

**ThermoFisher**  
S C I E N T I F I C

## Determination of Adsorbable Organic Halogen in Wastewater

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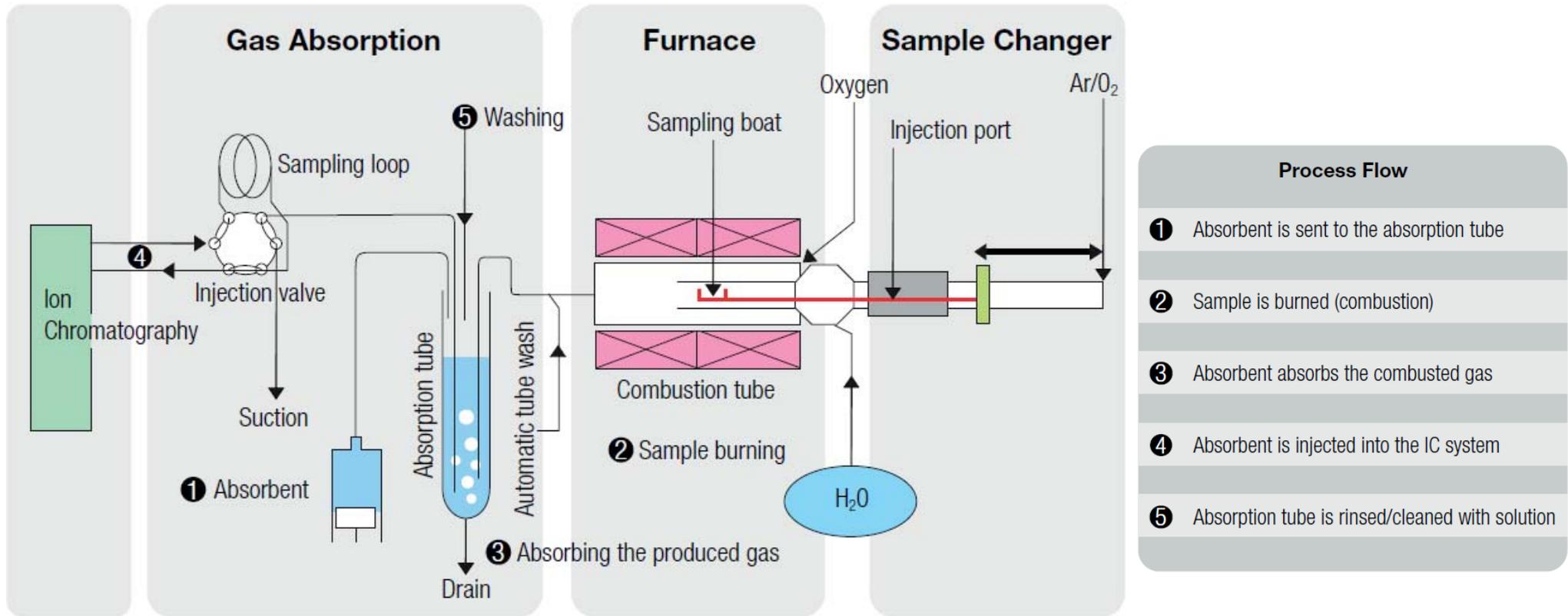
# Outline

