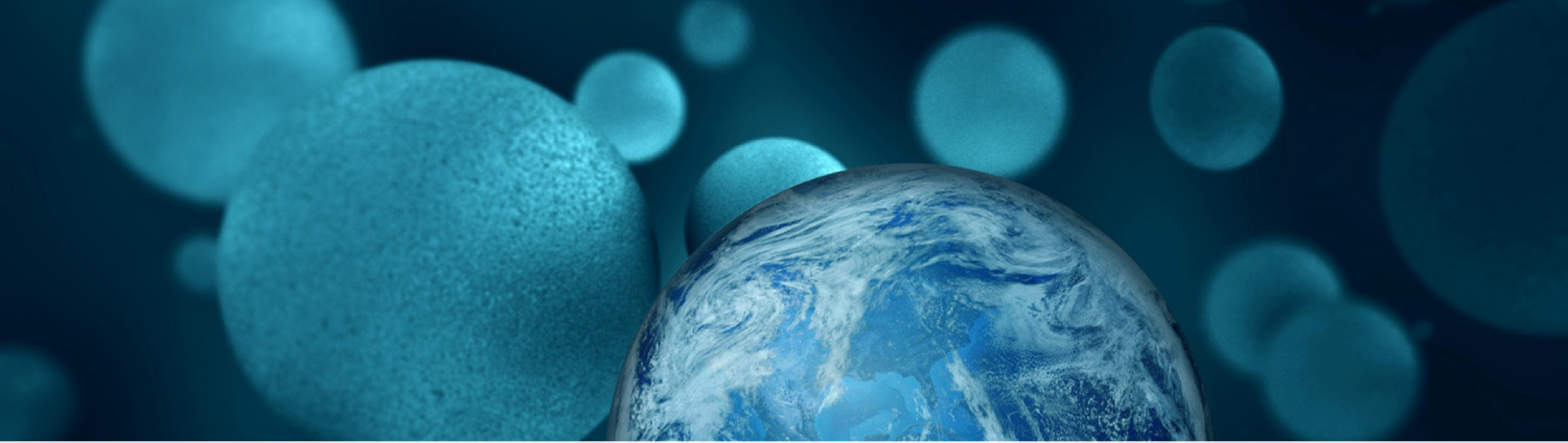


Determination of the Total Sulfur, Chlorine, Bromine, and Fluorine Contents of Solid Samples

Jeff Rohrer, Ph. D.
Thermo Fisher Scientific, Sunnyvale, CA

Outline

- The challenge of solid samples
- Combustion
- Ion chromatography (IC) basics and Combustion IC (CIC)
- Examples of using CIC to solve analysis problems
- Conclusions

Solid Samples for IC

- Those soluble in water will just require filtration.
- Samples soluble in an organic solvent* will probably require removal of the solvent and raise questions of recovery.
- Even without removal there can be questions of extraction efficiency.
- Acid solubility may or may not be useful.
- Is the goal to determine an ion (e.g., chloride) or an element (e.g., chlorine) content?

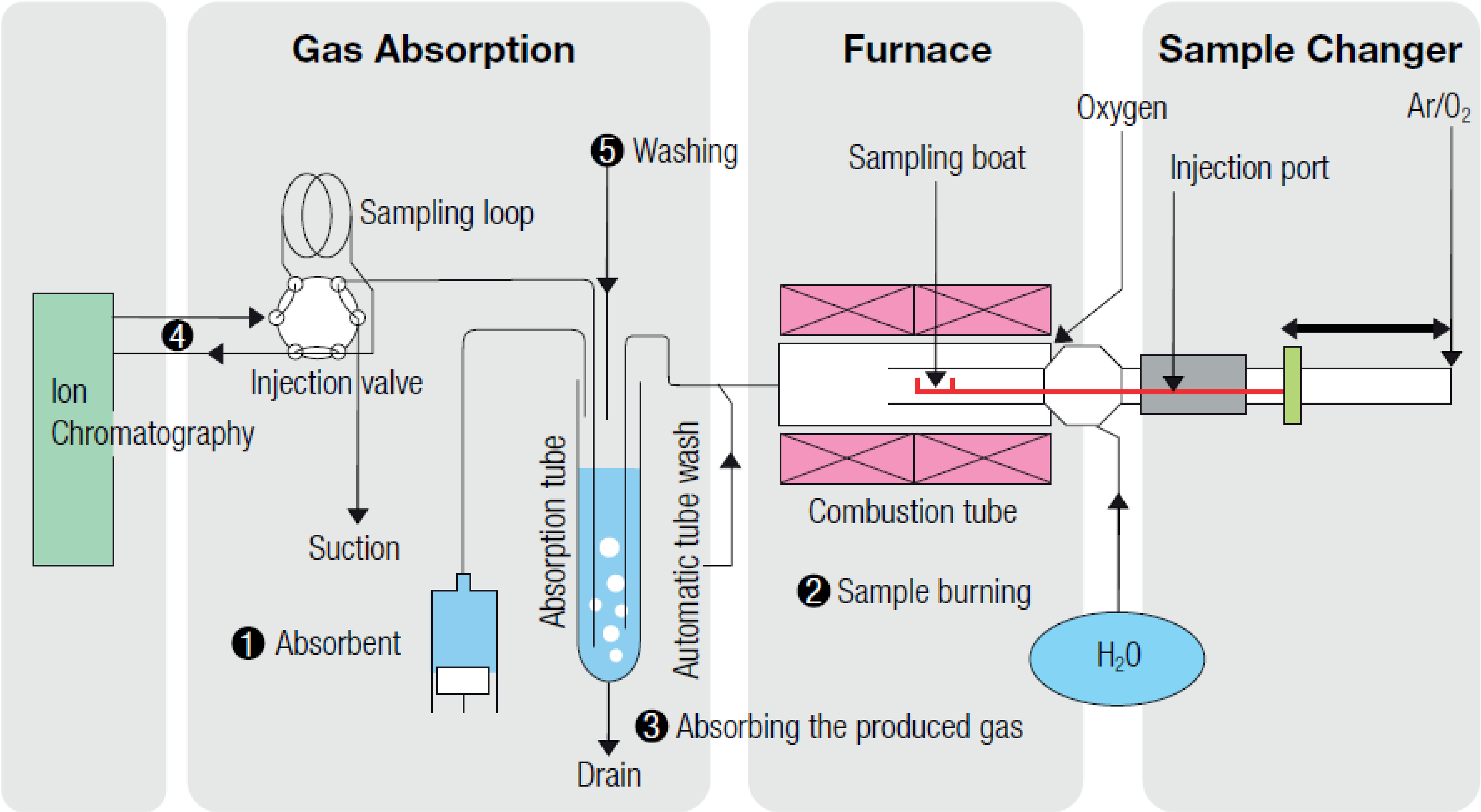
Combustion as Sample Preparation for Ion Chromatography

