



Determination of Adsorbable Organic Halogen in Wastewater

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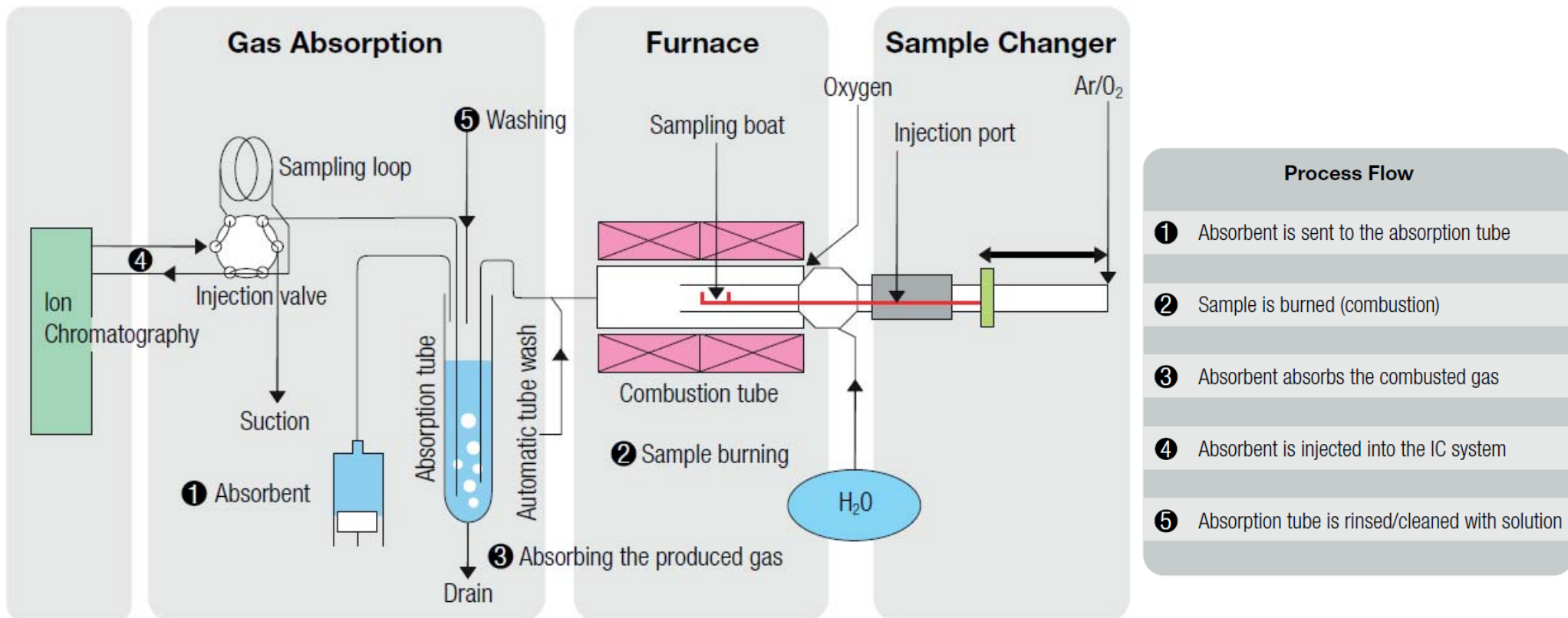
Outline