- 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



# CIC System Components



↑  
Ion  
Chromatography  
System

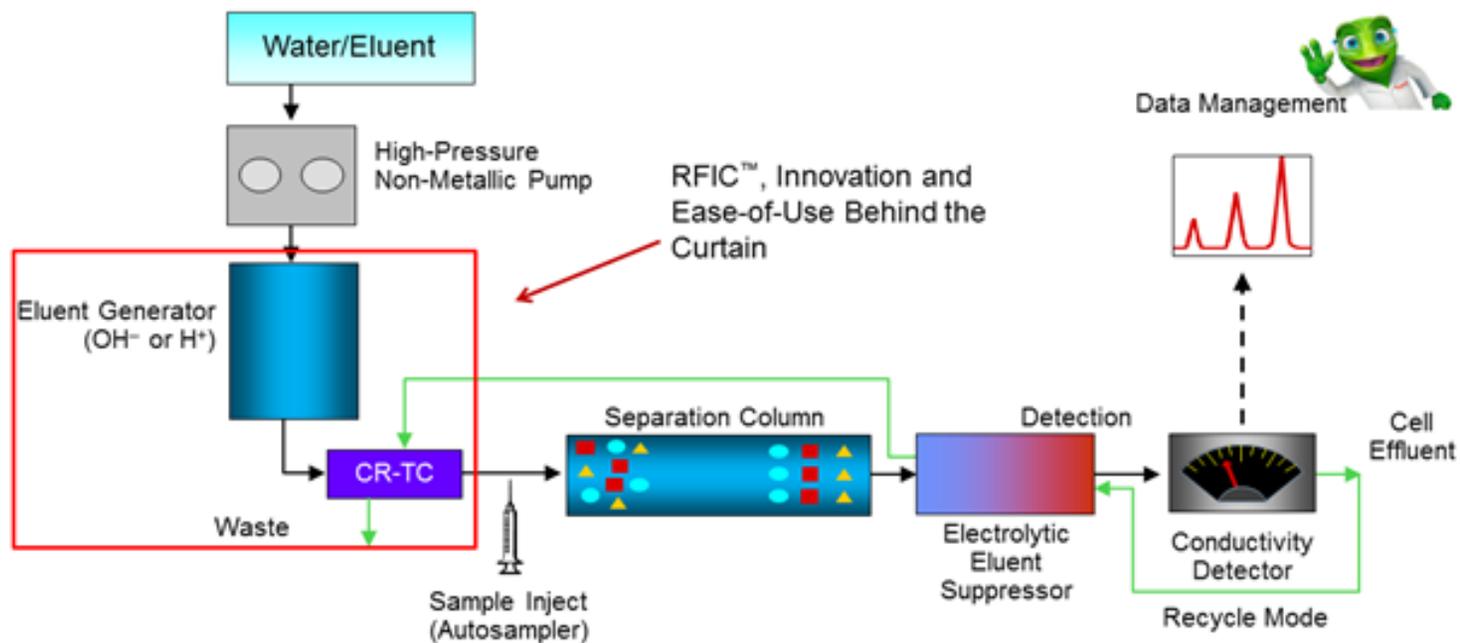
↑  
Gas Absorption  
Unit

↑  
Furnace

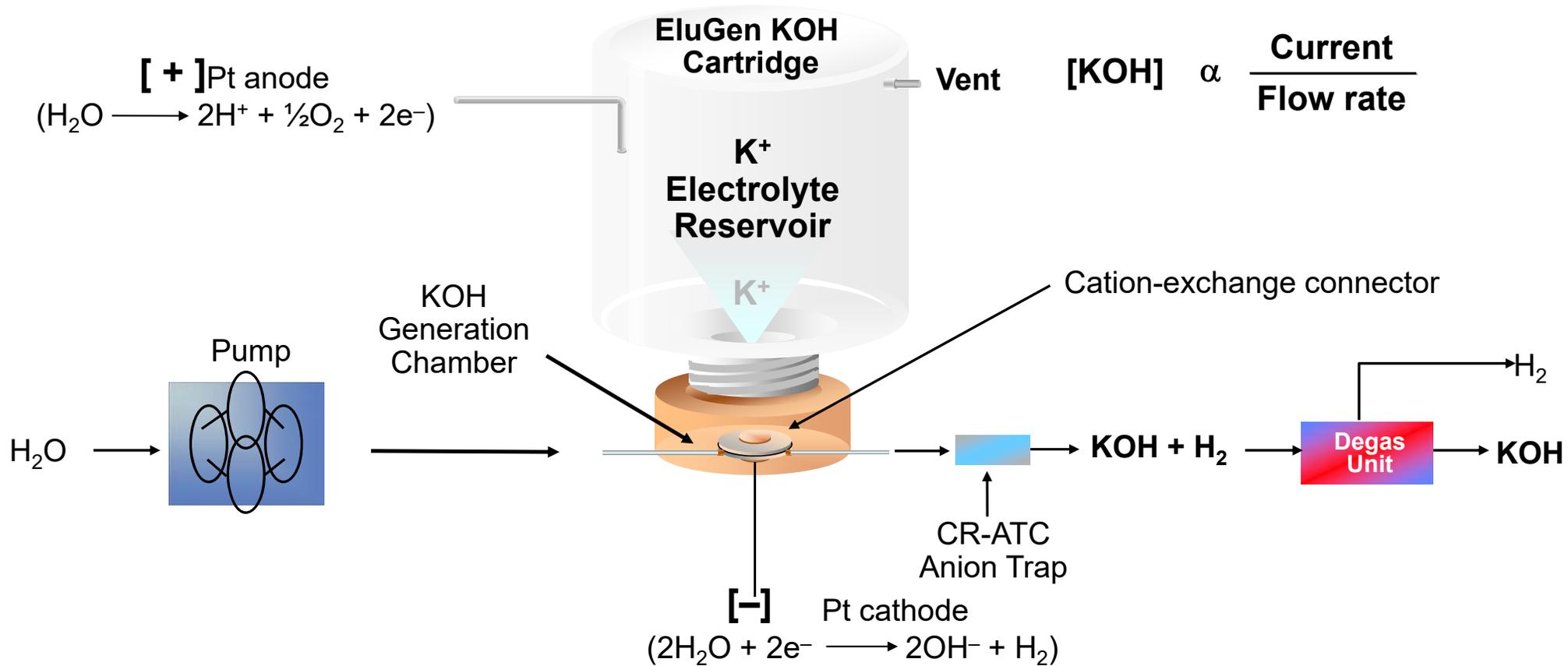