1. Samples are oxidized by oxygen (oxidative pyrolysis) at temperatures of about 1000 °C.

2. The combustion by-product gases, including HX and SO_2 /SO_3, are passed through an aqueous absorbing solution.

3. This solution is then directly injected into the IC instrument.

CIC System Diagram



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

Combustion Ion Chromatography (CIC)

Advantages of CIC system

- Eliminates complex sample preparation
- Sensitive
- Easy to use
- Produces fewer environmental contaminants

Applications of CIC

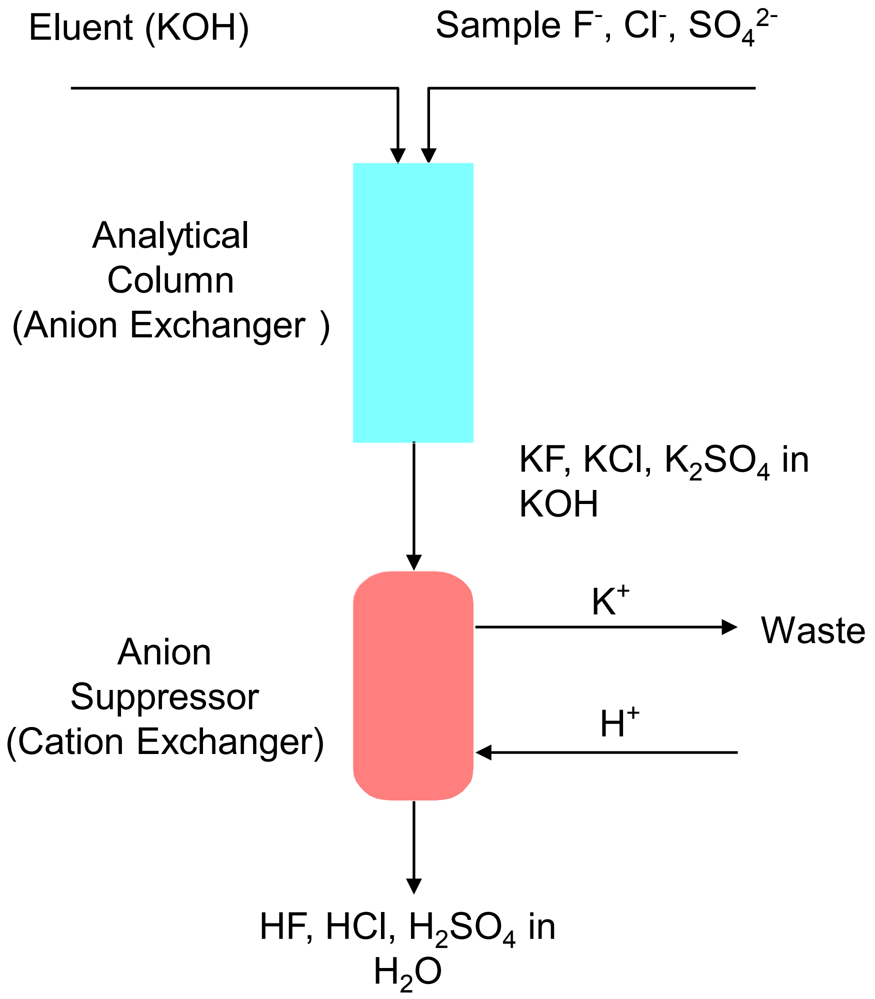
- Polymers and electronics
- Coal
- Petroleum
- LPG
- Wood chips
- Ethanol, biodiesel, alternative fuels