- 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

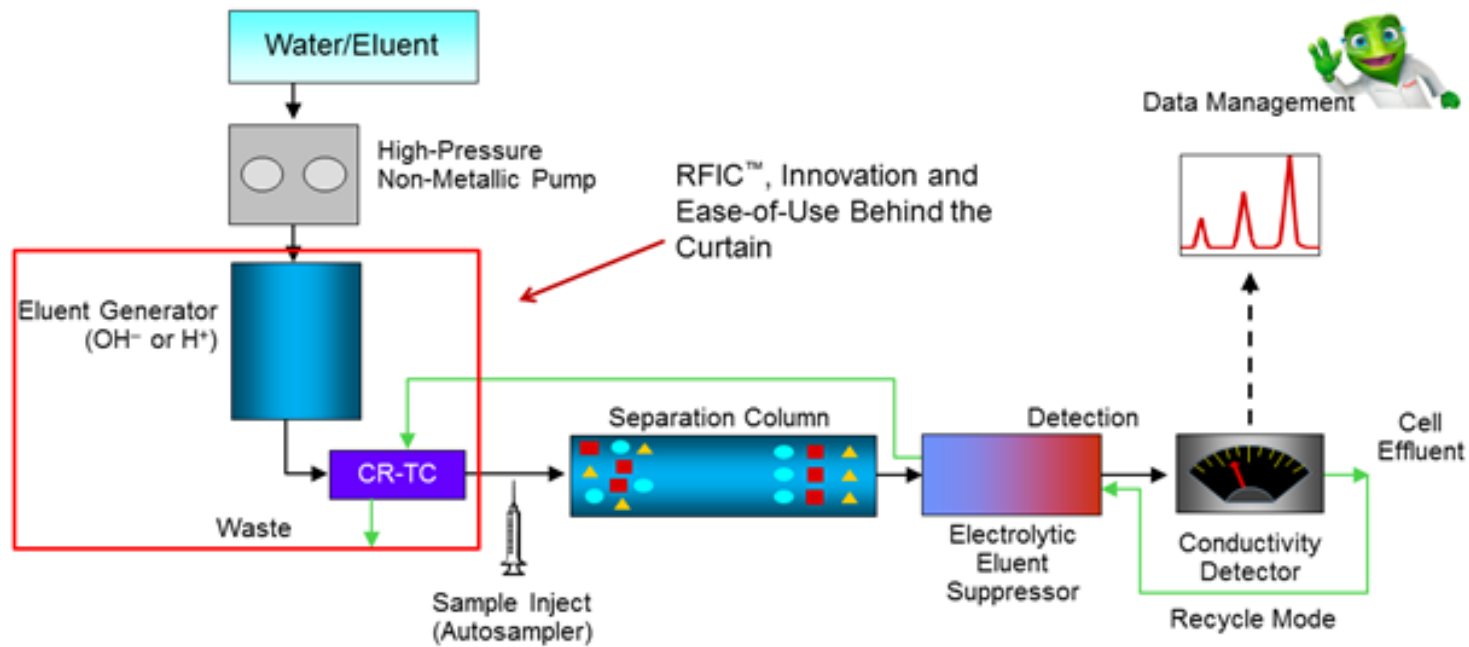
↑
Gas Absorption
Unit

↑
Furnace

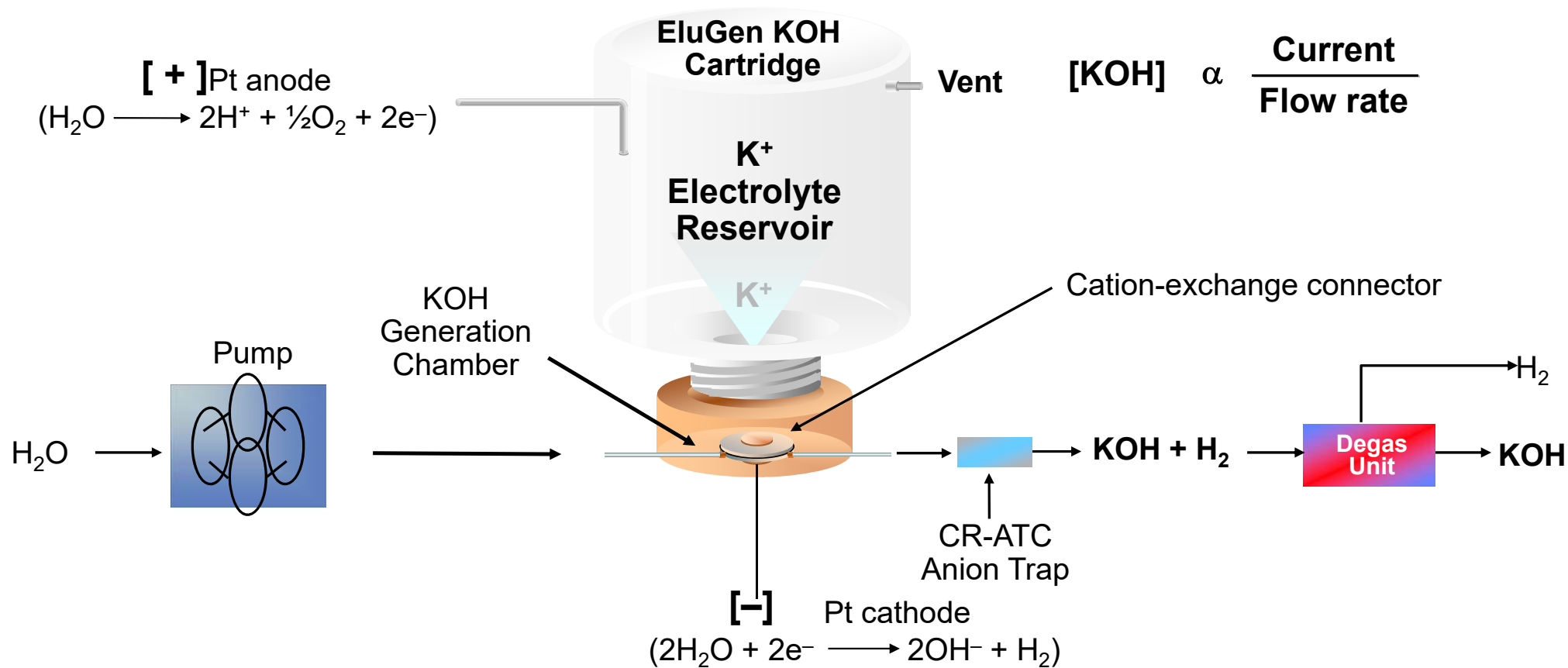
