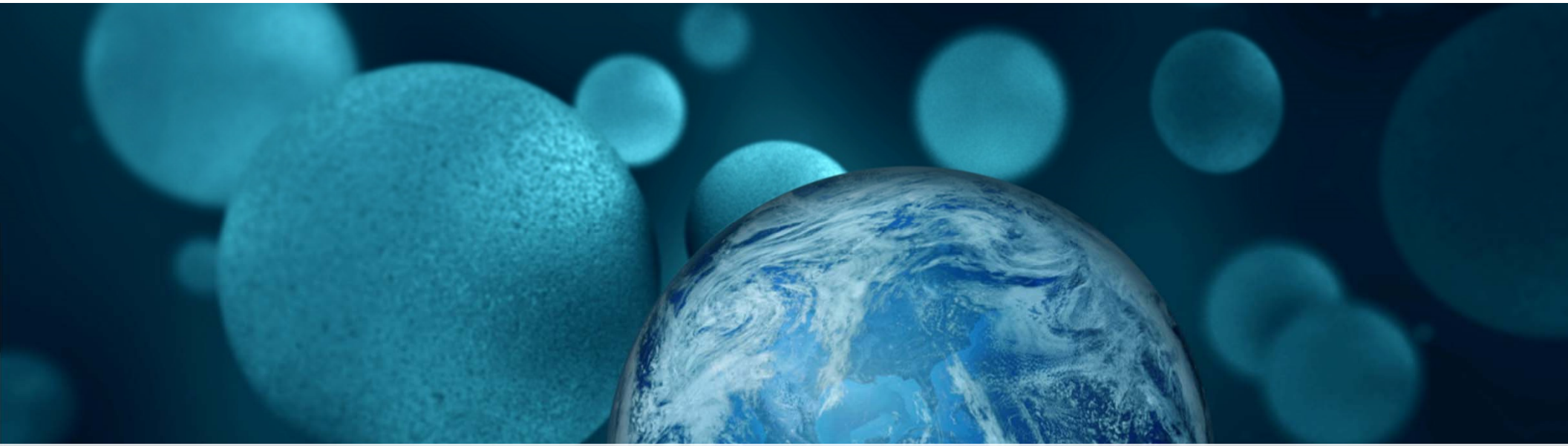

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Determination of Adsorbable Organic Halogen in Wastewater

Jingli Hu, Jeff Rohrer, and Kirk Chassaniol
Thermo Fisher Scientific, Sunnyvale, CA

