standard compounds listed in Table 2, transfer to a 100 mL volumetric flask, and fill to the mark with DI water. Mix thoroughly and store at 4 °C.

Table 3. Calibration standards preparation (mg/L).

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Fluoride	0.1	0.25	0.5	1	2.5	3.5	5
Chloride	0.2	0.5	1	2	5	7	10
Bromide	0.4	1	2	4	10	14	20

Table 2. Masses of standard compounds to prepare 100 mL of a 1,000 mg/L anion standard.

Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Chloride	Sodium chloride (NaCl)	164.9
Bromide	Sodium bromide (NaBr)	128.8

Working standard solutions

Seven calibration levels were used to cover the expected concentration range found in typical wastewater samples. Prepare the highest concentration working standard solutions (level 7) by pipetting the appropriate amount of 1,000 mg/L stock into a 100 mL volumetric flask and dilute to the mark with DI water (Table 3). Prepare levels 1–6 of the standard solutions by mixing the standard solution level 7 with DI water. Store the solutions at 4 °C.

Preparation of AOX standards

Trichlorophenol stock solution

Prepare the 1,000 mg/L Cl⁻ trichlorophenol stock solution by dissolving 186 mg of 2,4,6-trichlorophenol in 100 mL of HPLC grade methanol.

4-Fluorobenzoic acid stock solution

Prepare the 1,000 mg/L F⁻ 4-fluorobenzoic acid stock solution by dissolving 73.7 mg of 4-fluorobenzoic acid in 10 mL of HPLC grade methanol.

4-Fluorobenzoic acid working standard solution

Prepare the 100 mg/L F⁻ working standard solution by diluting the F⁻ stock solution 10-fold with HPLC grade methanol.

4-Bromoacetanilide stock solution

Prepare the 200 mg/L Br⁻ 4-bromoacetanilide stock solution by dissolving 5.36 mg of 4-bromoacetanilide in 10 mL of HPLC grade tetrahydrofuran.

Sample collection, preservation, and storage

Wastewater samples were obtained from a local water plant. All samples were collected in bottles with Teflon septa and were protected from light.

If the sample is known or suspected to contain free chlorine, the chlorine must be reduced to eliminate positive interference that may result from continued chlorination reactions. Test for residual chlorine using the following method:

- Dissolve a few crystals of potassium iodine in the sample and add three to five drops of a 1% starch solution. A blue color indicates the presence of residual chlorine. If residual chlorine is found, add 5 mL of sodium sulfite solution (0.2 M) to 100 mL of sample.
- Adjust the pH of aqueous samples to pH < 2 with nitric acid. Acidification inhibits biological activity and minimizes chemical degradation.
- Keep the sample at 0–4 °C from the time of collection until analysis. Analyze sample no more than six months after collection.

System preparation and configuration

IC 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 system operator's manual.^{7,8} Install and condition the guard and separation columns for 30 min prior to installing the column in line with suppressor.

Combustion system

Wastewater that contains high levels of alkali and alkaline earth metals such as sodium, potassium, and calcium can cause rapid devitrification of quartz components and combustion tubes, necessitating their frequent replacement and resulting in higher system maintenance costs. Additionally, accuracy and recovery of halides and sulfur are compromised by high temperature combustion in a quartz pyro-tube. As a result, this application requires the use of a ceramic pyro-tube insert. Refer to the Mitsubishi AQF-2100H instrument manual⁹ for complete system setup.

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 adsorption solution before injection into the IC.

Note: 15 min IC run time should be used for this test.

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

Calibration

Run the inorganic F, Cl, and Br calibration standard (Table 2) by IC with the external injection mode and build the calibration curves.

Combustion system test

1. NH₄Cl

This test can be used to assure that the combustion/IC system is performing properly without introduction of carbon. It should be done during initial instrument setup.