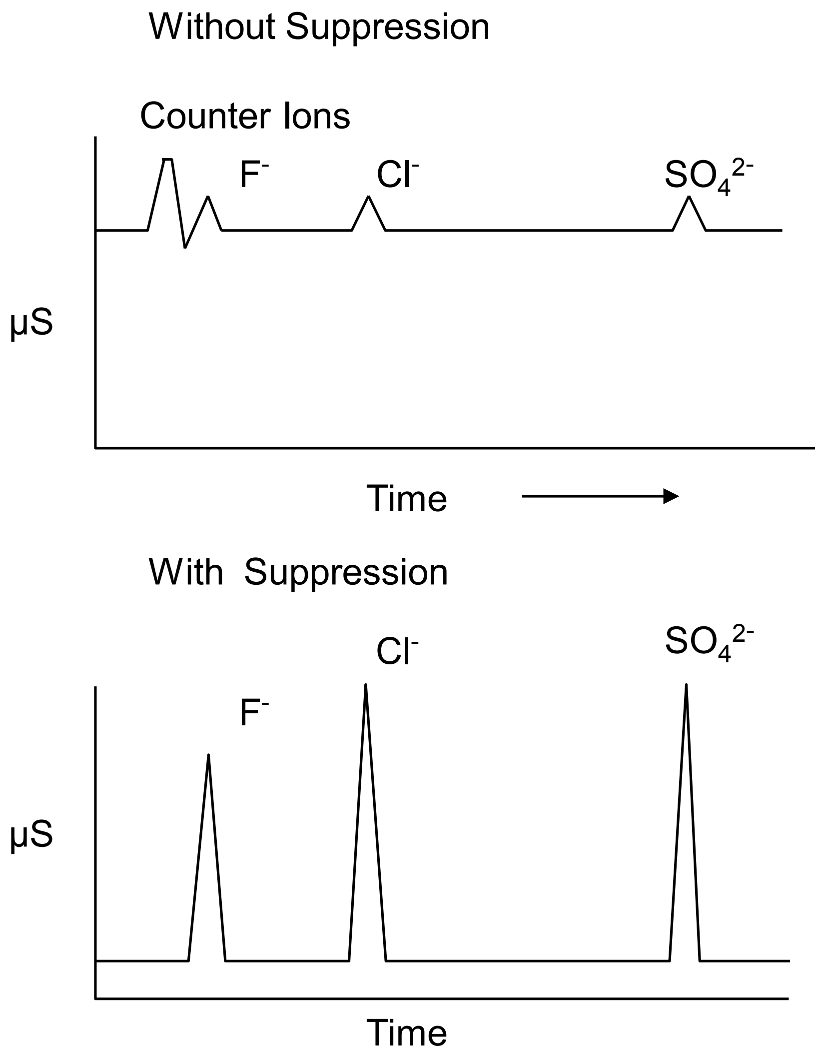
Ion Chromatography (IC)

At the most basic level….

Ion Chromatography = Ion-Exchange +
Chemically Suppressed Conductivity

The Role of Chemical Suppression (KOH)





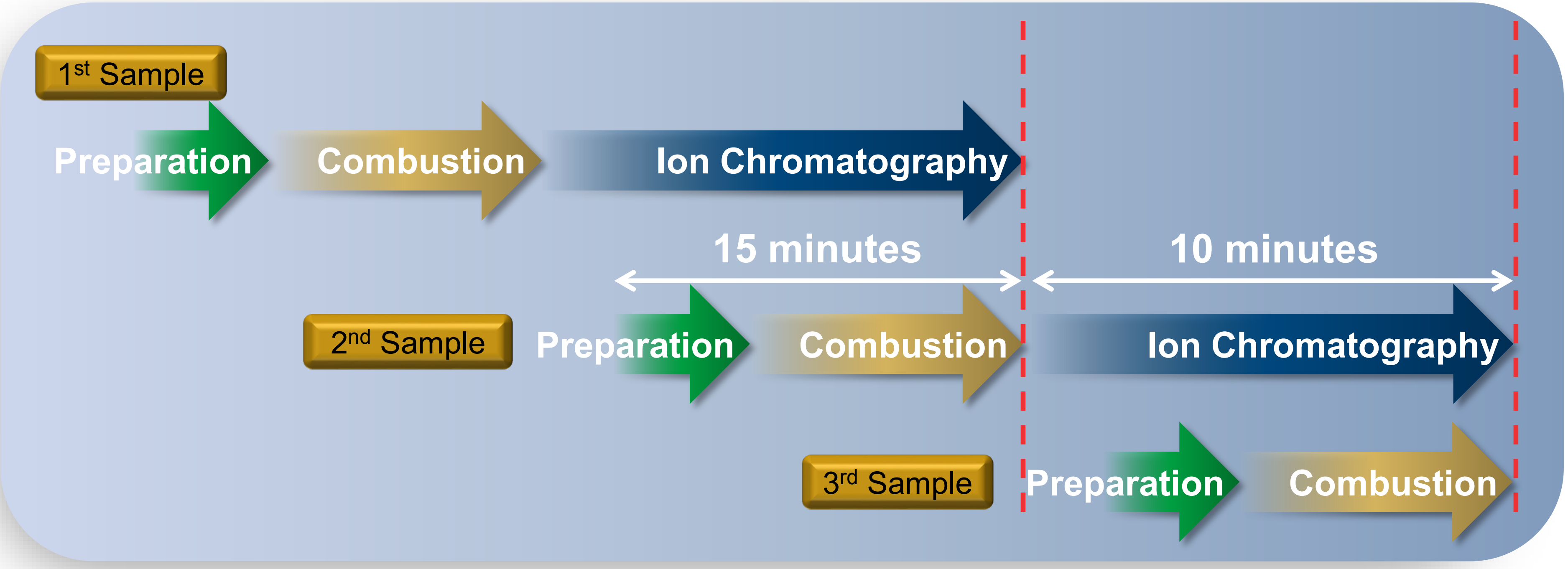
CIC System Components

IC   Gas Absorption Unit   Furnace   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

Software-Based Automation to Increase Productivity

- Established program controls total analysis
  - Capable of starting combustion of next sample to reduce waiting time

