Accurate and Reproducible Determination of Organic Halogens Using Combustion Ion Chromatography

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Thermo Fisher Scientific

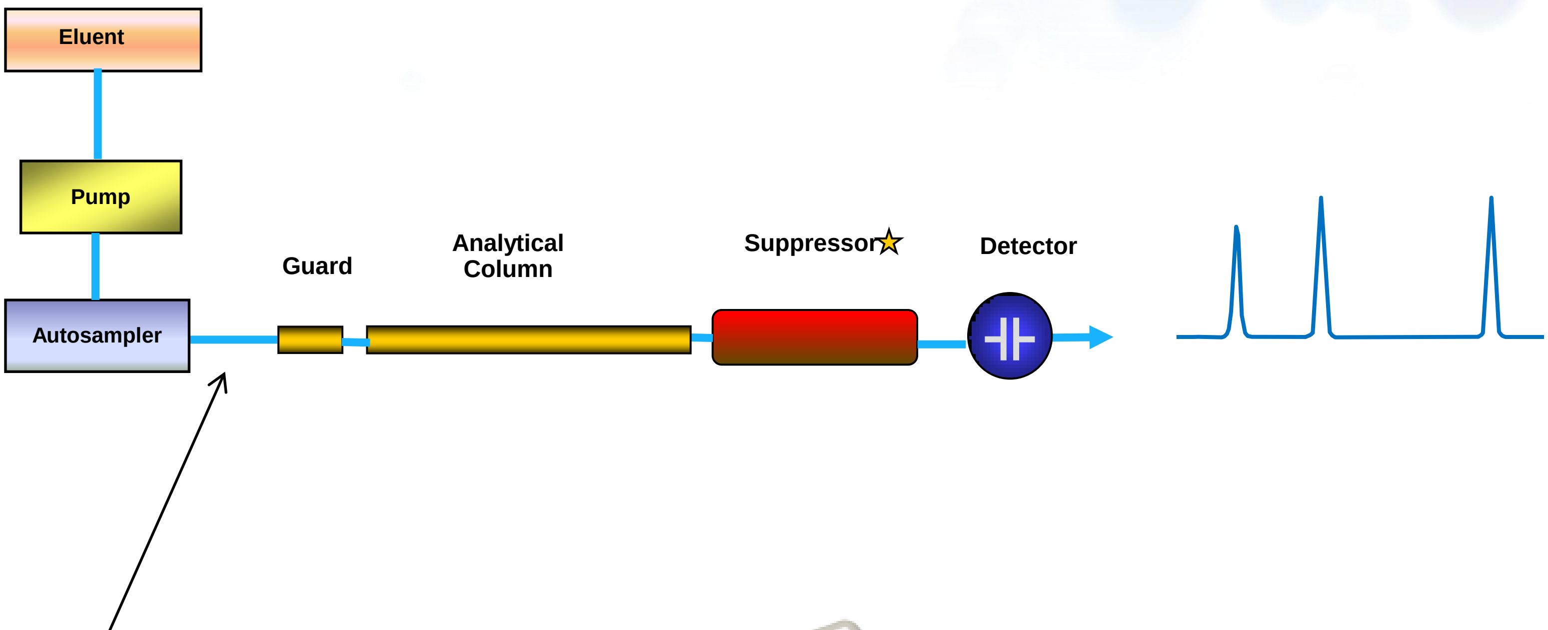
Overview

- Combustion Ion Chromatography (CIC) is rapidly becoming the preferred analytical technique for the measurement of fluoride, chloride, bromide, and sulfur in petrochemical and electronic industries
  - **ASTM D7359 - 13** Standard test method for total fluorine, chlorine, and sulfur in aromatic hydrocarbons and their mixtures by oxidative pyrohydrolytic combustion followed by ion chromatography detection (CIC)
  - **UOP991 – 13** Trace chloride, fluoride, and bromide in liquid organics by CIC
  - **KS M 0180:2009 –** Standard test method for halogen (F, Cl, Br) and sulfur content by oxidative pyrohydrolytic combustion followed by ion chromatography detection (CIC)

Agenda

- Overview of Ion Chromatography
- Benefits of Reagent-Free™ Ion Chromatography (RFIC™) and continuous suppression for CIC
- Overview of Mitsubishi AQF-2100H, new features and associated hardware for CIC
- Results on various sample types
- New trace enrichment approach to lower detection limits for critical CIC applications
- Questions

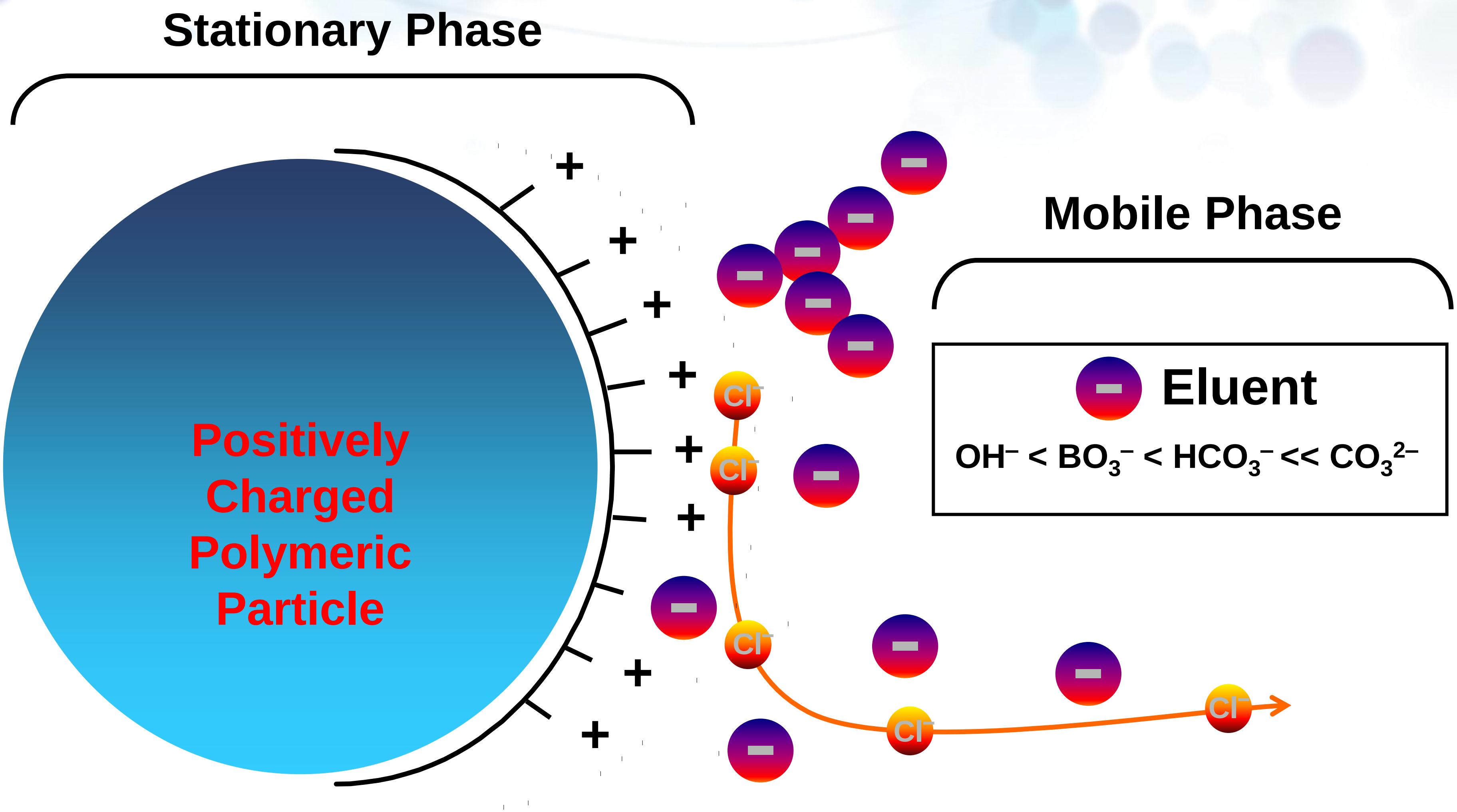
The Basic Components of an Ion Chromatograph