↑  
Solid/Liquid Autosampler

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

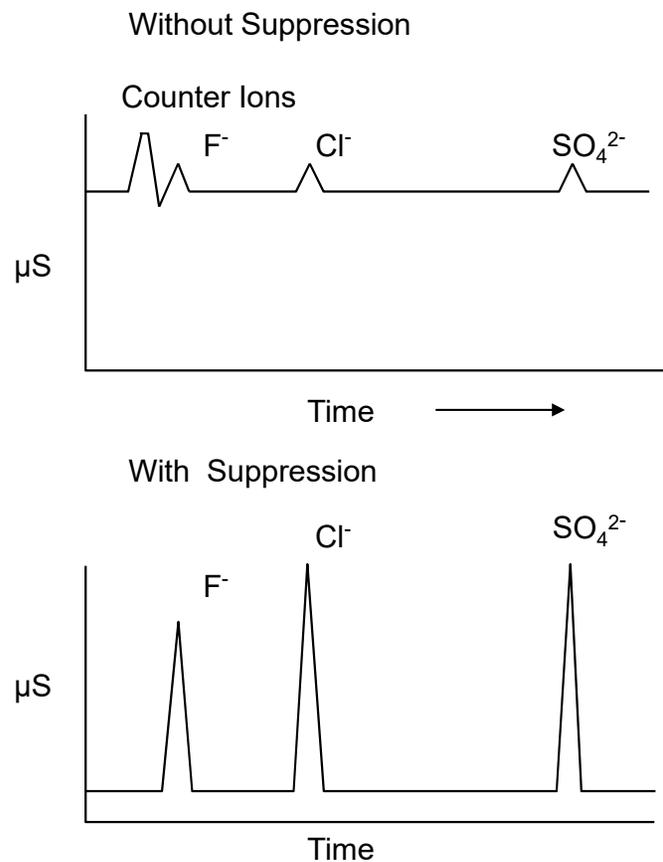
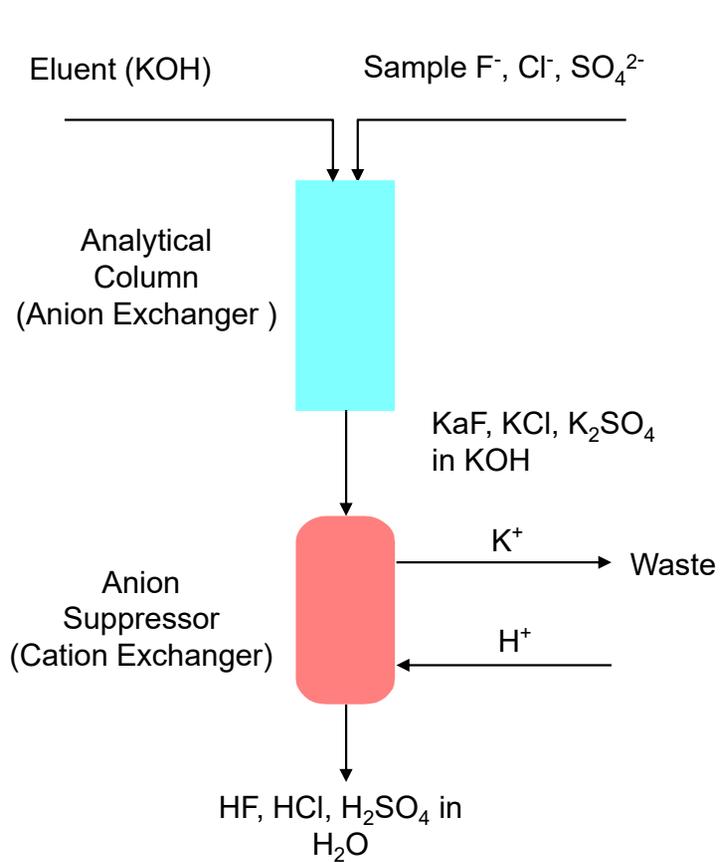
# Reagent-free Ion Chromatography (RFIC) System