↑
Solid/Liquid Autosampler

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

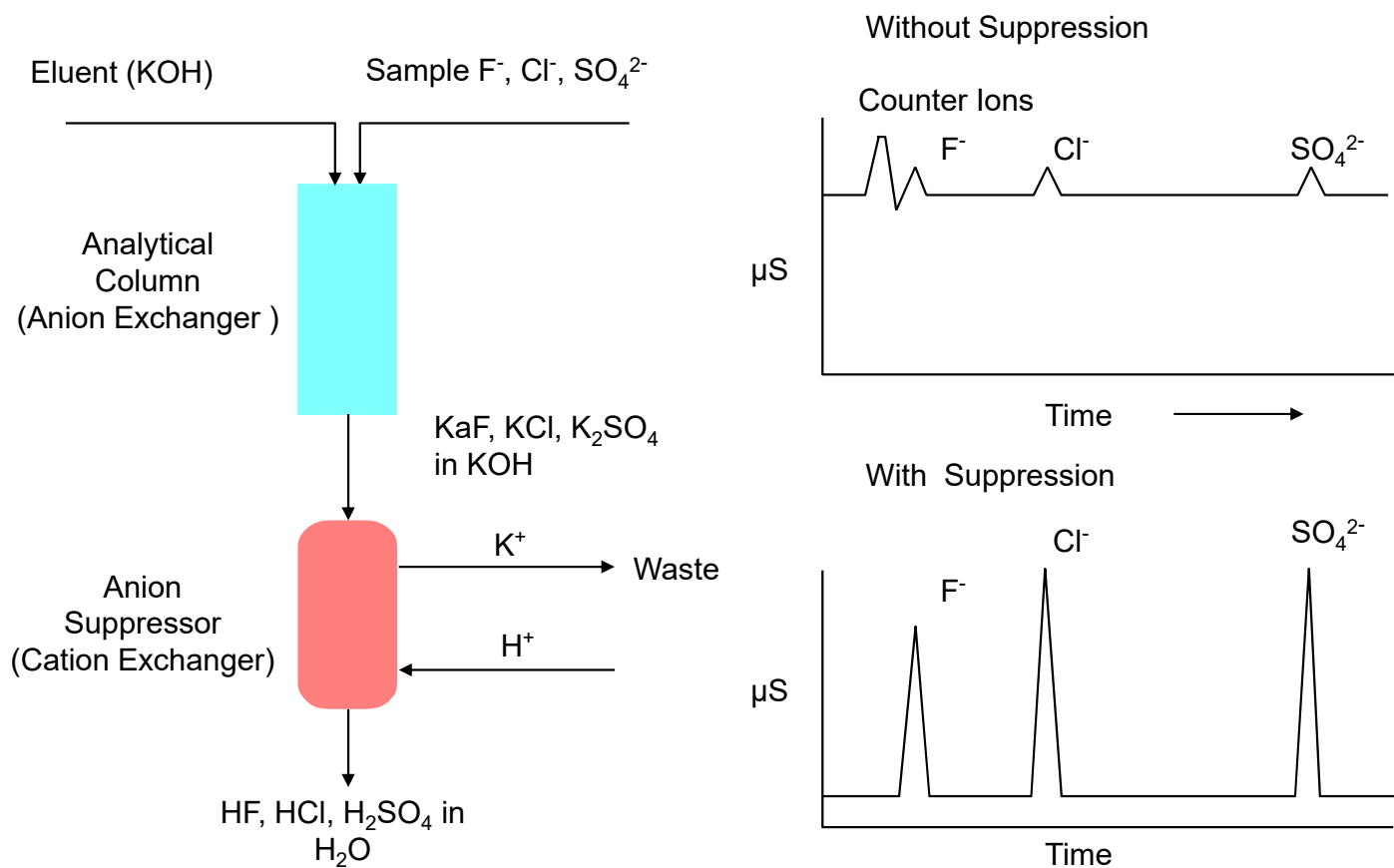
Reagent-free Ion Chromatography (RFIC) System