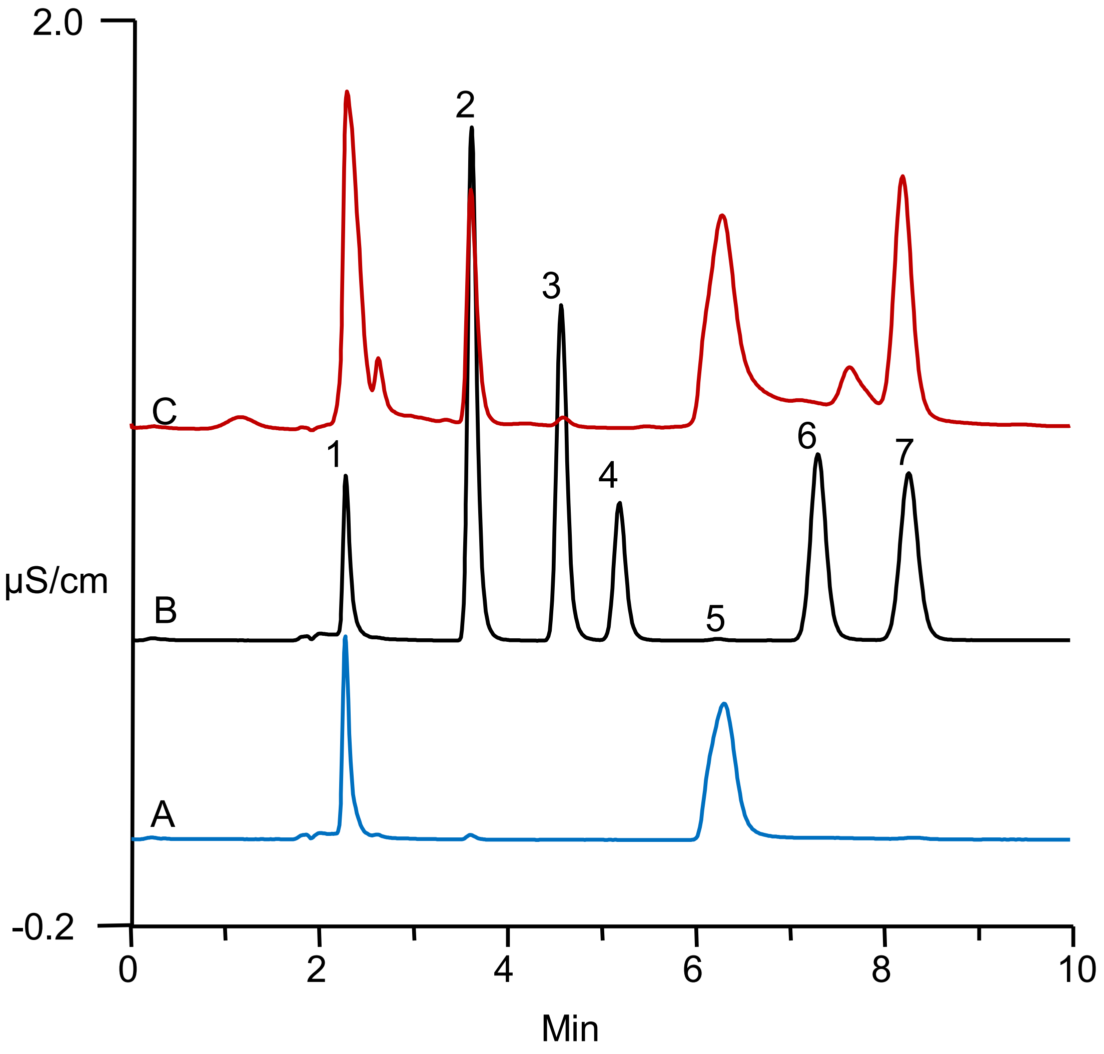


	1st Sample	2nd sample	3rd sample	4th sample	5th sample
Analysis time	25min (Data in 15+10 min)	40 min (Data in +15 min instead of 15+10 min)	55 min (Data in +15 min instead of 15+10 min)	@70min	@85min and so on…

Application Problem #1: Determination of Fluoride in Tea

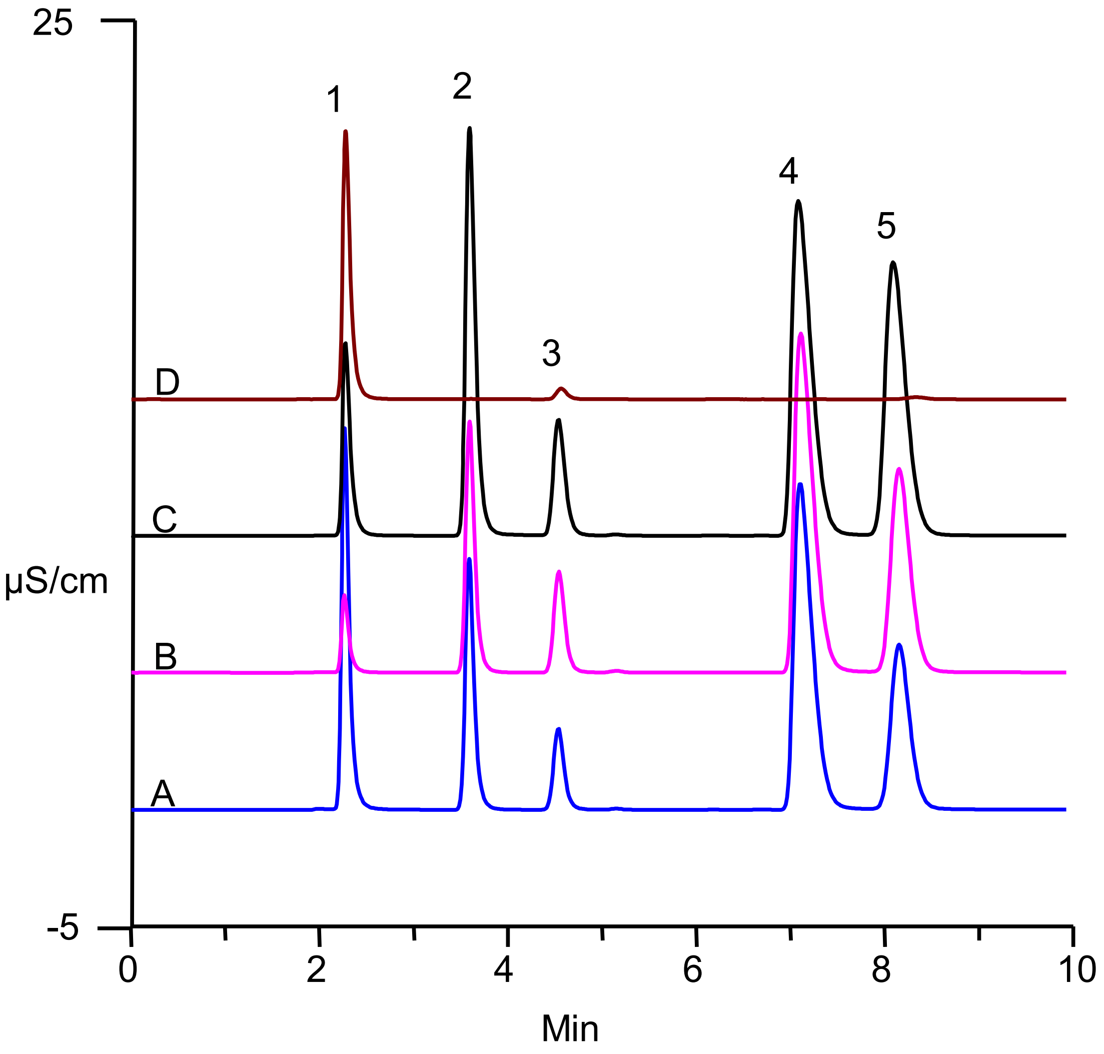
- Seems easy – Make tea and analyze by IC
- The problem: Too may other peaks interfere with fluoride separation
- The solution: Combust solid tea to remove other compounds and obtain fluoride