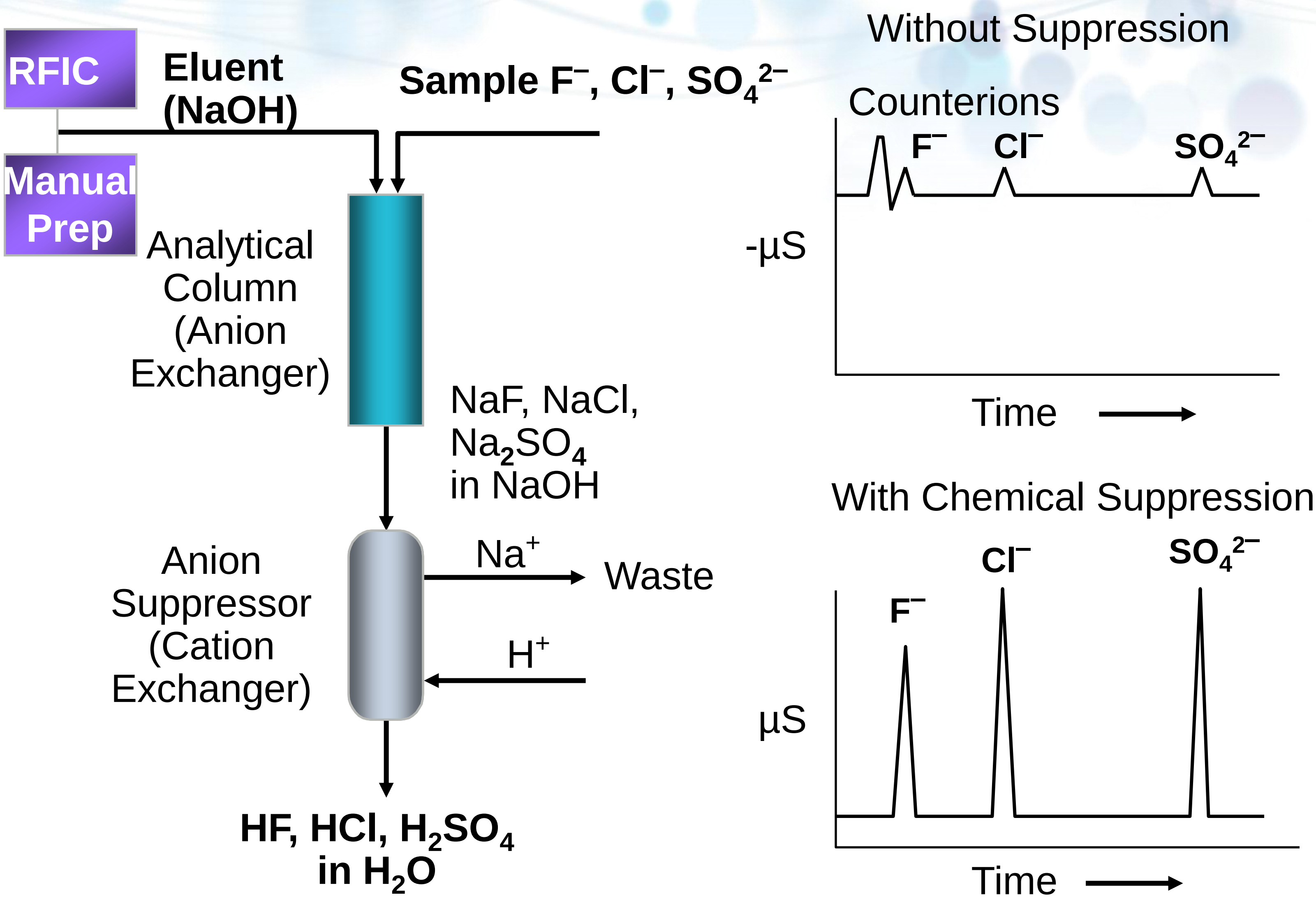
All inert flow path
with PEEK tubing

☆Suppression
is the key to IC

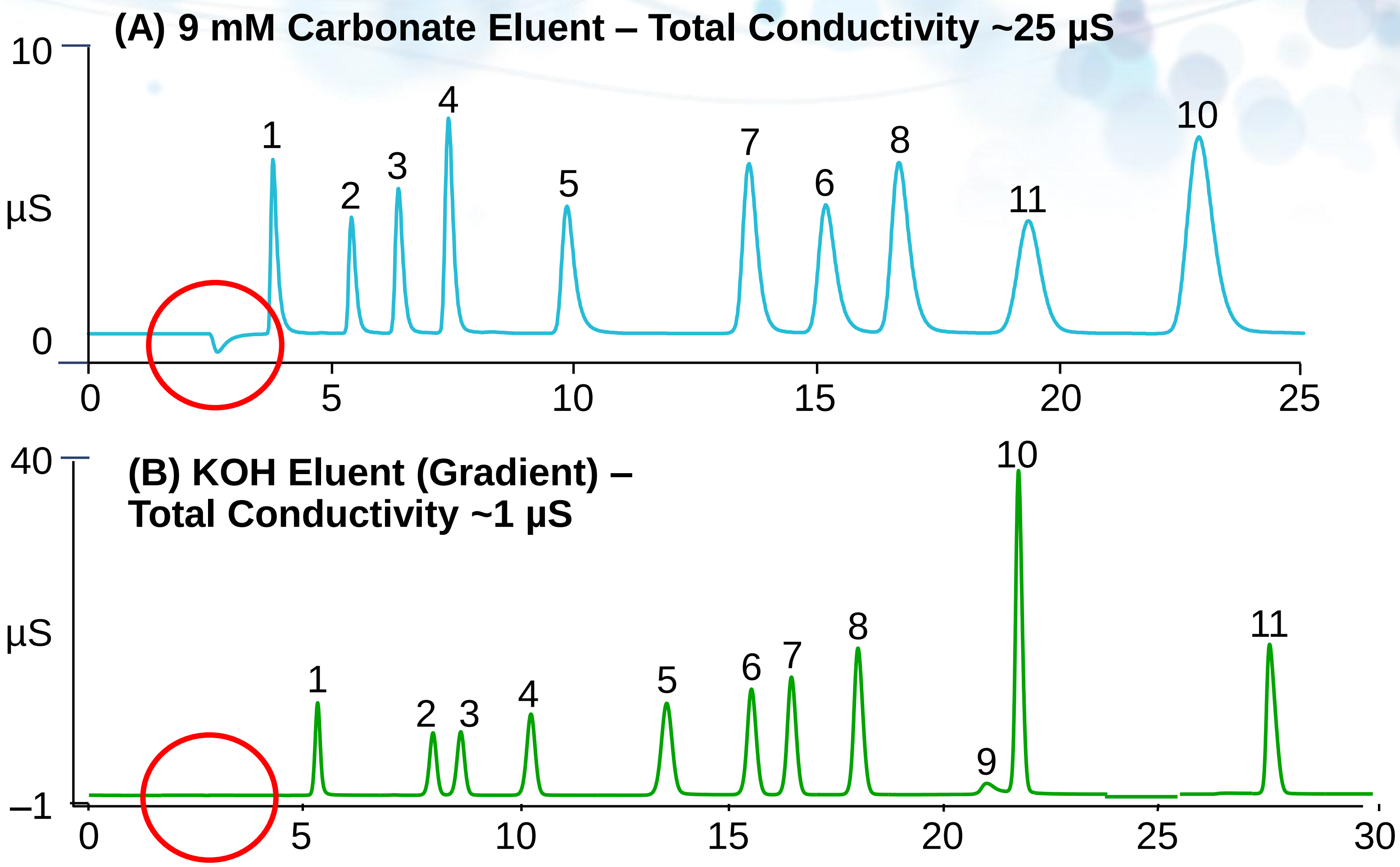
Anion-Exchange Mechanism



The Role of Suppression Using Hydroxide Eluents

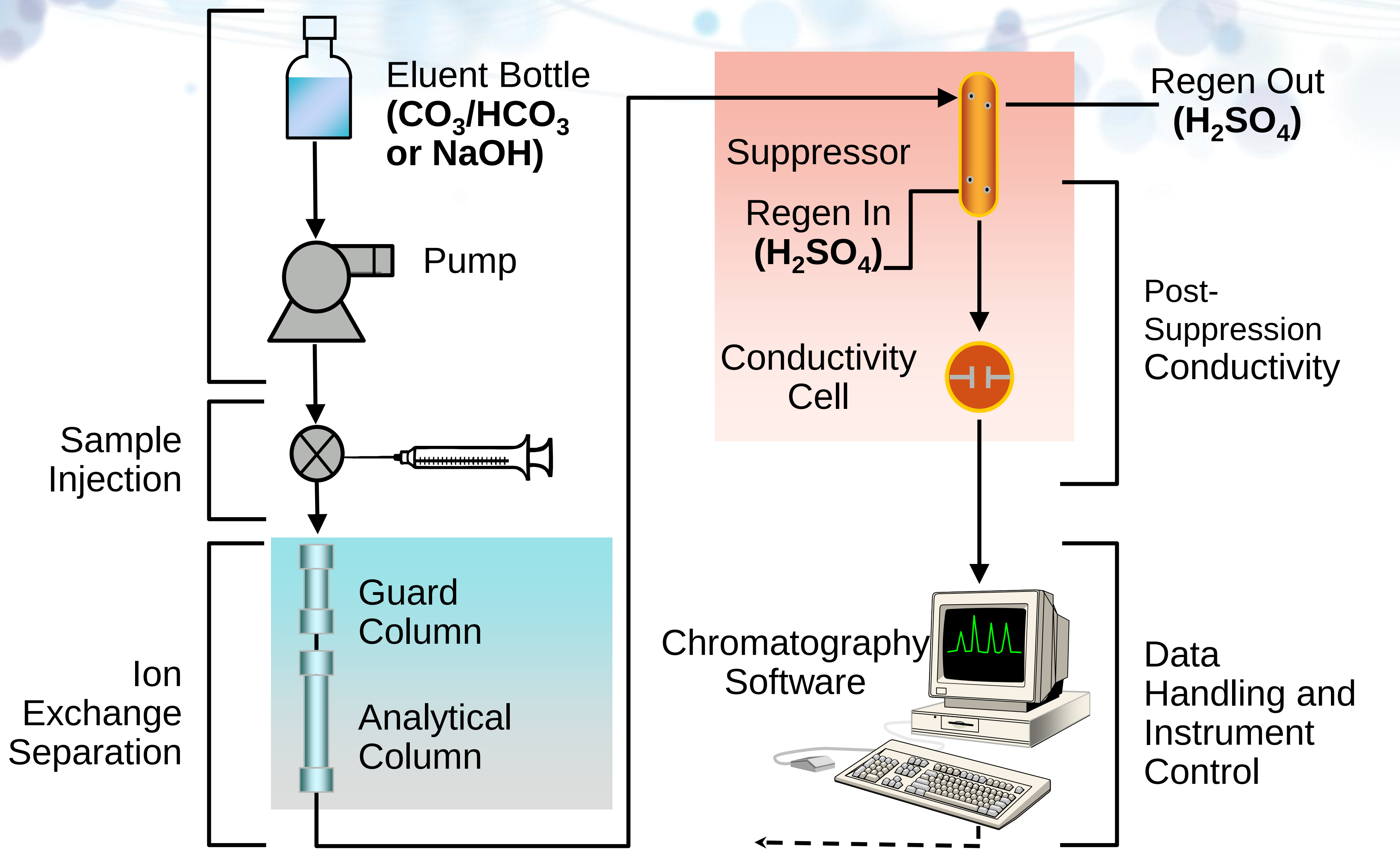


Carbonate Eluent Water Dip

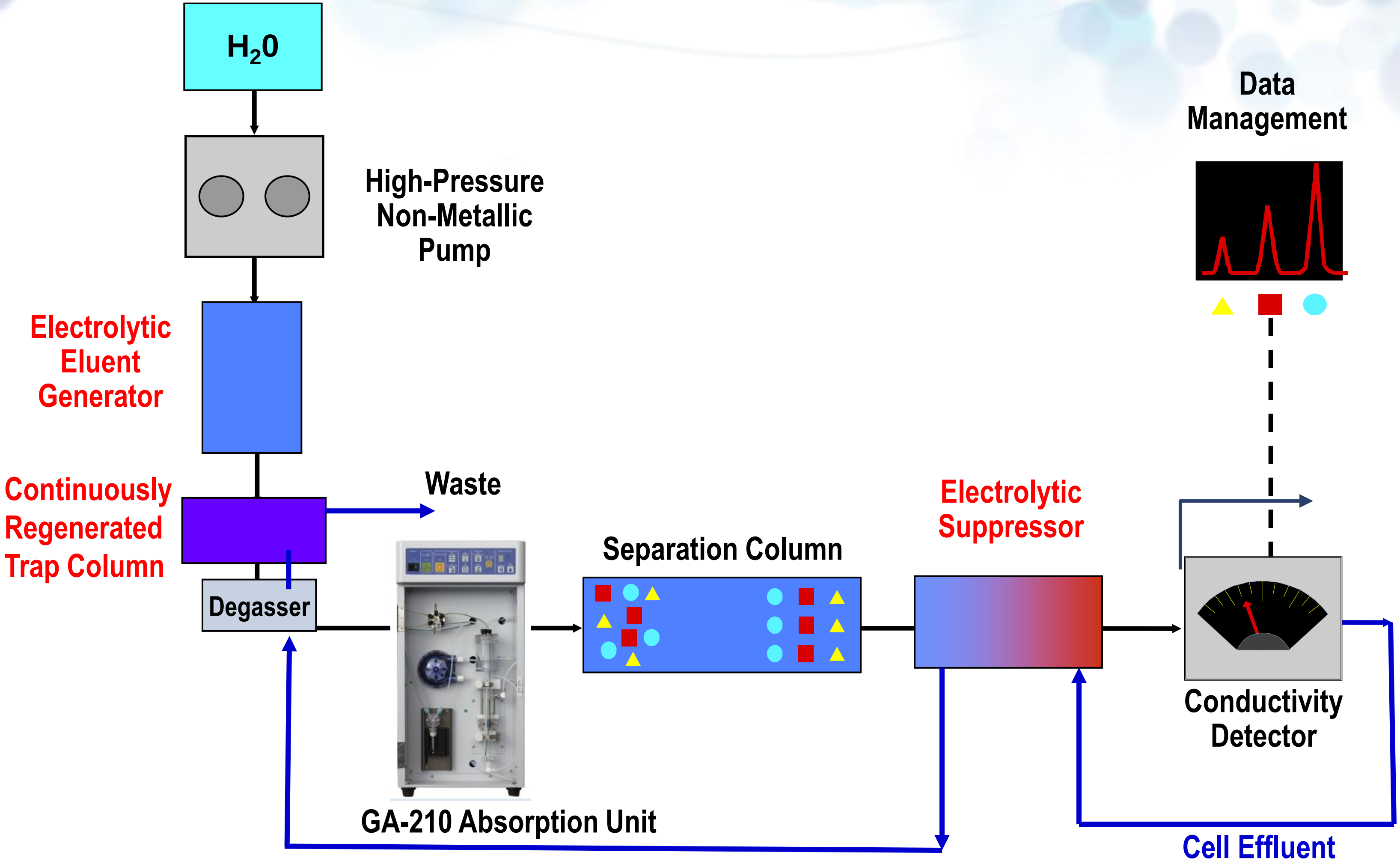


The larger the sample injected, the larger the water dip.