Inject 100 µL of NH₄Cl solution (100 mg/L of Cl⁻) into the sample boat and proceed with analysis. The result should be between 9.5 and 10.5 µg Cl⁻. If the recovery is not within these limits, check the temperature of the combustion system, verify that there are no leaks in the combustion system, confirm that IC is performing properly, and then repeat the test.

2. Trichlorophenol combustion test

This test can be used to assure that the combustion/IC system is performing properly.

Inject 10 µL of the 1,000 mg/L trichlorophenol stock solution onto sample boat, and immediately proceed with the analysis to prevent loss of trichlorophenol. The result should be between 9.0 and 11.0 µg of Cl⁻. If the recovery is not within these limits, the combustion system should be adjusted by changing combustion conditions and then the test repeated.

Sample AOX analysis procedure

1. Column adsorption

A. Column preparation. Using the push rod, place some glass wool into the end of a clean glass column (5 cm long × 6 mm O.D. × 2 mm I.D.), fill the glass column with 40–50 mg of granular activated carbon (GAC), and insert some glass wool into the open end of the column to hold the carbon in place. Store the columns in a glass jar with a PTFE-lined screw cap to prevent infiltration of halide vapors from the air. Prepare active carbon columns and use the same day. Alternately, purchase a prepacked GAC column.

B. Column setup. Set up the column with a peristaltic pump or nitrogen pressure as shown in Figure 2.

C. Sample flow rate adjusted by peristaltic pump or nitrogen pressure. Because the flow rate used to load the sample onto the column can affect the ability of the GAC to adsorb organic halides, the flow rate of the sample is measured, and the pump or glass pressure used to process the sample is adjusted accordingly. The flow rate should be adjusted to 2–3 mL/min.

Note: This application uses a manual column adsorption apparatus. However, the Mitsubishi TXA-03 column adsorption module can accept the GAC column and automatically perform the AOX adsorption and the nitrate washing.

2. Reservoir filling

Fill the sample reservoir with the sample (50 mL) and adsorb to the GAC column at 2–3 mL/min.

3. Column washing

Wash the GAC with 20 mL of sodium nitrate washing solution (0.01 mol/L) at 2–3 mL/min to displace inorganic chloride ions.

4. Combustion

Using the push rod, push the carbon and glass wool from the column into a sample boat and then proceed with the automated sequence.

5. Determination of F⁻, Cl⁻, and Br⁻

Determine F⁻, Cl⁻, and Br⁻ in the adsorption tube using IC external calibration curves.

Note: For an unknown sample, try 50 mL and 100 mL. If the difference in determined values is more than 15%, dilute the sample.

Blank determination

For the blank, prepare 50 mL of DI water and then proceed with carbon adsorption and combustion IC.

Validation with a known concentration of trichlorophenol

For validation, prepare 50 mL of trichlorophenol (0.5 mg/L Cl⁻) and then proceed with carbon adsorption and combustion IC.

Data analysis and calculation

The concentration of adsorbable organic halogens was calculated as follows.⁴

$$C_{(AOCl)} = \frac{(CCl - CoCl)V_2 D}{V_1}$$

$C_{(AOCl)}$: Concentration of adsorbable organic chloride in wastewater sample, µg/L

CCl : Cl⁻ Concentration of sample determined by IC external standard curve, mg/L

$CoCl$: Cl⁻ Concentration of reagent water blank determined by IC external standard curve, mg/L

V_1 : Wastewater sample volume, L

V_2 : Total volume of absorption tube, mL

D : Dilution factor of the wastewater sample

$$C_{(AOF)} = \frac{(CF - CoF)V_2 D}{V_1}$$

$C_{(AOF)}$: Concentration of adsorbable organic fluoride in wastewater sample, $\mu\text{g/L}$

CF : F^- Concentration of sample determined by IC external standard curve, mg/L

CoF : F^- Concentration of reagent water blank determined by IC external standard curve, mg/L