Analysis of Tea for Fluoride



Columns:	Thermo Scientific™ Dionex™ IonPac™ AG18-4µm and AS18-4µm, 4 mm
Eluent:	20 mM KOH
Eluent source:	Thermo Scientific Dionex EGC 500 KOH cartridge
Flow rate:	1.0 mL/min
Inj. volume:	100 µL
Column temp.:	30 °C
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ AERS 500 electrolytically regenerated suppressor, 4 mm, 35 °C, 50 mA, recycle mode Compartment temp. 25 °C
Sample prep.:	Brew 5 g tea in 50 mL DI water for 5 min, filter - 0.2 µm filter
Sample :	A 0.02 ppm fluoride (Direct inj.) B 20 µL tea solution through CIC C 1000x diluted tea solution (Direct inj.)
Peaks:	1. Fluoride 2. Chloride 3. Nitrite 4. Unknown 5. Carbonate 6. Sulfite 7. Sulfate

CIC of Tea Samples



Columns:	Dionex IonPac AG18-4µm, and Dionex IonPac AS18-4µm, 4 mm
Eluent:	20 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge
Flow rate:	1.0 mL/min
Inj. volume:	100 µL
Column temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 4 mm, 35 °C, 50 mA, recycle mode Compartment temp. 25 °C
Sample size:	~20mg

Sample :		Fluoride (mg/Kg)
A	Tea 1	279
B	Tea 2	55
C	Tea 3	129
D	200 ppm F^-(NH_4F)	200

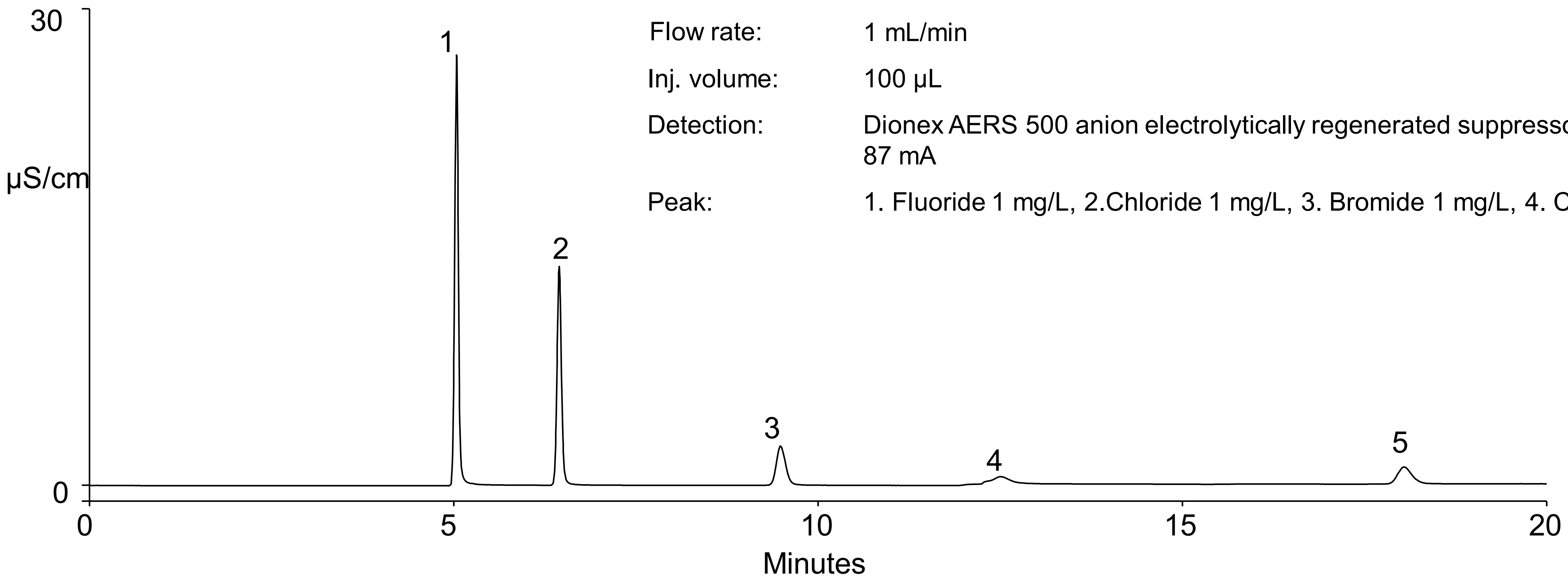
Peaks:
1. Fluoride
2. Chloride
3. Nitrite
4. Sulfite
5. Sulfate

Application Problem #2: Determining Halogens in Electronic Components

- Need to know for recycling purposes
- Possibly can be used to assess the potential for failure
- Ideal for combustion and IC
- ISO Method in progress