Typical Ion Chromatographic System – Anion Analysis



Reagent-Free Ion Chromatography System in CIC Mode



Benefits of Continuous Chemical and Electrolytic Suppression

- Electrolytically regenerated suppressors generate the ions necessary for eluent suppression through the electrolysis of water
  - This means no regenerant solutions to make and no need for off-line regeneration of the suppressor to achieve low background and high signal-to-noise levels
- Chemically regenerated suppressors continuously suppress the baseline using external reagents
  - This requires chemicals but is continuous and does not rely on a rotating suppressor device

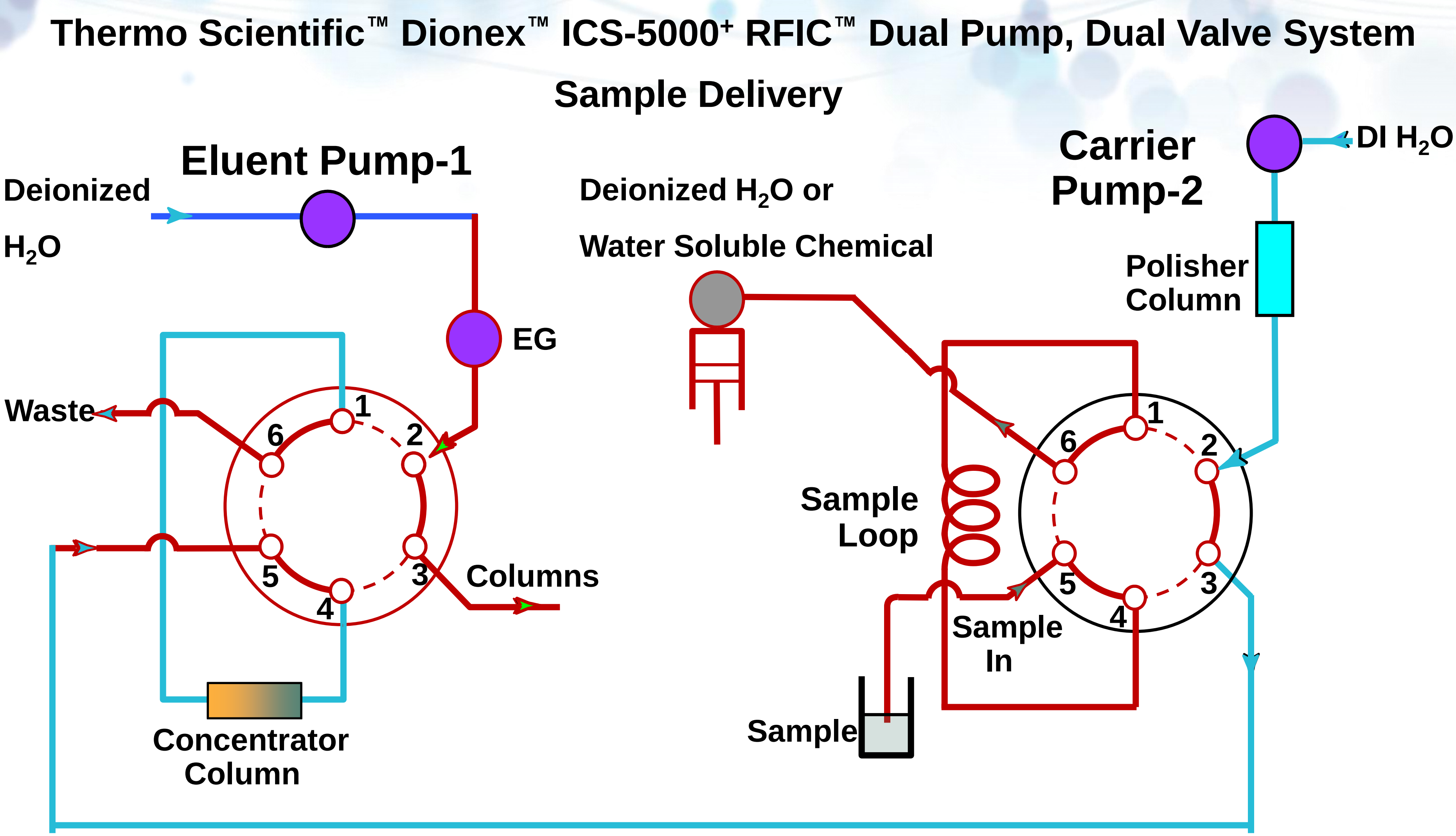
Benefits of Continuous Chemical and Electolytic Suppression