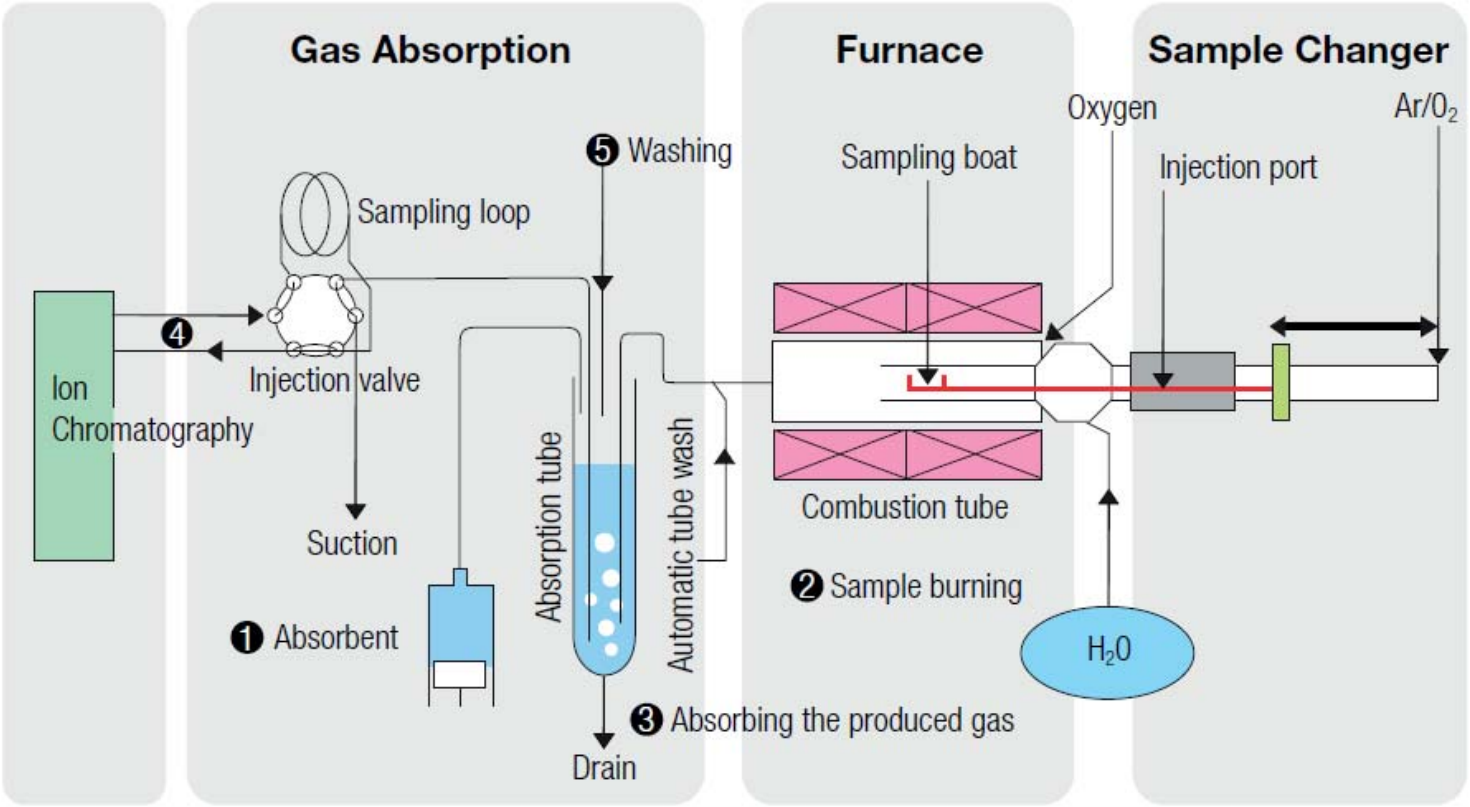
Outline

- AOX (Adsorbable Organic Halogen)
- Combustion IC
- Ion Chromatography
- Methods
- Results and Conclusions

AOX Introduction

- Organohalogens are toxic and persistent compounds
- Given high priority in the monitoring and control of environmental pollution
- 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
- 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.

Diagram of a CIC System



Process Flow

1. Absorbent is sent to the absorption tube
2. Sample is burned (combustion)
3. Absorbent absorbs the combusted gas
4. Absorbent is injected into the IC system
5. Absorption tube is rinsed/cleaned with solution