Halogen Separation

Column:	Dionex IonPac AG17-C guard, 4 × 50 mm Dionex IonPac AS17-C analytical, 4 × 250 mm
Eluent:	1 mM KOH 0-3 min, 10 mM 3-10 min, 35 mM 10-18 min, 1 mM 18.1-20 min
Eluent source:	Dionex EGC 500 KOH eluent generator cartridge with Thermo Scientific™ Dionex™ CR-ATC 600 continuously regenerated anion trap column
Temperature:	30˚C
Flow rate:	1 mL/min
Inj. volume:	100 µL
Detection:	Dionex AERS 500 anion electrolytically regenerated suppressor, 4mm, recycle mode, 87 mA
Peak:	1. Fluoride 1 mg/L, 2.Chloride 1 mg/L, 3. Bromide 1 mg/L, 4. Carbonate, 5. Iodide 1 mg/L



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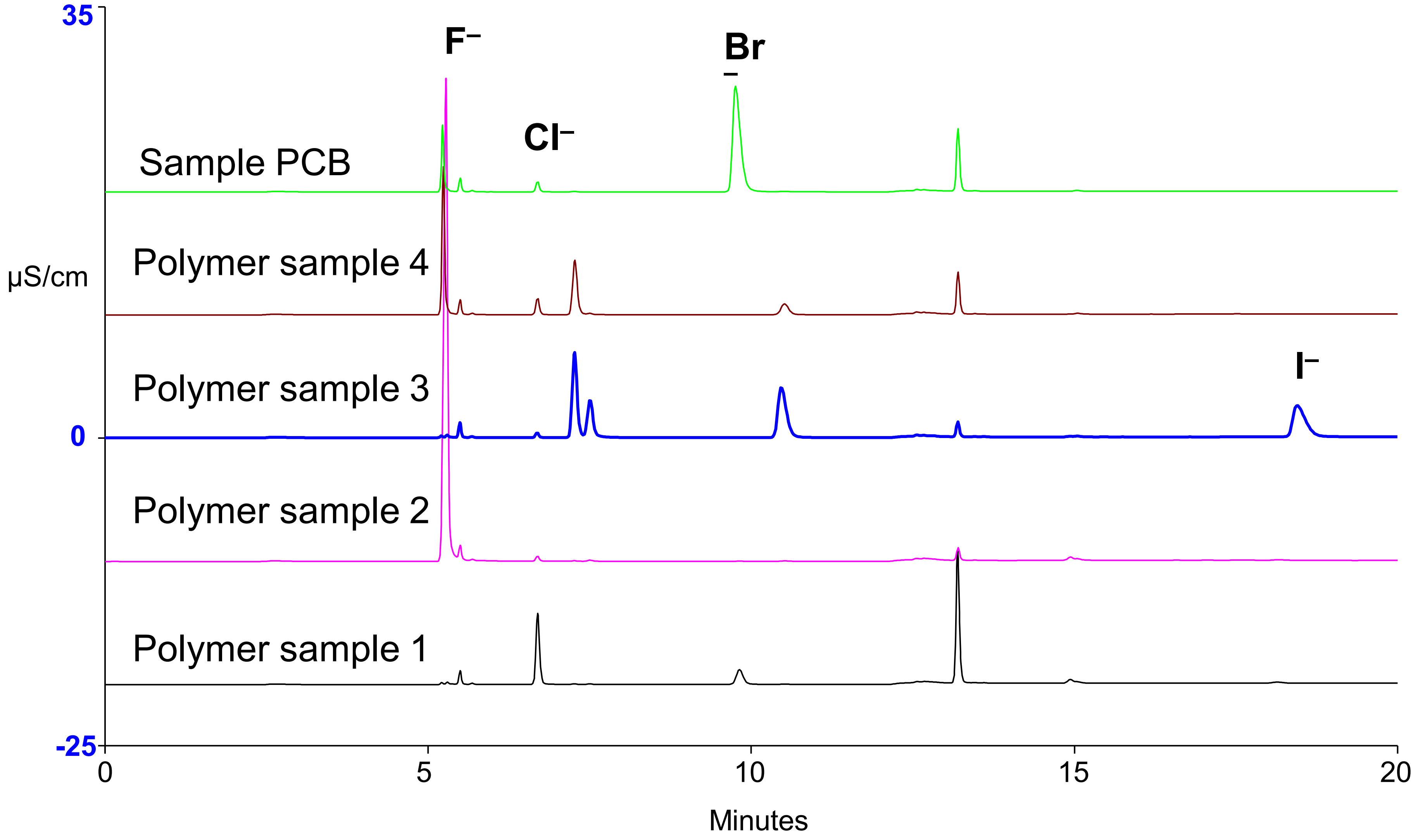
Chromatograms of Halogens in Polymers and Electronics