- Continuous Suppression using either chemical suppression or electrolytic suppression offers greater chromatographic flexibility
  - Longer runtimes if needed
  - Stronger mobile phases are still suppressed
- Gradient elution in conjunction with high capacity columns
- A continuously regenerated suppressor allows for easy to implement gradient elution
- A continuously regenerated suppressor is easy to validate

Packed Bed Suppressor - Limitations

- Limited run times due to limited capacity of suppressor
- Multiple packed bed chambers (2 or 3) still require off-line regeneration using pumps or spent eluent
- Cannot run with stronger mobile phases
- Does not do well with gradient runs
- Chambers are impossible to validate
- Old technology; must have sulfuric acid regenerant and DI water available for rinsing
- Requires additional hardware in the form of peristaltic pumps
- More maintenance, more labor

General Approach to Matrix Elmination



Thermo Scientific Dionex IC Product Line

RFIC

HPIC

Dionex ICS-900

Starter Line
IC System

Smallest Footprint
Drinking Water
Analysis

Dionex ICS-1100

Basic Integrated
RFIC System

Routine IC
Drinking & Wastewater
Analysis

Dionex ICS-1600

Standard
Integrated RFIC
System

Routine
Drinking & Wastewater
Analysis

Dionex ICS-2100

Superior
Integrated
RFIC System

Award Winning
Great Performance
High Purity Water and
Beverage Analysis

Dionex ICS-4000

Integrated Dedicated
Capillary HPIC System

Capillary HPIC
RFIC-EG Technology
CD, ED, QD
Carbohydrate Analysis
Drinking & Wastewater
Analysis

Dionex ICS-5000$^+$

Premier
High-End HPIC & RFIC
System

Flexible HPIC
RFIC Technology
Dual Channel
Ion Analysis
CD, ED, QD
2D-IC, AM
Carbohydrate & Amino Acid
Analysis

Integrated and Modular IC Systems

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Types of Samples Analyzed for Halides and Sulfur

- Petrochemical, refinery products, and fine chemicals
- Gases and LPG's
- Plastics, polymers, and rubber
- Consumer products and testing
- Gasoline, diesel, and jet fuel
- Ethanol, biodiesel, and alternative fuels
- ASTM D7359 - 08
- Pharmaceuticals and lyophilized proteins

Standard test method for total fluorine, chlorine, and sulfur in aromatic hydrocarbons and their mixtures by oxidative pyrohydrolytic combustion followed by ion chromatography detection (CIC)

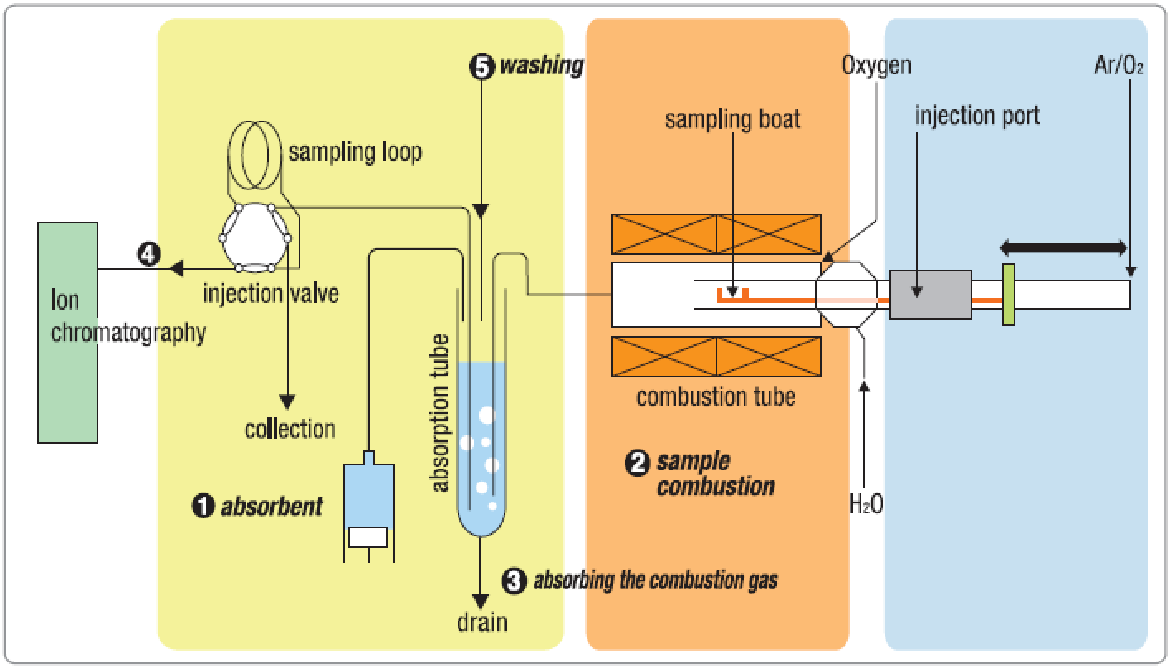
Features of the Mitsubishi AQF-2100H

- Measure fluorine, chlorine, bromine, and sulfur simultaneously with one instrument
- Replaces wickbold, oxygen bombs, and other dangerous combustion methods
- Fast analysis time; sample results in under 12 minutes
- Fully automated sample preparation and analysis with one system
- Solid and liquid autosamplers available
- Measure solids, liquids, gases, and LPG’s with one instrument

Combustion IC System

Sample — Sulfur → **In the combustion tube** — SO_x → **In the absorbent** — SO_4^{2-} → Ion Chromatograph

Sample — Halogen → **In the combustion tube** — HX, X_2 → **In the absorbent** — X^- → Ion Chromatograph