CIC System Components

Ion Chromatography System

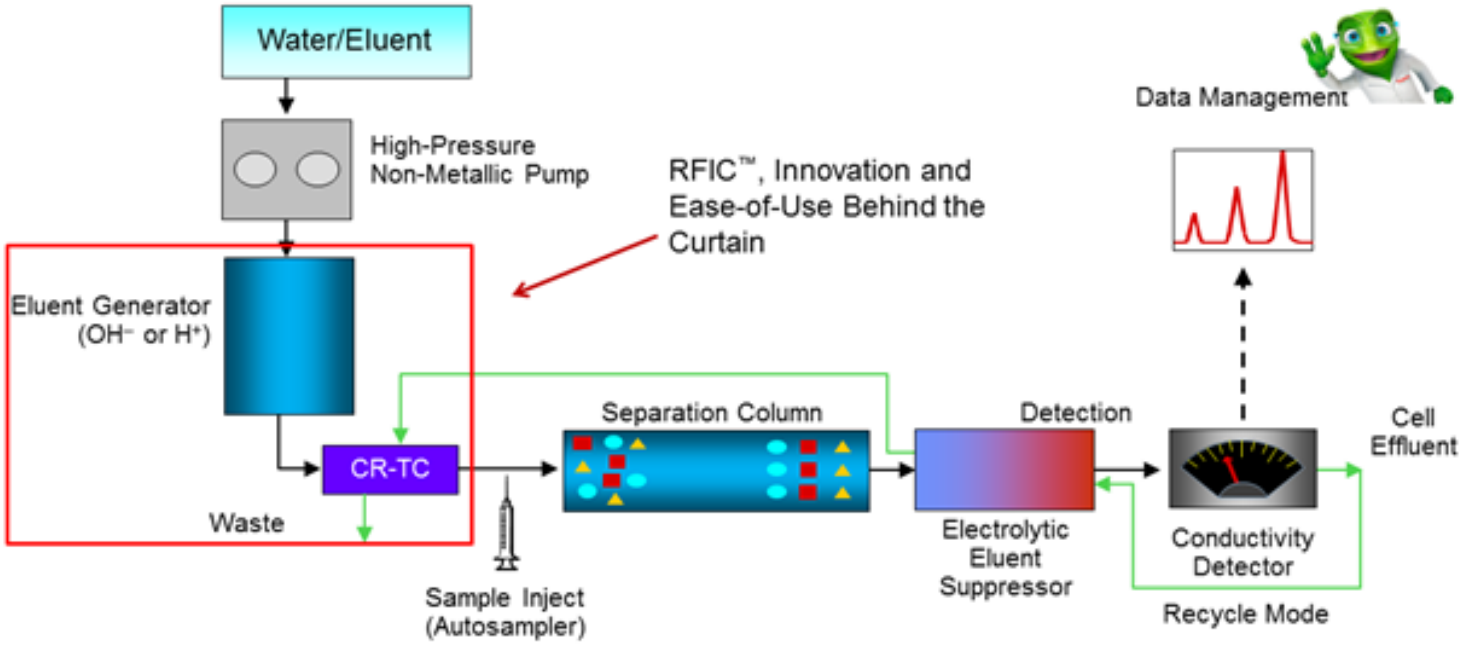
Gas Absorption Unit

Furnace

Solid/Liquid Autosampler

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 system

Reagent-free Ion Chromatography (RFIC) System



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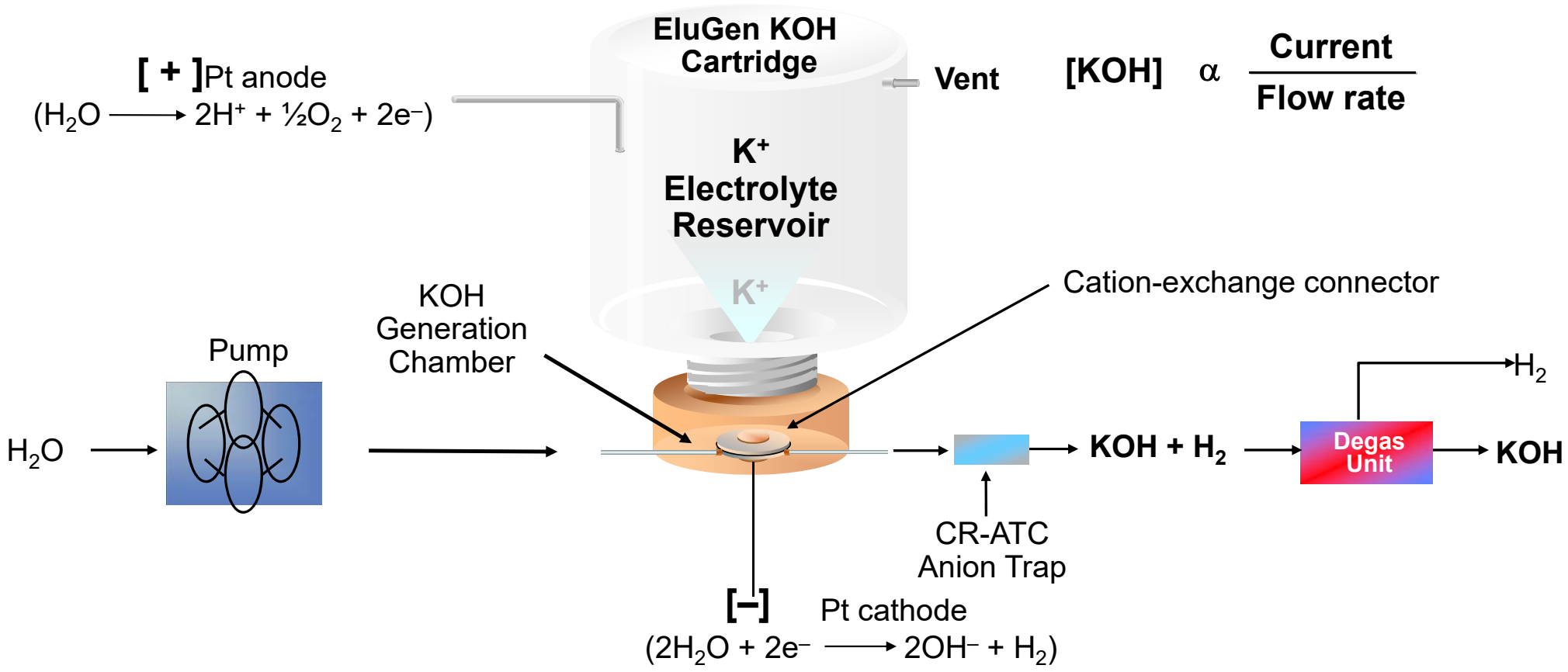
Hydroxide Eluent Generation