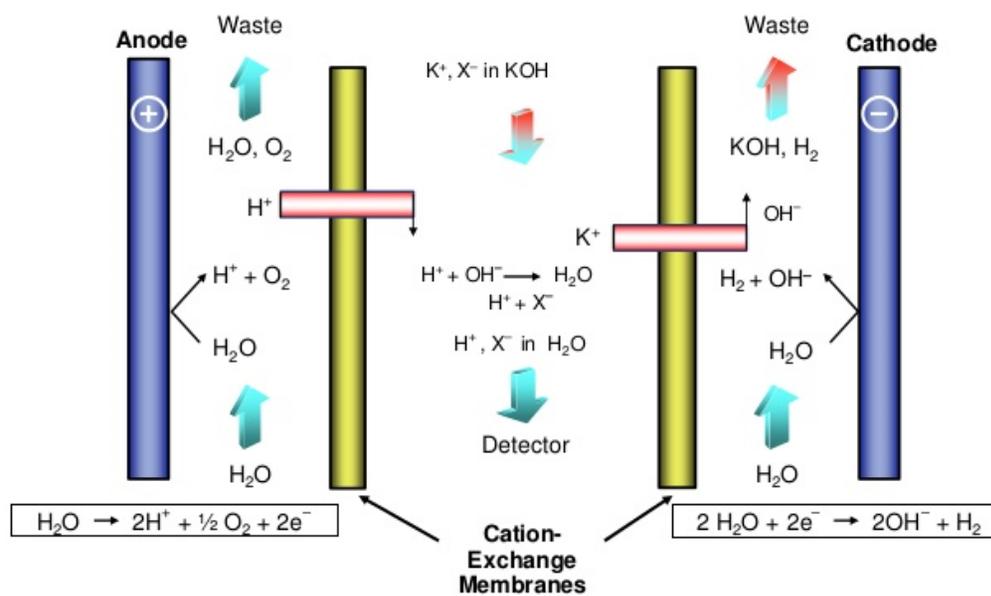
# Hydroxide Eluent Generation



# The Role of Chemical Suppression (KOH)



# Thermo Scientific Dionex Electrochemically Regenerated Suppressors



## 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

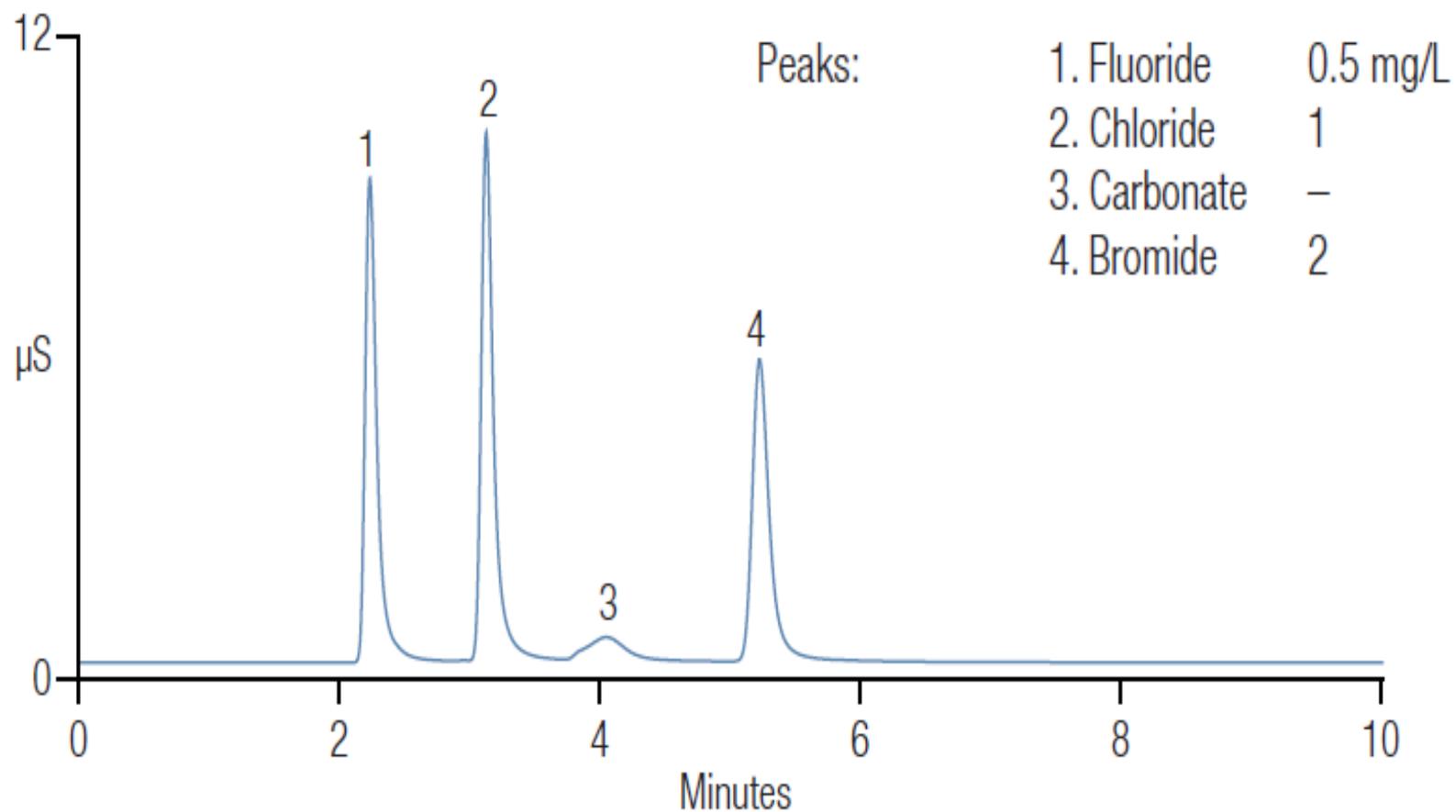
<b>Furnace Inlet Temp.</b>	900 ° C
<b>Furnace Outlet Temp.</b>	1,000 ° C
<b>Argon Flow (Carrier)</b>	200 mL/min
<b>Oxygen Flow (Combustion Agent)</b>	400 mL/min
<b>Humidified Argon Flow</b>	100 mL/min
<b>Pyrolysis Tube</b>	Quartz tube with ceramic insert and quartz wool
<b>Sample Boat</b>	Ceramic
<b>Absorption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