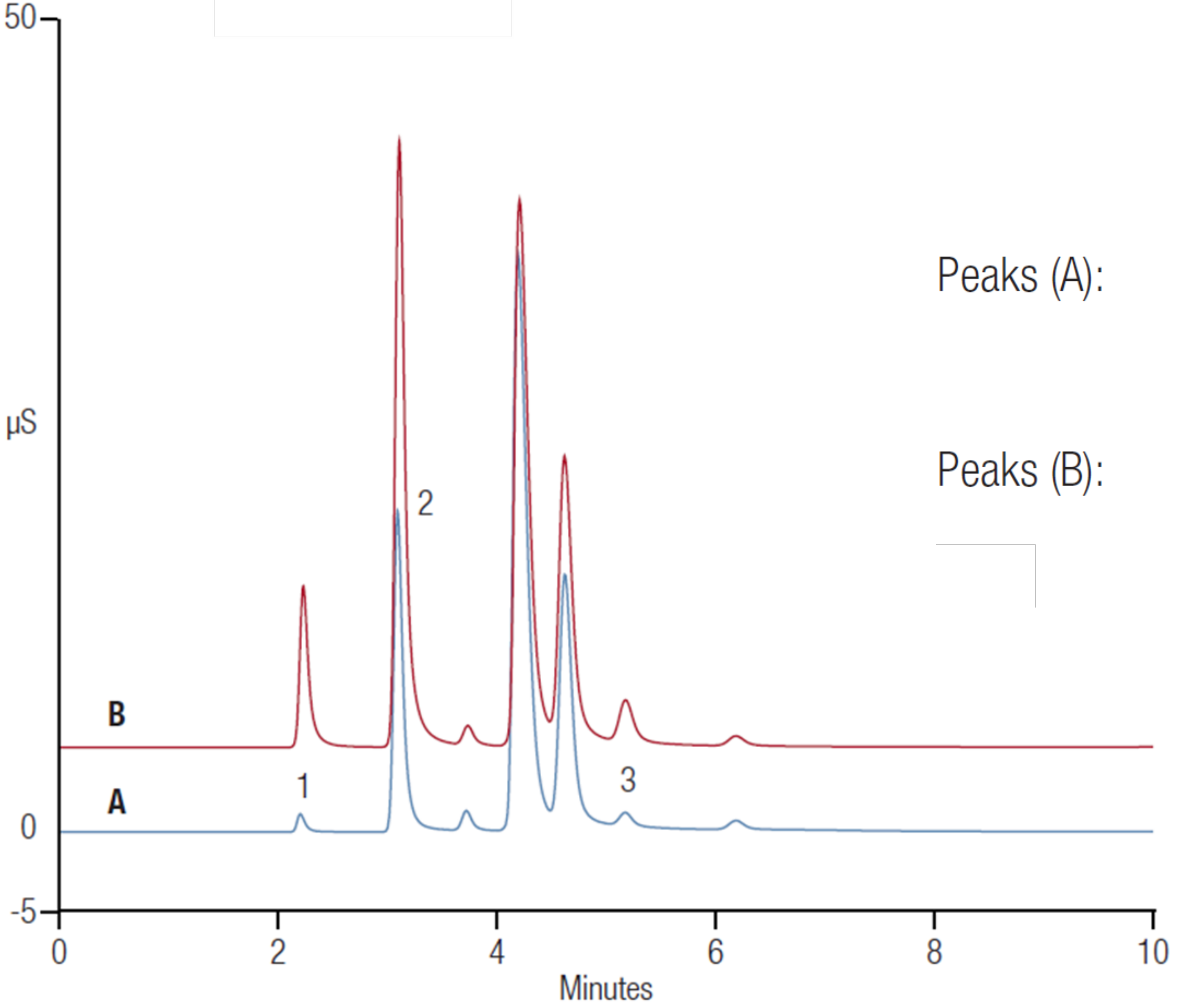
Application Problem #3: Absorbable Organic Halogen in Wastewater

- Absorbable Organic Halogens (AOX) are general indicators of pollution as many are toxic and persistent compounds.
- 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.
- With so many compounds and at varying concentrations, how do you determine them all?
- Capture, combust, and IC

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.