V_1 : Wastewater sample volume, L

V_2 : Total volume of absorption tube, mL

D : Dilution factor of the wastewater sample

$$C_{(AOBr)} = \frac{(CBr - CoBr)V_2 D}{V_1}$$

$C_{(AOBr)}$: Concentration of adsorbable organic bromide in wastewater sample, $\mu\text{g/L}$

CBr : Br^- Concentration of sample determined by IC external standard curve, mg/L

$CoBr$: Br^- Concentration of reagent water blank determined by IC external standard curve, mg/L

V_1 : Wastewater sample volume, L

V_2 : Total volume of absorption tube, mL

D : Dilution factor of the wastewater sample

$$C_{AOX} = C_{AOCl} + 1.86 C_{AOF} + 0.444 C_{AOBr}$$

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 3 shows the separation of calibration standard level 3. As seen in the chromatogram, fluoride, chloride, and bromide were well resolved within 10 min.

Columns:	Dionex IonPac AG18-4 μm Guard Column, 4 \times 30 mm Dionex IonPac AS18-4 μm Analytical Column, 4 \times 150 mm
Eluent:	30 mM KOH
Eluent Source:	Dionex EGC 500 KOH cartridge with CR-ATC 600
Temperature:	30 $^{\circ}\text{C}$
Flow Rate:	1 mL/min
Injection Volume:	100 μL
Detection:	Dionex AERS 500 suppressor, 4 mm, recycle mode, 75 mA
Peaks:	1. Fluoride 0.5 mg/L 2. Chloride 1 3. Carbonate - 4. Bromide 2

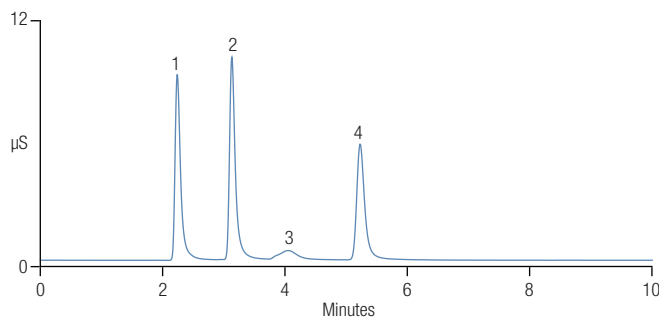


Figure 3. Separation of a standard anion mixture.

Linearity

To determine the linear calibration ranges, the peak responses to concentration were determined using triplicate injections of calibration standards. Table 4 shows the 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 4) and bromide calibration curve (Figure 5). The exception was fluoride, which exhibited a quadratic relationship to concentration (Figure 6). Coefficients of determination (r^2) ranged from 0.99997 to 0.99998. 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 and reducing the time required for method development.

Table 4. Calibration data, retention time, and peak area precisions (n = 3).

Analyte	Range (mg/L)	Coefficient of Determination	Calibration Type	Peak Area Precision (RSD)	Retention Time Precision (RSD)
Fluoride	0.1–5	0.99998	Quad, WithOffset	<0.5	<0.2
Chloride	0.2–10	0.99998	Lin, WithOffset	<0.5	<0.2
Bromide	0.4–20	0.99997	Lin, WithOffset	<1	<0.2

Note: Peak area and retention time precision data is based on the highest level of calibration standard.

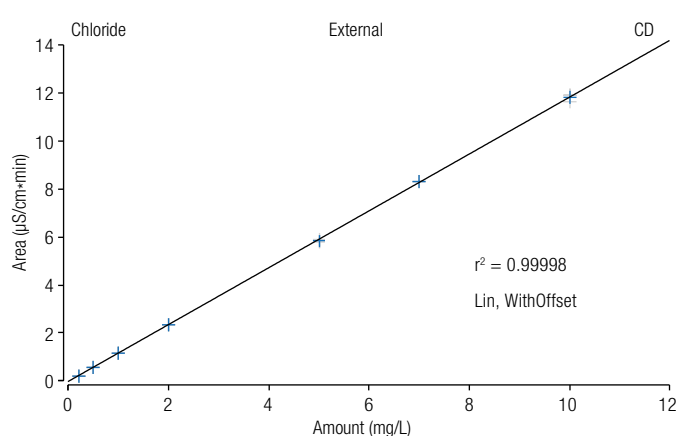


Figure 4. Chloride calibration curve.