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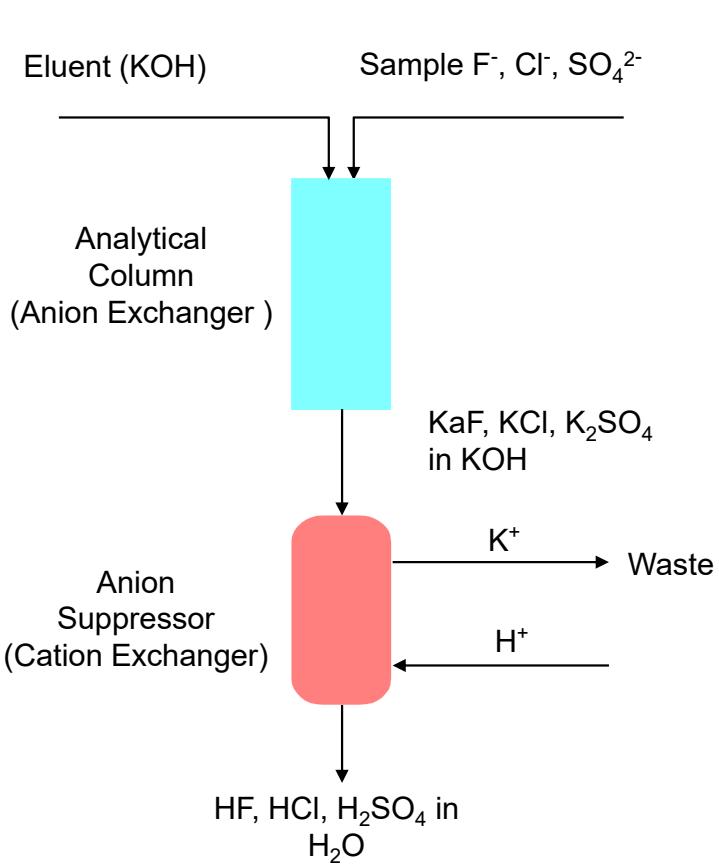
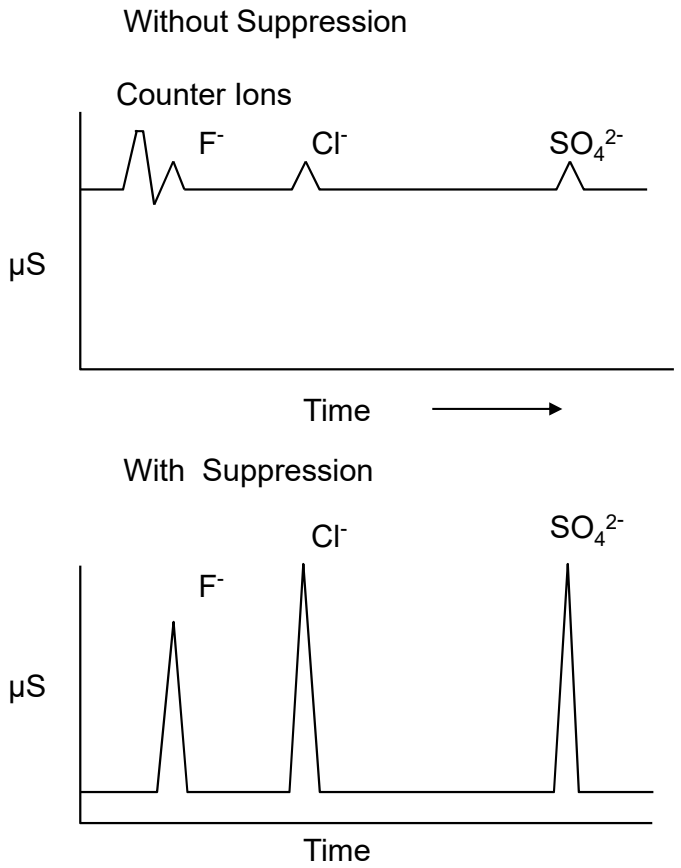
The Role of Chemical Suppression (KOH)