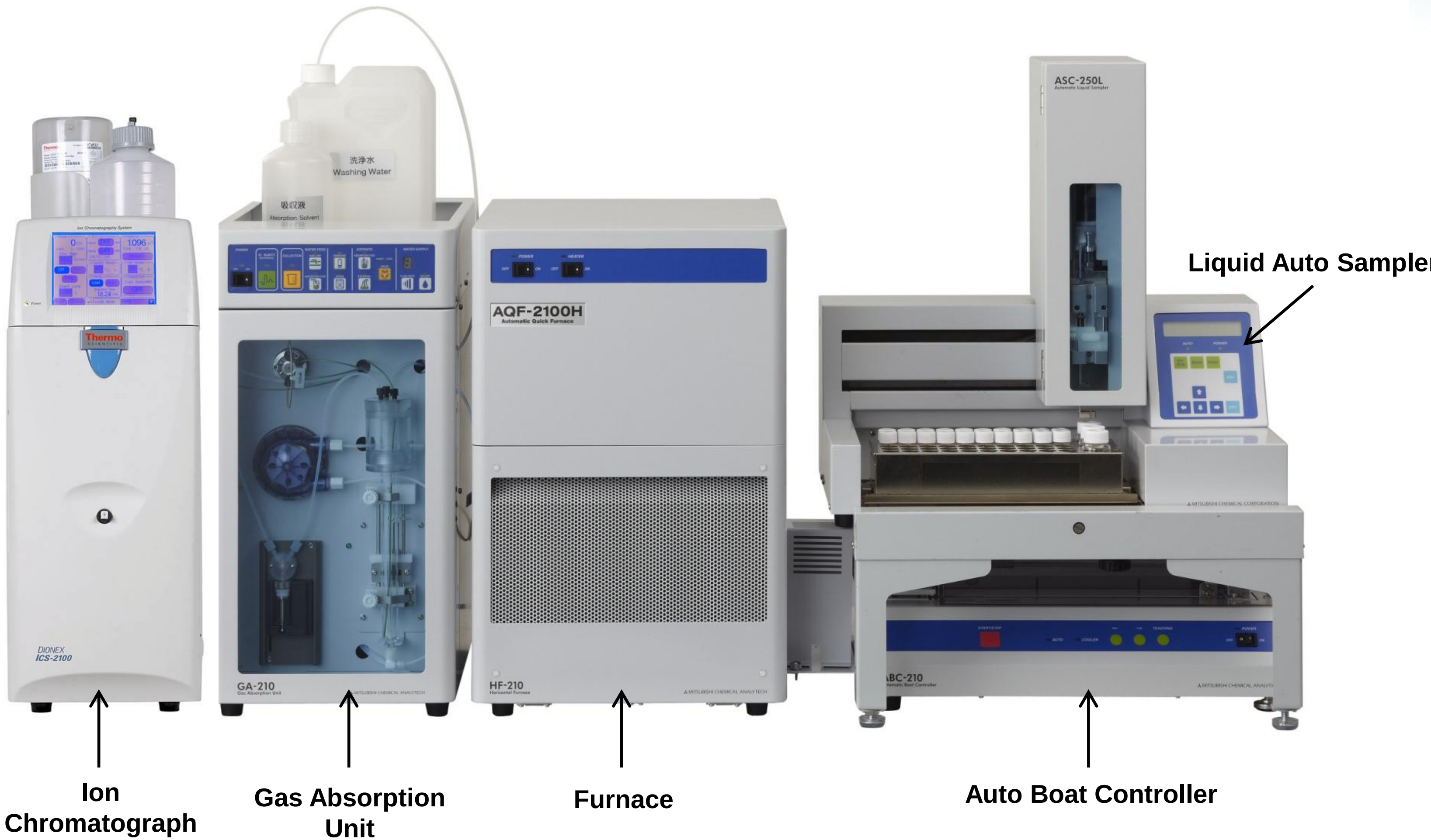


Process Flowchart

1. set absorbent
2. pyrohydrolytic combustion of sample
3. combusted gas is absorbed by absorbent
4. absorbent is injected into the Ion chromatograph
5. clean absorption tube

Thermo Scientific Combustion IC

Mitsubishi AQF-2100H with Liquid Autosampler



Thermo Scientific Combustion IC

Mitsubishi AQF-2100H with Solid Autosampler

Ion Chromatograph **Gas Absorption Unit** **Furnace** **Solid Autosampler (with built-in Auto Boat Controller)**

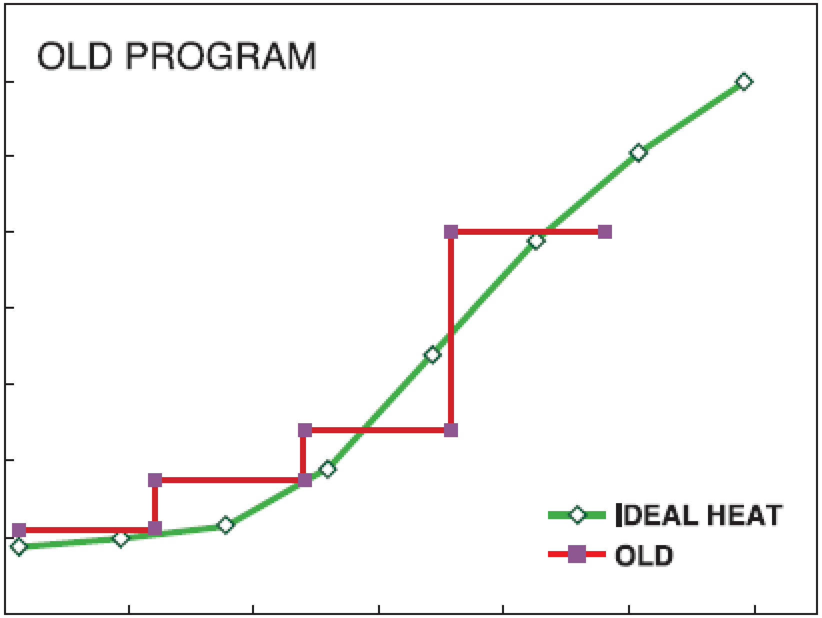
Electric Furnace - Mitsubishi HF-210

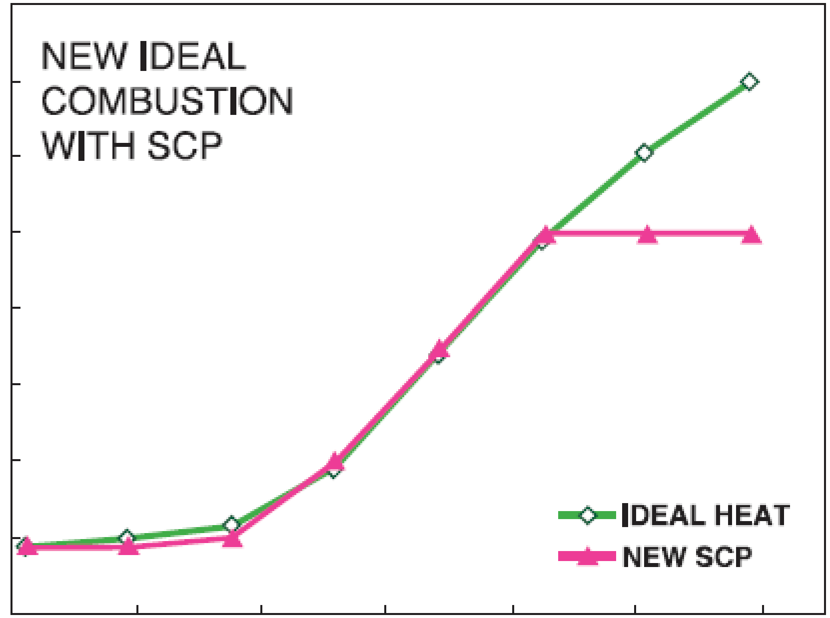
New hinged furnace design with easy open/close feature allows easy access to pyrolysis tube

Easily inspect and replace pyrolysis tube

Model HF-210 Horizontal Furnace

SCP – Secure Combustion Programming





- Allows complete combustion of large amount and complex sample matrix without test run
- Use of the optional combustion monitor can shorten time to 5 min