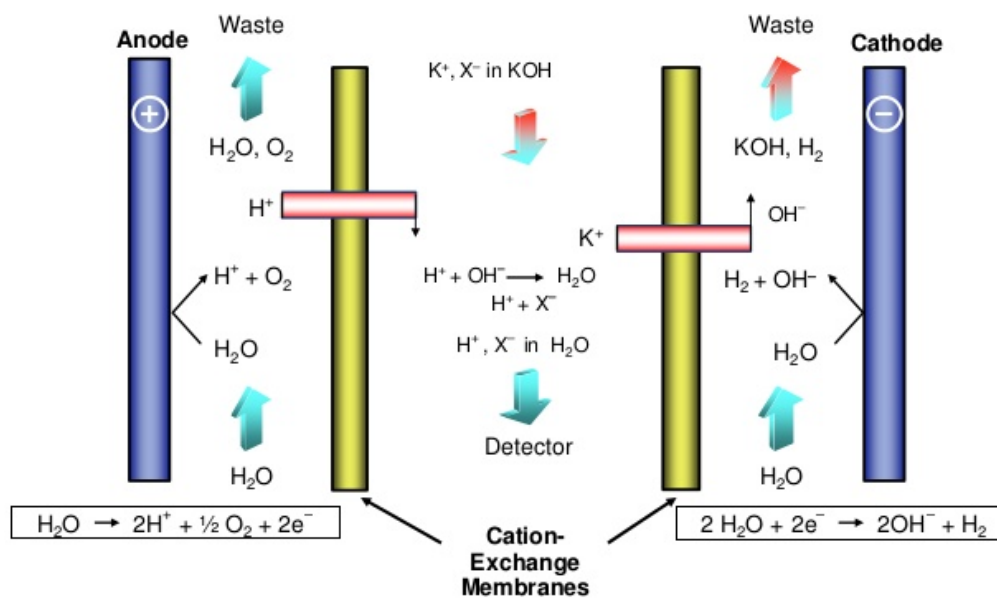
Hydroxide Eluent Generation



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

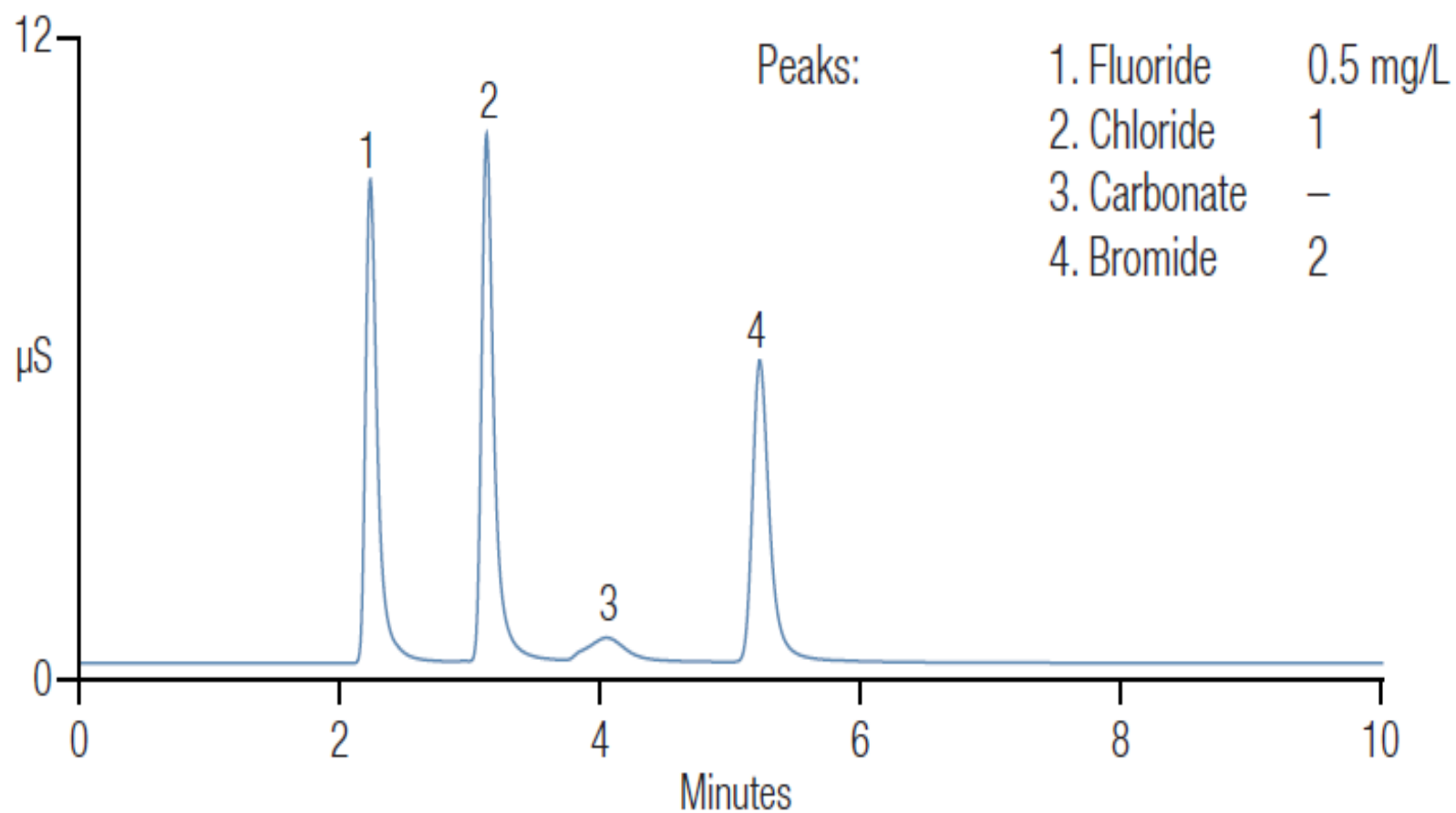
| | |
|---------------------------------------|---|
| Furnace Inlet Temp. | 900 ° C |
| Furnace Outlet Temp. | 1,000 ° C |
| Argon Flow (Carrier) | 200 mL/min |
| Oxygen Flow (Combustion Agent) | 400 mL/min |
| Humidified Argon Flow | 100 mL/min |
| Pyrolysis Tube | Quartz tube with ceramic insert and 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