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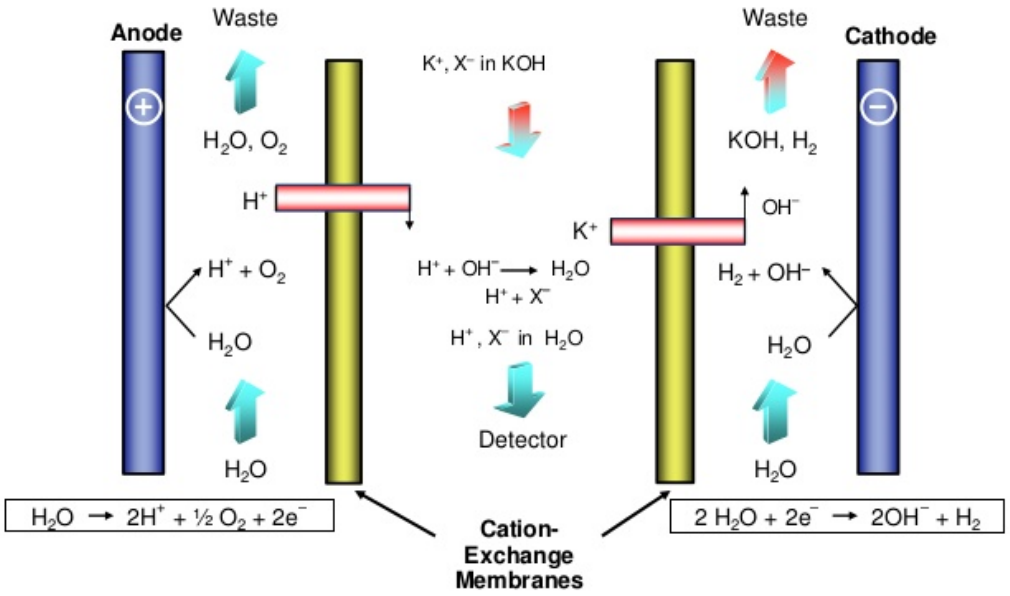
Thermo Scientific Dionex Electrochemically Regenerated Suppressors



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Sample Preparation

- Wastewater samples (50 mL) were absorbed onto granular activated carbon (GAC) columns
- The column was then washed with 20 mL of sodium nitrate washing solution (0.01 M) at 2–3 mL/min to displace inorganic chloride ions
- A rod was used to push the carbon from the column into a sample boat
- Samples were analyzed with CIC