Combustion Gas Absorption Module

Injection Valve

Drain Pump

Dispensing Syringe

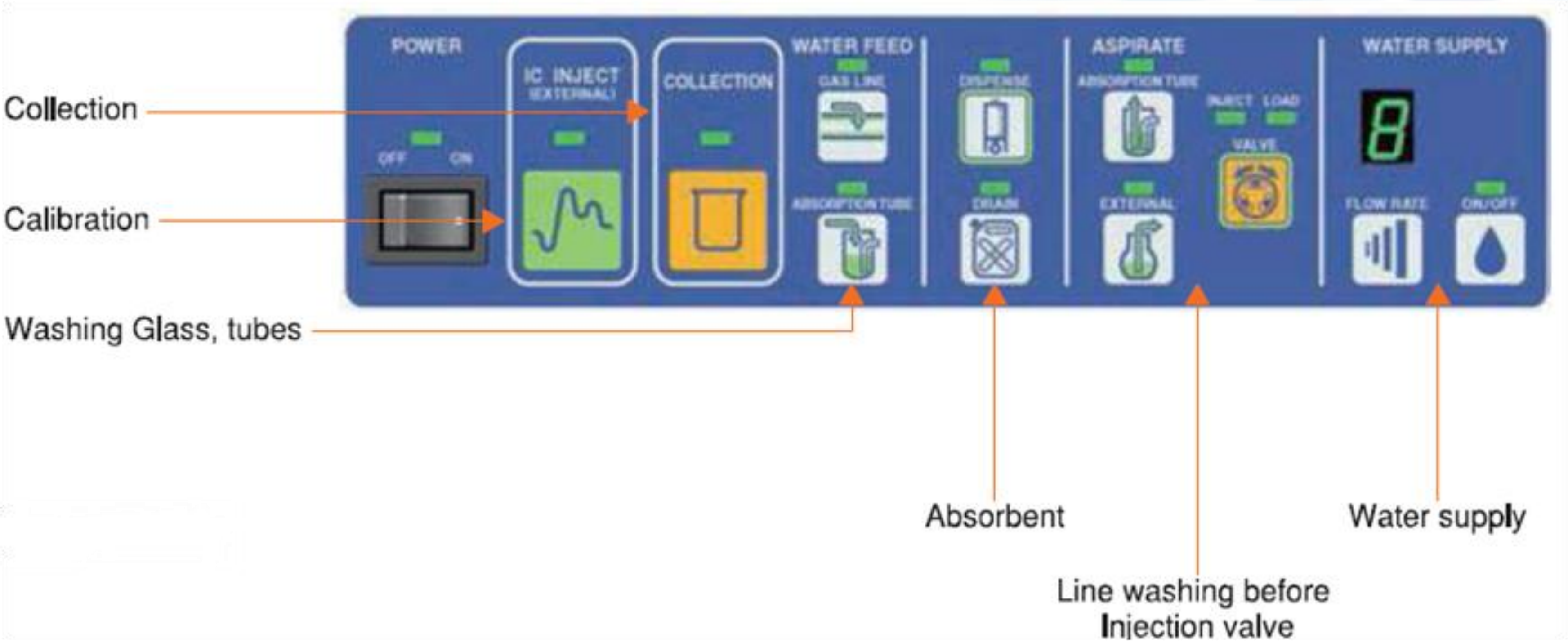
Absorption Tube

Mitsubishi ES-210 External Solution Selector
Four aqueous solutions/standards can be injected without combustion

Channel Indicator LED’s

Switching Valve

Intuitive Control of Gas Absorption Module



Sample Changers for CIC

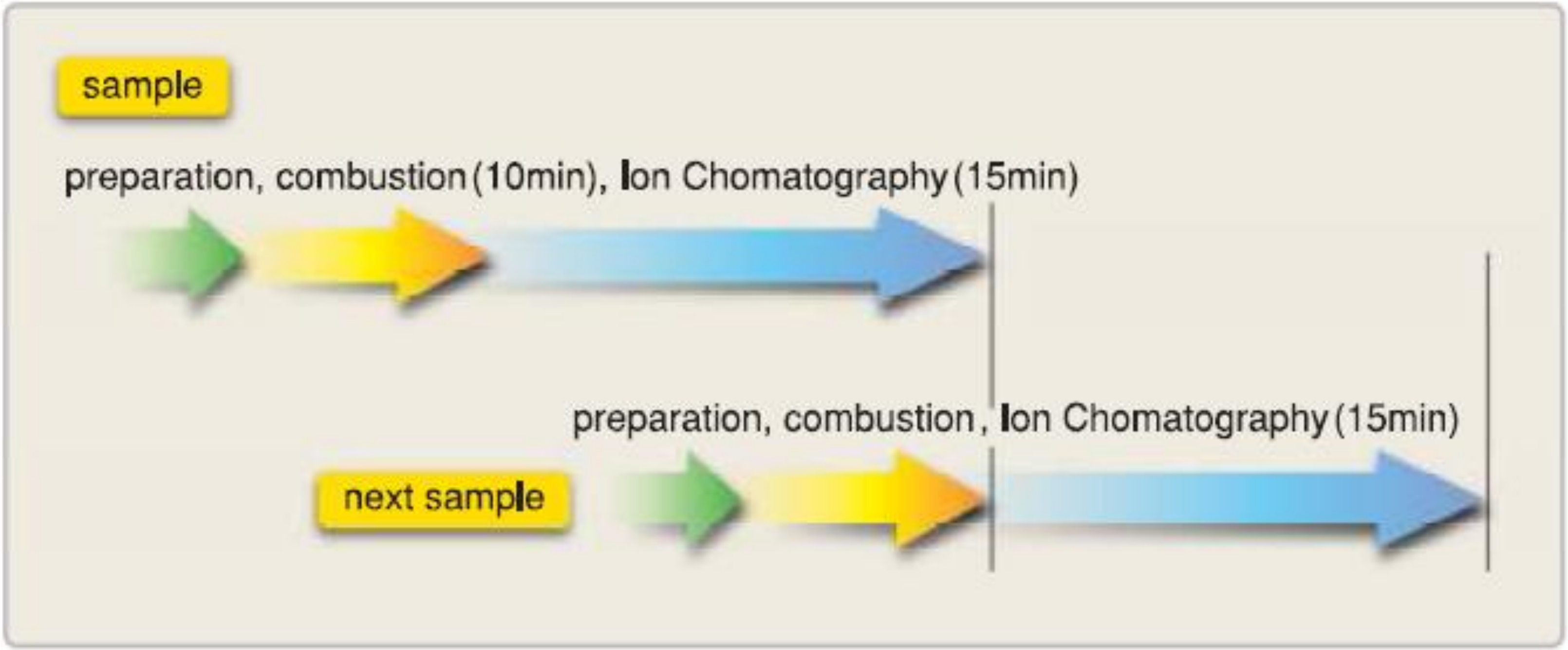
Mitsubishi ASC-250L
Liquid Sample Changer

Mitsubishi ASC-240S
Solid Sample Changer

Mitsubishi GI-240
Gas/LPG Injector

Software Based Automation to Increase Productivity

Established program controls total analysis and able to start combustion of the next sample to minimize analysis time.