## IC Conditions

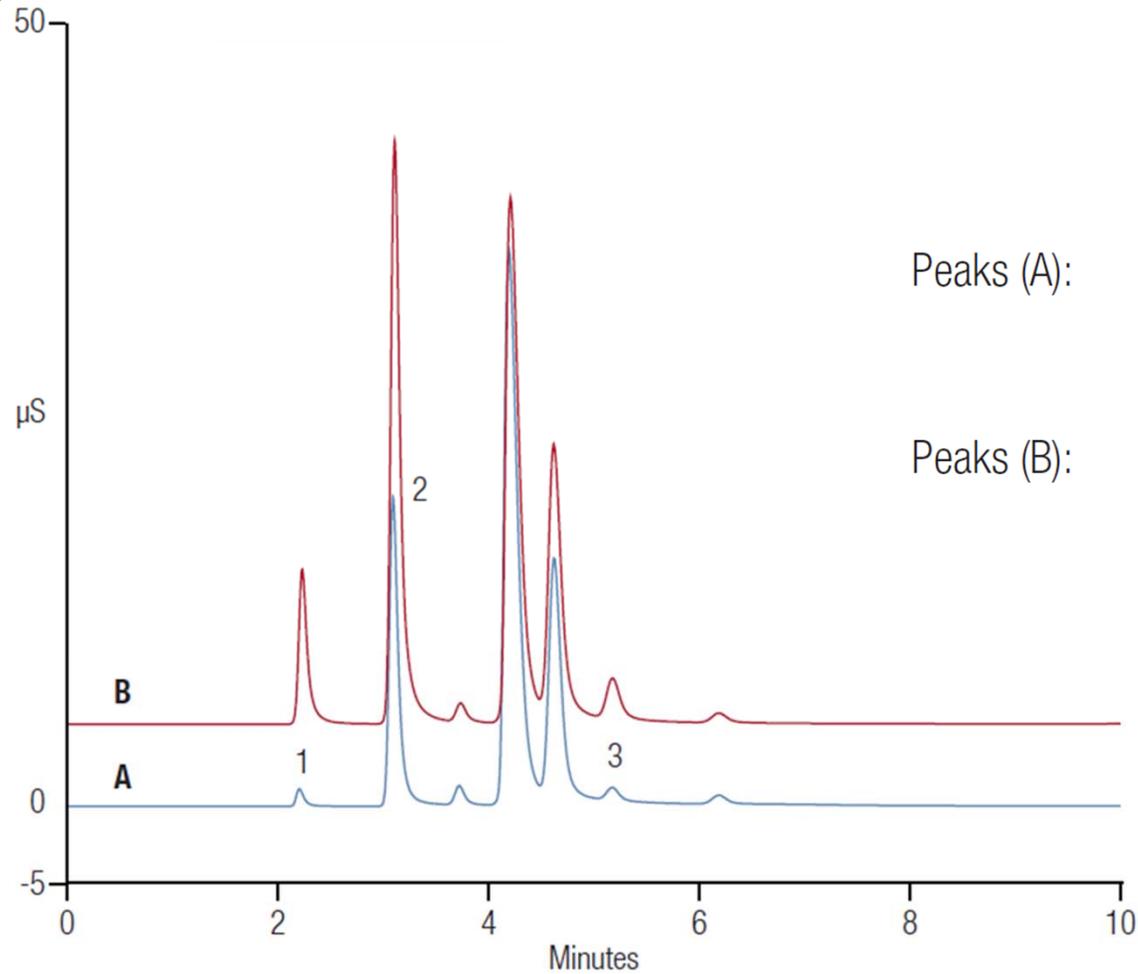
### Thermo Scientific™ Dionex™ Integrion™ HPIC™ System

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



# 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 (%)
<b>Fluoride</b>	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
<b>Chloride</b>	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
<b>Bromide</b>	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)

Analyte	Wastewater 1			Wastewater 2		
	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
<b>Fluoride</b>	1.71	101	103	2.69	101	104
<b>Chloride</b>	315	400	102	80.5	100	103
<b>Bromide</b>	293	230	103	27.3	115	102

Analyte	Wastewater 3		
	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
<b>Fluoride</b>	8.86	101	103
<b>Chloride</b>	399	400	98.3
<b>Bromide</b>	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 AS18-4 $\mu$ m 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>

The screenshot shows the Thermo Scientific AppsLab Library website. At the top, the ThermoFisher Scientific logo is on the left, and navigation links for 'Getting Started', 'Virtual Column Online', and 'Contact Us' are on the right. A search bar is located in the top right corner with the placeholder text 'enter compound, matrix or instrument type'. Below the search bar is a large blue banner with the text 'Welcome to the Thermo Scientific AppsLab Library of Analytical Applications!' and 'Find methods for your needs'. A central workflow diagram consists of three circular icons connected by arrows: a magnifying glass labeled 'find a method', a download icon labeled 'download 1-click workflow', and a bottle, chromatogram, and document icon labeled 'run, process, report'. To the left of the banner are social media sharing icons for Facebook, Twitter, LinkedIn, Google+, and RSS. Below the banner, the text reads 'AppsLab Library: Find your Methods, eWorkflows and more'. This is followed by three columns of text: 'The AppsLab Library of Analytical Applications is a fully searchable online, analytical method repository where you can find applications with detailed method information, chromatograms and related compound information.', 'Discover the latest applications from Thermo Fisher Scientific for LC, IC, GC, GC-MS and LC-MS instruments. Search by compound, column, instrument or any other method parameter and view key method parameters.', and 'Download one-click eWorkflows, created and tested by Thermo Fisher Scientific application scientists, which can be directly executed in your chromatography data system.' To the right, a 'Latest Methods' section features two entries, each with a chromatogram and a title: 'Quantification of paclitaxel, its degradants and related substances using UHPLC with charged aerosol detector' (Instrument Type: HPLC-CAD) and 'Simultaneous high-performance ultra-highperformance liquid chromatographic analysis of acetaminophen impurities using UHPLC' (Instrument Type: UHPLC). At the bottom of the main content area, a blue cloud icon with a magnifying glass is next to the text: 'All the information needed to run, process and report the analysis is available in ready-to-use eWorkflows.'

# 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