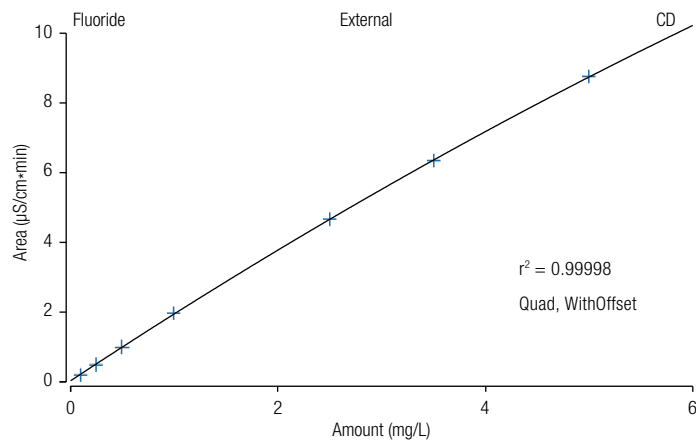


Figure 6. Fluoride calibration curve.

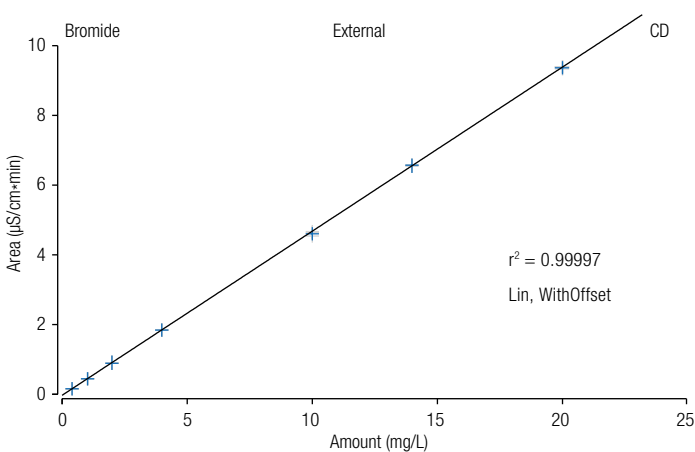


Figure 5. Bromide calibration curve.

Sample accuracy and precision

Working AOX standard trichlorophenol stock solution (1,000 mg/L Cl⁻), 4-fluorobenzoic acid solution (100 mg/L F⁻), and 4-bromoacetanilide stock solution (200 mg/L Br⁻) were used to spike AOX into DI water. Four spike levels were chosen and three replicate analyses were done on each level to determine the analysis accuracy and precision. Table 5 shows the recovery for AOF, AOCl, and AOBr spiked in DI water at all four levels. All three organic halides demonstrate acceptable recovery (85–115%). Good precision was achieved as evidenced by the relative standard deviation (RSD) values calculated from the three replicates (1.4–5.1).

Table 5. Recovery of AOX spiked in DI water.

Analyte	Amount Spiked (µg/L)	Measured value (µg/L)			Average (µg/L)	RSD	Recovery %
		Repetition 1	Repetition 2	Repetition 3			
Fluoride	50.0	51.8	56.6	52.7	53.7	4.75	107
	80.1	86.1	85.8	87.9	86.6	1.31	108
	160	171	175	175	173.7	1.33	109
	250	286	276	263	275	4.19	110
Chloride	50.0	43.6	41.8	45.9	43.8	4.70	87.6
	80.0	76.9	74.3	78.8	76.7	2.95	95.9
	160	150	146	147	147.4	1.41	92.1
	320	288	305	279	291	4.54	90.8
Bromide	115	118	112	124	118	5.08	103
	184	196	194	205	198	2.95	108
	367	416	399	393	402.7	2.96	110
	574	658	676	632	656	3.38	114