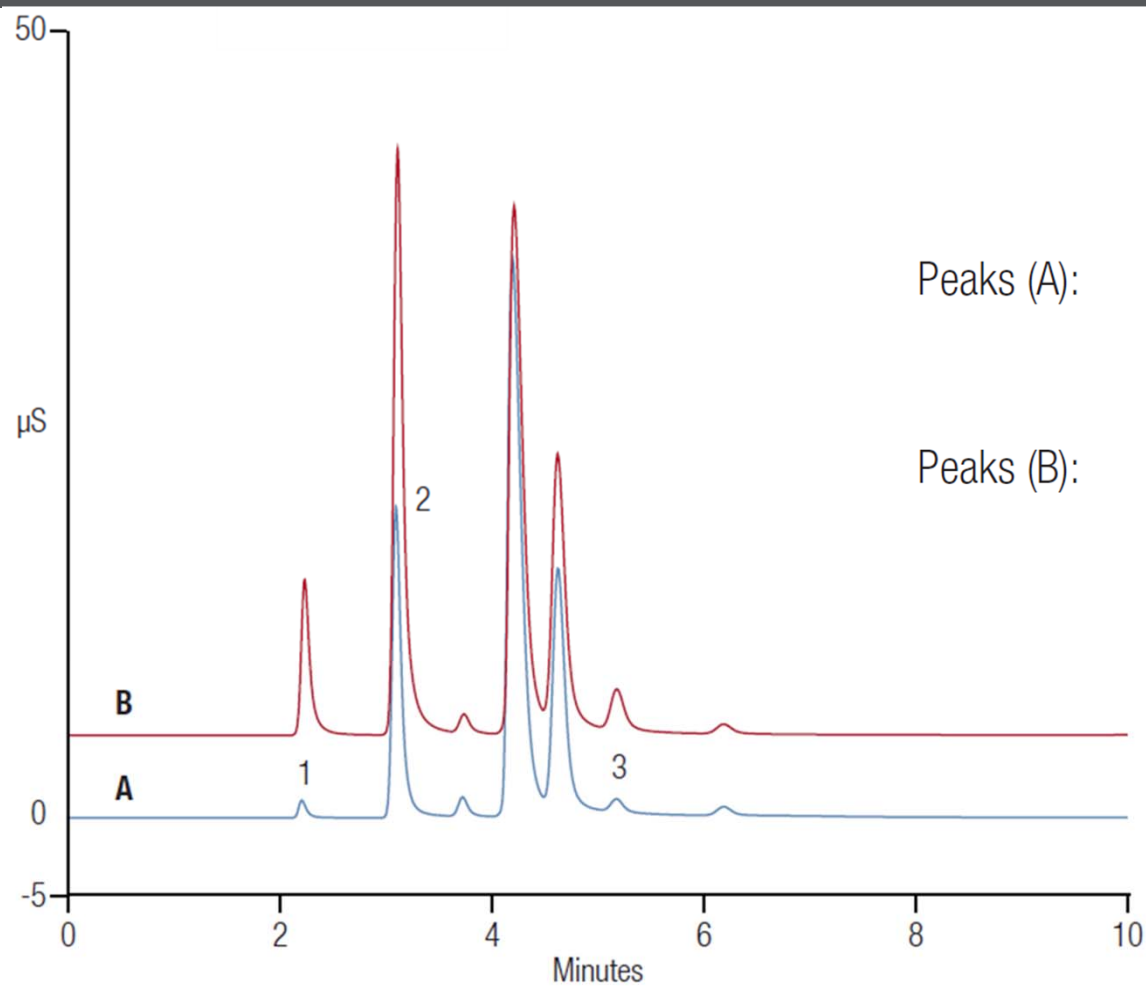
Thermo Scientific™ Dionex™ Integrion™ HPIC™ System

| 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



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 AS18-4 μ 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 homepage. At the top, the ThermoFisher Scientific logo and 'AppsLab Library' are on the left, and navigation links for 'Getting Started', 'Virtual Column Online', and 'Contact Us' are on the right. A welcome message reads: 'Welcome to the Thermo Scientific AppsLab Library of Analytical Applications!'. To the right of this is a search bar with the placeholder text 'Find methods for your needs' and 'enter compound, matrix or instrument type'. Below the welcome message is a three-step workflow diagram: 1. 'find a method' (magnifying glass icon), 2. 'download 1-click workflow' (download icon), and 3. 'run, process, report' (icons of a vial, chromatogram, and document). To the left of the workflow are social media share buttons for Facebook, Twitter, LinkedIn, Google+, and ResearchGate. Below the workflow, the text 'AppsLab Library: Find your Methods, eWorkflows and more' is followed by three columns of descriptive text. The first column states the library is a fully searchable online repository. The second column describes the range of applications from LC to GC-MS. The third column mentions the availability of one-click eWorkflows. To the right, under 'Latest Methods', two method cards are shown: 'Quantification of paclitaxel, its degradants and related substances using UHPLC with charged aerosol detection' and 'Simultaneous high-performance ultra-highperformance liquid chromatographic analysis of acetaminophen impurities using UHPLC'. Each card includes a small chromatogram plot and the instrument type.

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Download one-click eWorkflows, created and tested by Thermo Fisher Scientific application scientists, which can be directly executed in your chromatography data system.

Latest Methods

Quantification of paclitaxel, its degradants and related substances using UHPLC with charged aerosol detection
Instrument Type: HPLC-CAD

Simultaneous high-performance ultra-highperformance liquid chromatographic analysis of acetaminophen impurities using UHPLC
Instrument Type: UHPLC

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