Combustion Conditions

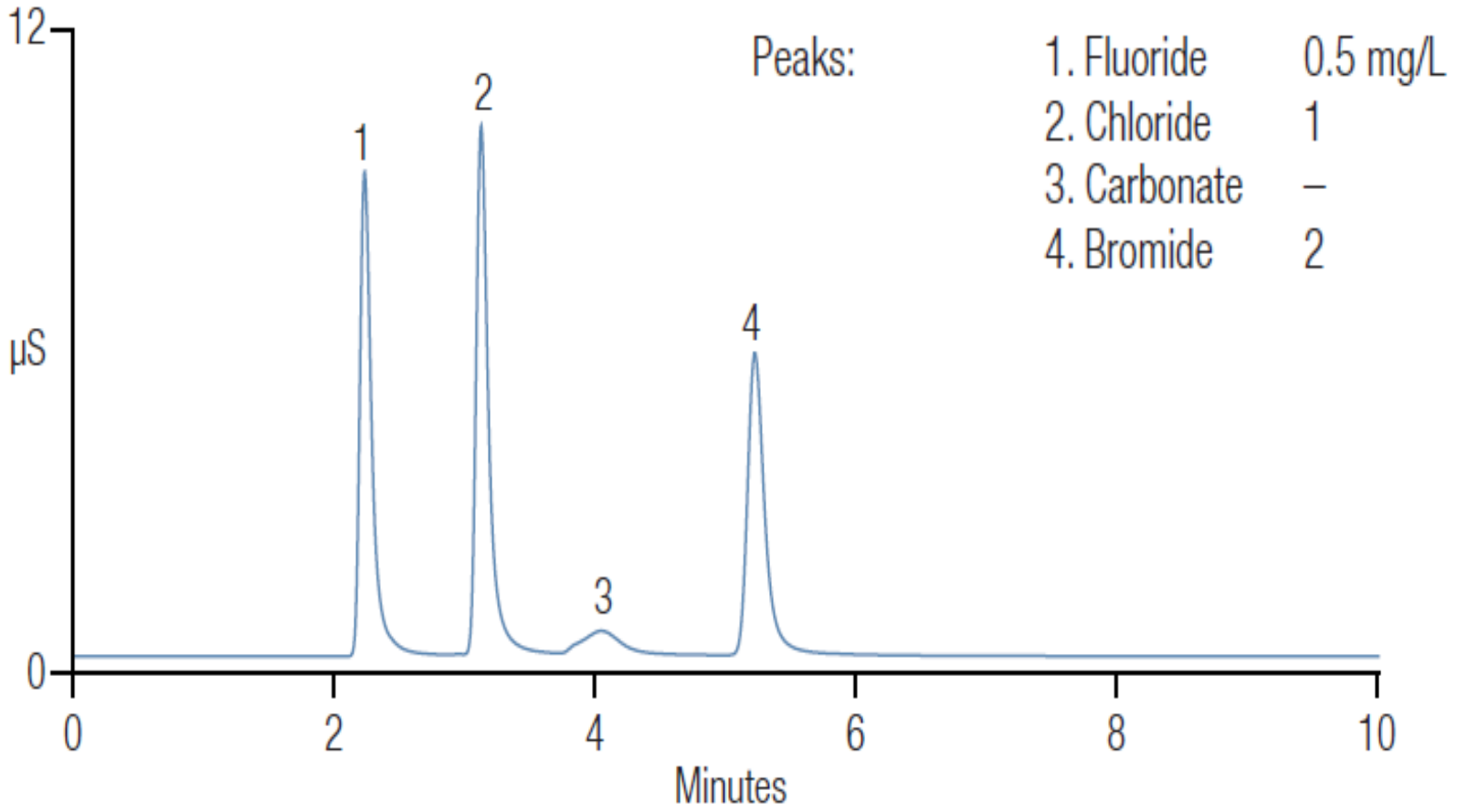
Furnace Inlet Temp.	900 ° C
Furnace Outlet Temp.	1,000 ° C
Argon Flow (Carrier)	200 mL/min
Oxygen Flow (Combustion Agent)	400 mL/min
Humidified Argon Flow	100 mL/min
Pyrolysis Tube	Quartz tube with ceramic insert and quartz wool
Sample Boat	Ceramic
Absorption Solution	Water
Absorption Solution Volume	3.5 mL
Mass Combusted	Contents of the GAC column (40–50 mg)

IC Conditions

Thermo Scientific™ Dionex™ Integrion™ HPIC™ System

IC Conditions	
Columns	Thermo Scientific™ Dionex™ IonPac™ AG18-4µm column set, 4 mm
Eluent Source	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge
Eluent Concentration	30 mM KOH
Flow Rate	1.0 mL/min
Column Temp.	30 ° C
Inj. Volume	100 µL
Detection	Suppressed conductivity