Determination of AOX in wastewater

Three wastewater samples were obtained from local wastewater plants. Three replicates were performed for each sample. Table 6 summarizes the recoveries for AOX spiked in wastewater samples. AOF, AOCl, and AOBr all demonstrated excellent recovery (95–105%). Figure 7 shows an overlay of chromatograms of unspiked and spiked wastewater 3. As the figure shows, the Dionex IonPac AS18-4µm column and suppressed conductivity detection achieve excellent resolution and sensitive detection for AOX.

Table 6. Recoveries of AOX spiked in wastewaters (n = 3).

Analyte	Wastewater 1			Wastewater 2			Wastewater 3		
	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Fluoride	1.71	101	103	2.69	101	104	8.86	101	103
Chloride	315	400	102	80.5	100	103	399	400	98.3
Bromide	293	230	103	27.3	115	102	68.7	115	104

Columns: Dionex IonPac AG18-4 μ m Guard Column, 4 \times 30 mm
 Dionex IonPac AS18-4 μ m Analytical Column, 4 \times 150 mm
 Eluent: 30 mM KOH
 Eluent Source: Dionex EGC 500 KOH cartridge with CR-ATC 600
 Temperature: 30 $^{\circ}$ C
 Flow Rate: 1 mL/min
 Injection Volume: 100 μ L
 Detection: Dionex AERS 500 suppressor, 4 mm, recycle mode, 75 mA

Peaks (A):
 1. Fluoride 0.0425 mg/L
 2. Chloride 1.90
 3. Bromide 0.340

Peaks (B):
 1. Fluoride 0.543 mg/L
 2. Chloride 3.92
 3. Bromide 0.908

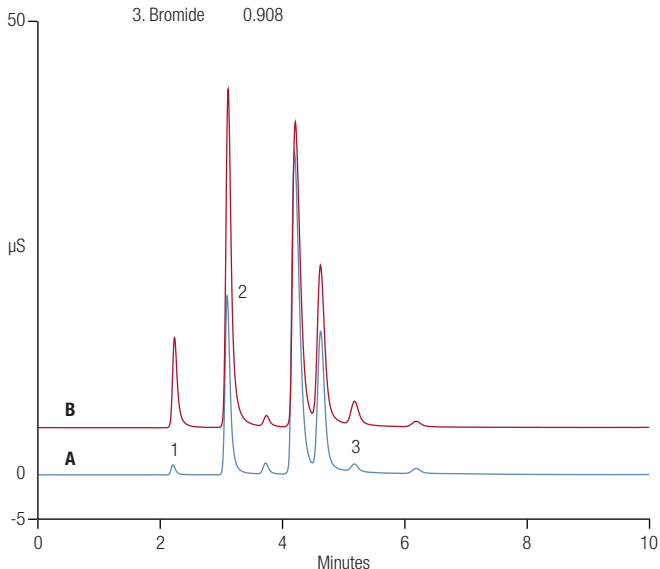


Figure 7. Determination of AOX in (A) wastewater 3 and (B) spiked wastewater 3.

Conclusion

This application note demonstrates that AOX can be precisely and accurately determined in wastewater using combustion ion chromatography. Analysis was automated using the Mitsubishi AQF-2100H system in combination with the Dionex Integrion HPIC system with a Dionex IonPac AS18-4 μ m column. The HPIC feature allows use of small 4- μ m-particle-size columns for shorter analysis and better sensitivity compared to the use of traditional larger-particle-sized columns. Suppressed conductivity detection selectivity detects only anionic species in aqueous solution from the absorbed combustion gas. Eluent generation frees the analyst from the need to prepare eluent, eliminates the handling of strong base, and removes a possible source of error (i.e. improperly prepared eluent).

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