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

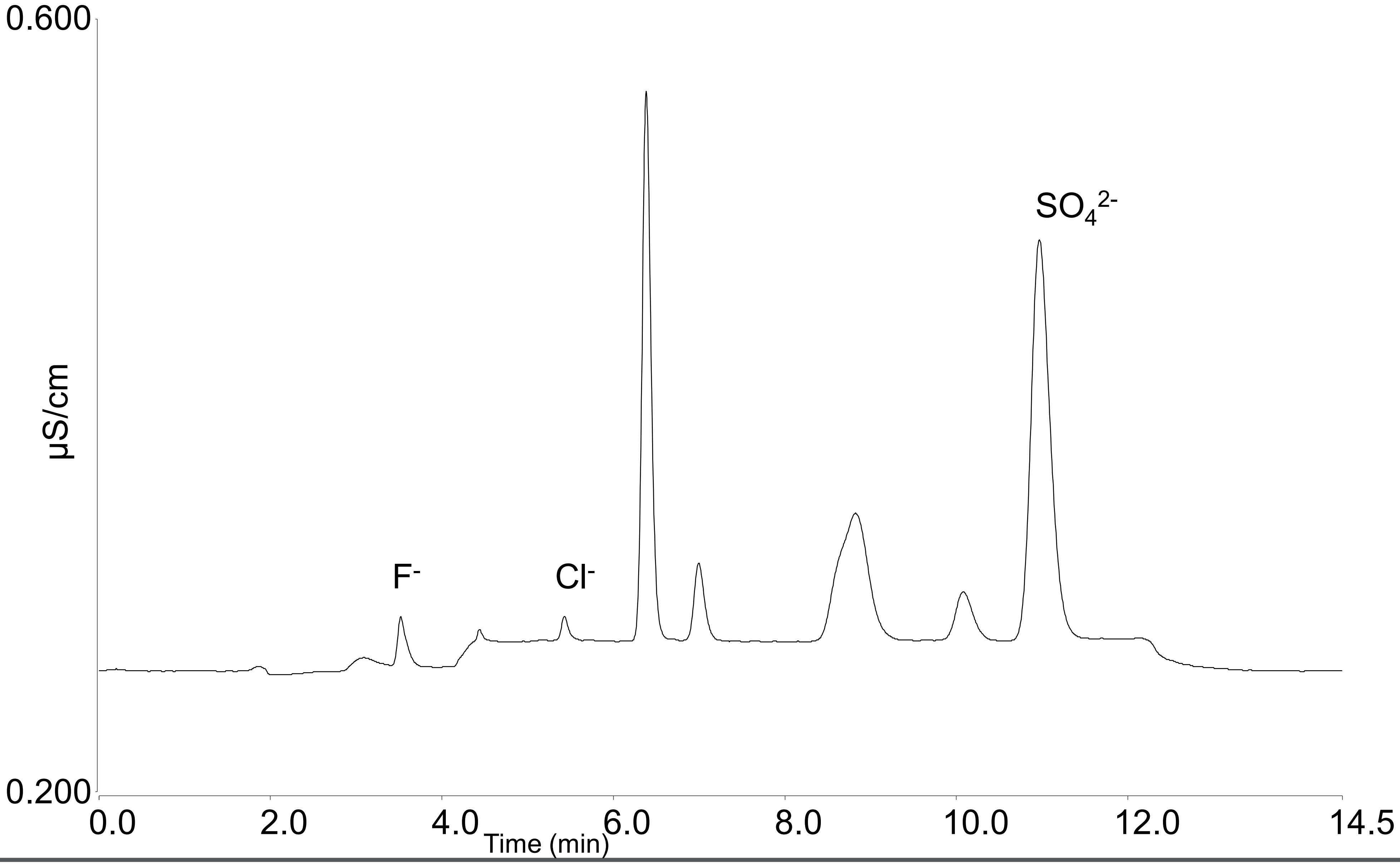


Peaks (A):	1. Fluoride	0.0425 mg/L
	2. Chloride	1.90
	3. Bromide	0.340
Peaks (B):	1. Fluoride	0.543 mg/L
	2. Chloride	3.92
	3. Bromide	0.908

Application Problem #4: Total F, Cl, and S in Aromatic Hydrocarbons

- Need to know for environmental issues as well as performance issues
- ASTM Method D7359-14A
- Used for other fuels

Combustion IC Chromatogram of a Gasoline Sample



Spike Recovery Results

Spike conc (mg/L)	F		Cl		SO_4	
	Average amount (mg/L)	% Recovery	Average amount	% Recovery	Average amount (mg/L)	% Recovery
0 (Premium gasoline)	0.24		0.22		4.37	
0.5	0.75	102.2	0.71	96.5	4.82	91.0
1	1.22	98.0	1.08	85.9	5.30	93.0
2	2.11	93.7	2.03	90.5	6.30	96.3

CIC Application Documents

- Application note 72268: Determination of fluoride in tea using a combustion ion chromatography system
- Application note 1145: Determination of halogens in coal using combustion ion chromatography.
- Application note 72349: Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion ion chromatography
- Application note 72573: Determination of halogens in polymers and electronics using a combustion ion chromatography system
- Application note 72693: Determination of total fluorine, chlorine, and sulfur in aromatic hydrocarbons by oxidative pyrolytic combustion followed by ion chromatography
- Application note 72333: Determination of adsorbable organic halogen in wastewater using a combustion ion chromatography system

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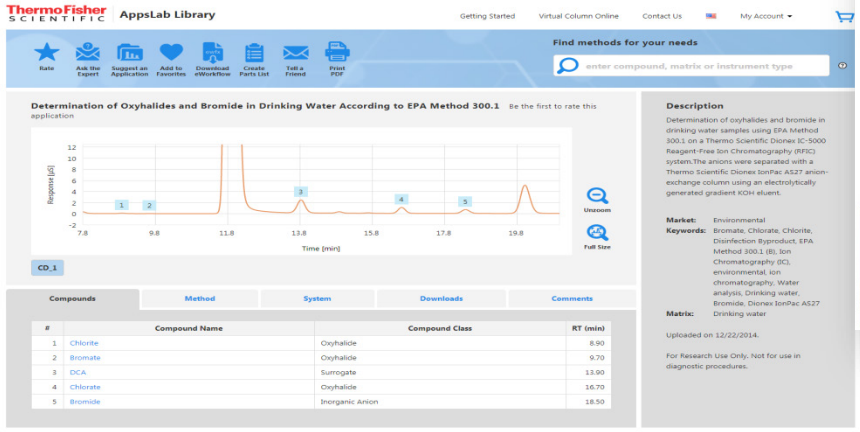

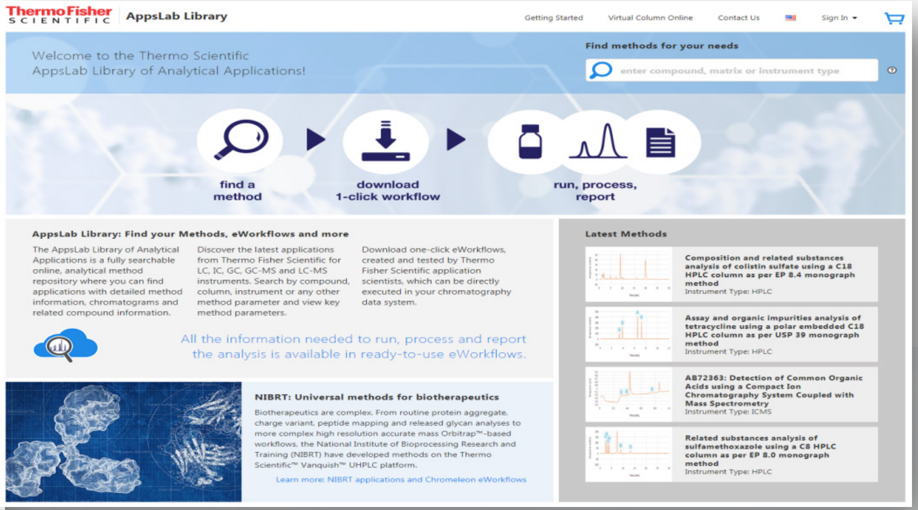

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Conclusions

- AOX can be precisely and accurately determined in wastewater using CIC
- Fluoride in tea can be accurately measured by CIC.
- Halogens and sulfur can be measured in gasoline and other soils by CIC.
- CIC is also useful for determining halogens in electronic waste.
- Other solid and liquid samples may be amenable to CIC.

Thank you!

- Questions?