Separation of a Standard Anion Mixture



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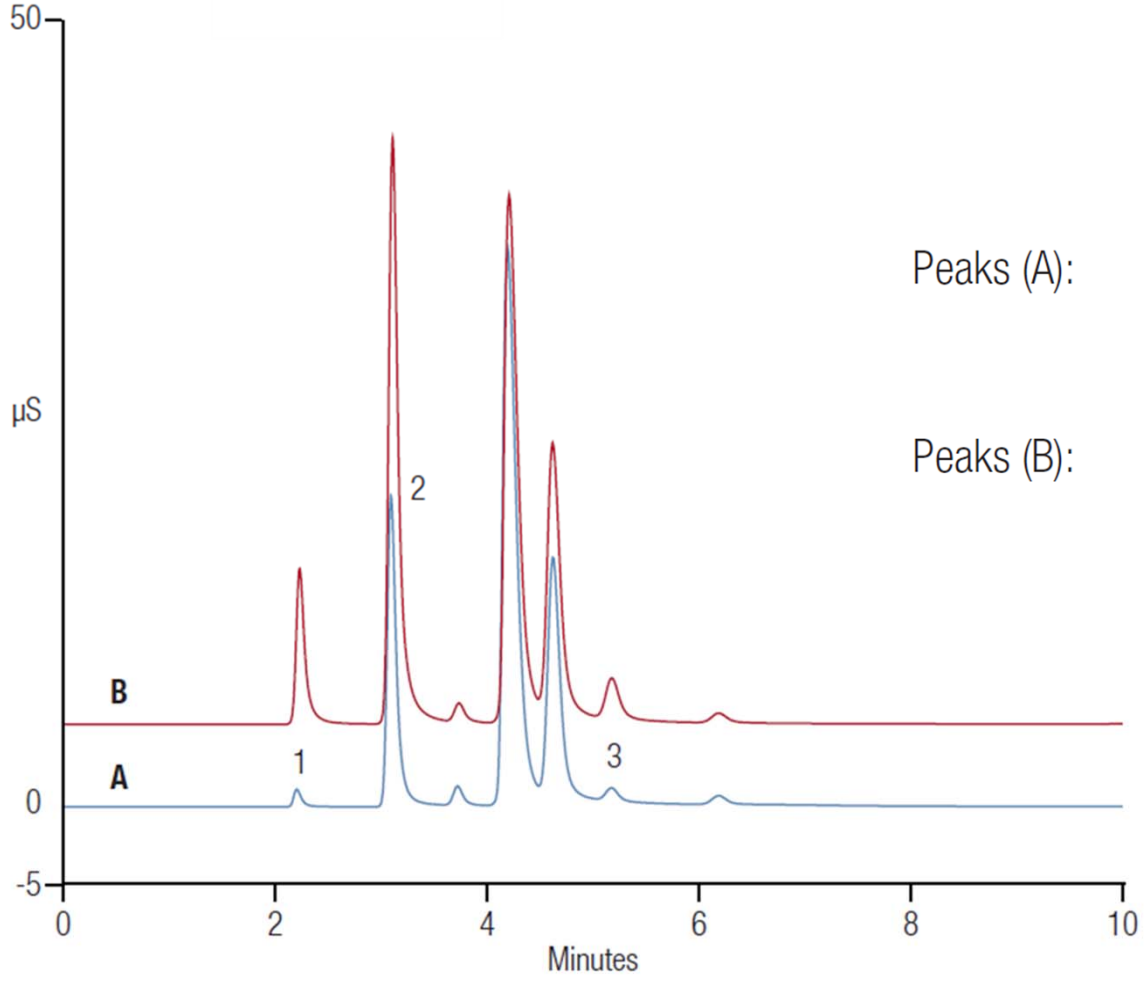
Determination of AOX in (A) Wastewater and (B) Spiked Wastewater



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

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

Recovery of AOX Spiked in DI Water (n=3)

	Amount Spiked (µg/L)	Average (µg/L)	RSD	Recovery (%)
Fluoride	50.0	53.7	4.75	107
	80.1	87.9	1.31	108
	160	173.7	1.33	109
	250	275	4.19	110
Chloride	50.0	43.8	4.70	87.6
	80.0	76.7	2.95	95.9
	160	147	1.41	92.1
	320	291	4.54	90.8
Bromide	115	118	5.08	103
	184	198	2.95	108
	367	403	2.96	110
	574	656	3.38	114

Recoveries of AOX Spiked in Wastewaters (n = 3)

	Wastewater 1			Wastewater 2		
Analyte	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
Chloride	315	400	102	80.5	100	103
Bromide	293	230	103	27.3	115	102

	Wastewater 3		
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Fluoride	8.86	101	103
Chloride	399	400	98.3
Bromide	68.7	115	104

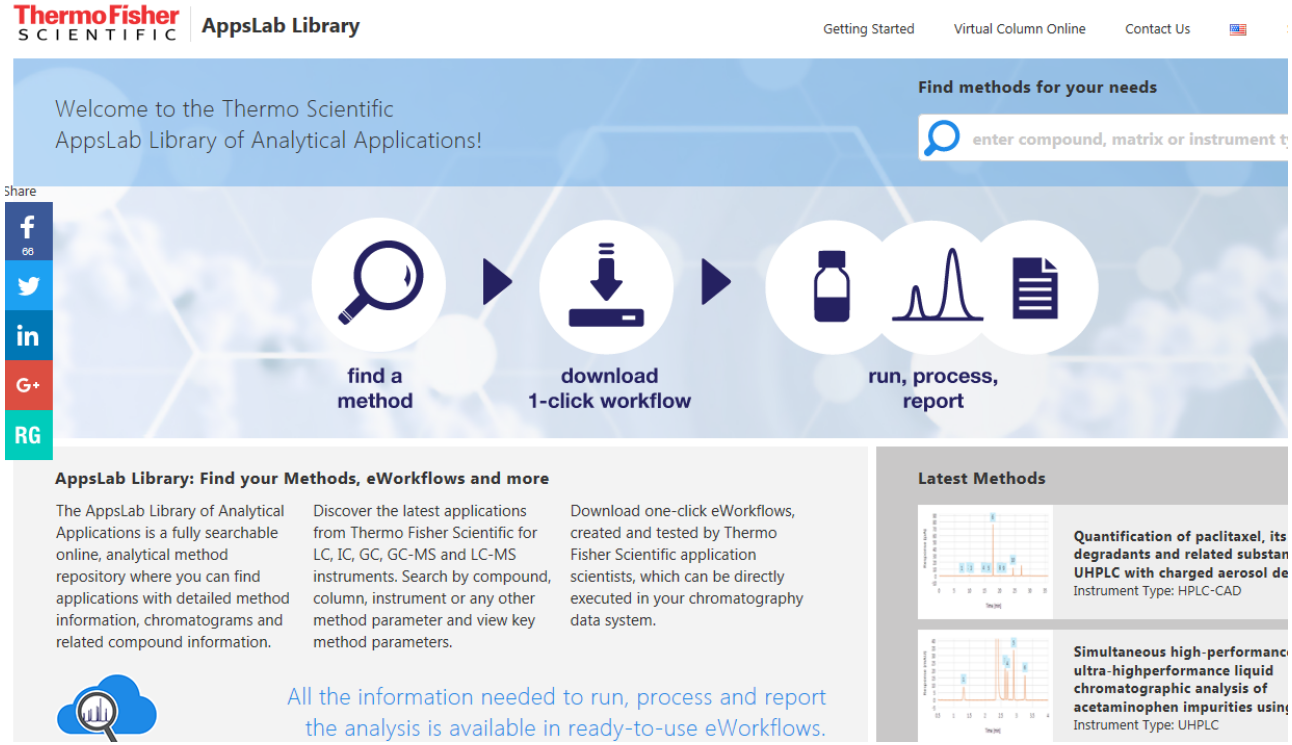
Conclusions

- 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 AS18-4µm column
- 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

Thermo Scientific AppsLab Library of Analytical Applications

Thermo Scientific Application Note 72333: Determination of adsorbable organic halogen in wastewater using a combustion ion chromatography system

https://appslab.thermofisher.com



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CIC Application Notes

- AN72693: Determination of total fluorine, chlorine, and sulfur in **aromatic hydrocarbons** by oxidative pyrolytic combustion followed by ion chromatography
- AU72588: Determination of Chlorine, Bromine, and Sulfur in **Polyethylene** Materials using Combustion IC with a Carbonate/Bicarbonate Eluent
- AN72573: Determination of Halogens in **Polymers** and **Electronics** using a Combustion Ion Chromatography System
- AN72349: Determination of Chlorine, Bromine, and Sulfur in **Polyethylene** Materials using Combustion Ion Chromatography
- AN72333: Determination of Adsorbable Organic Halogen in **Wastewater** using a Combustion Ion Chromatography System
- AN72268: Determination of Fluoride in **Tea** using a Combustion Ion Chromatography System
- AN1145: Determination of Halogens in **Coal** Using Combustion Ion Chromatography
- TN72211: Combustion Ion Chromatography with a Dionex **Integrion** HPIC System