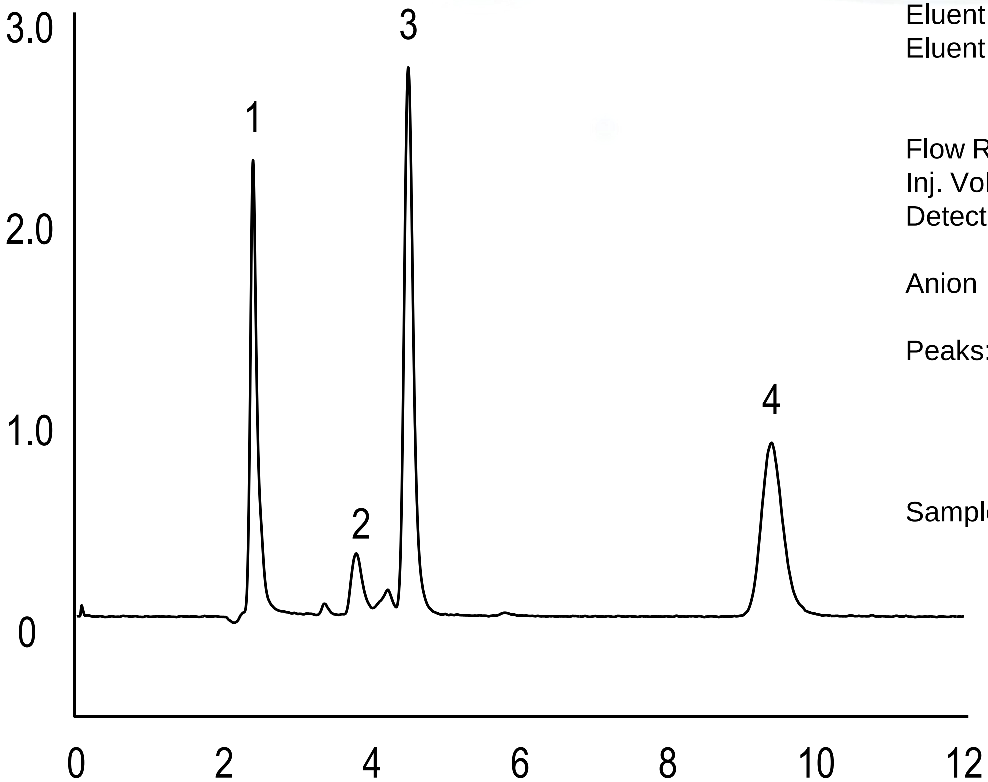


Precision and Recovery Data for Organic Standards Using Inorganic Ion Calibration

Analyte	0.5 mg/L (ppm) Std				1.0 mg/L (ppm) Std				2.5 mg/L (ppm) Std				5.0 mg/L (ppm) Std			
	Avg	SD	%RSD	% Rec	Avg	SD	%RSD	% Rec	Avg	SD	%RSD	% Rec	Avg	SD	%RSD	% Rec
Fluoride [1]	0.51	0.12	22.70	***102.5***	1.05	0.23	21.59	***104.5***	2.44	0.26	10.71	***97.7***	5.02	0.25	5.05	***100.4***
Chloride [2]	0.49	0.02	4.86	***97.6***	0.98	0.02	2.43	***97.7***	2.51	0.03	1.25	***100.2***	5.00	0.02	0.47	***100.1***
Bromide [3]	0.52	0.02	4.64	***103.6***	1.01	0.06	6.17	***101.3***	2.45	0.03	1.15	***97.8***	5.08	0.09	1.85	***101.7***
Sulfur [4]	0.52	0.02	4.18	***103.4***	0.98	0.02	1.70	***97.6***	2.48	0.03	1.14	***99.0***	5.02	0.02	0.30	***100.3***

1. Fluorobenzoic acid
2. 1,3, 5 – Trichlorophenol
3. Bromoacetanilide
4. Dibenzothiophene

Halides and Sulfur in Liquified Petroleum Gas by On-Line CIC with RFIC



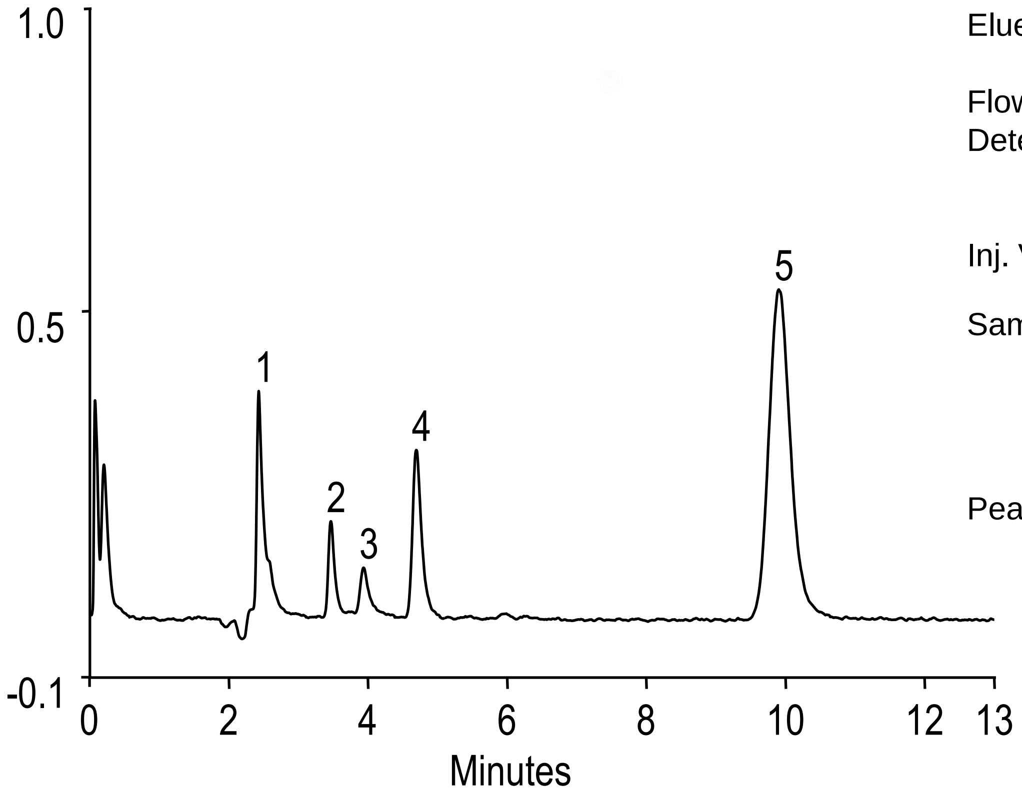
Column:	Thermo Scientific™ Dionex ™ IonPac™ AS11-HC
Eluent :	25 mM KOH
Eluent Source:	Thermo Scientific Dionex EGC cartridge with Thermo Scientific Dionex CR-ATC Continuously Regenerating Anion Trap column
Flow Rate:	1.3 mL/min
Inj. Volume:	100 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA
Anion	Self-Regenerating Suppressor, recycle mode

Peaks:

1. Fluoride	1.5 mg/L
2. Chloride	0.019
3. *S* as Sulfate	3.0
4. Phosphate (int. std)	2.0

Sample Preparation: Mitsubishi AQF-100 combustion system

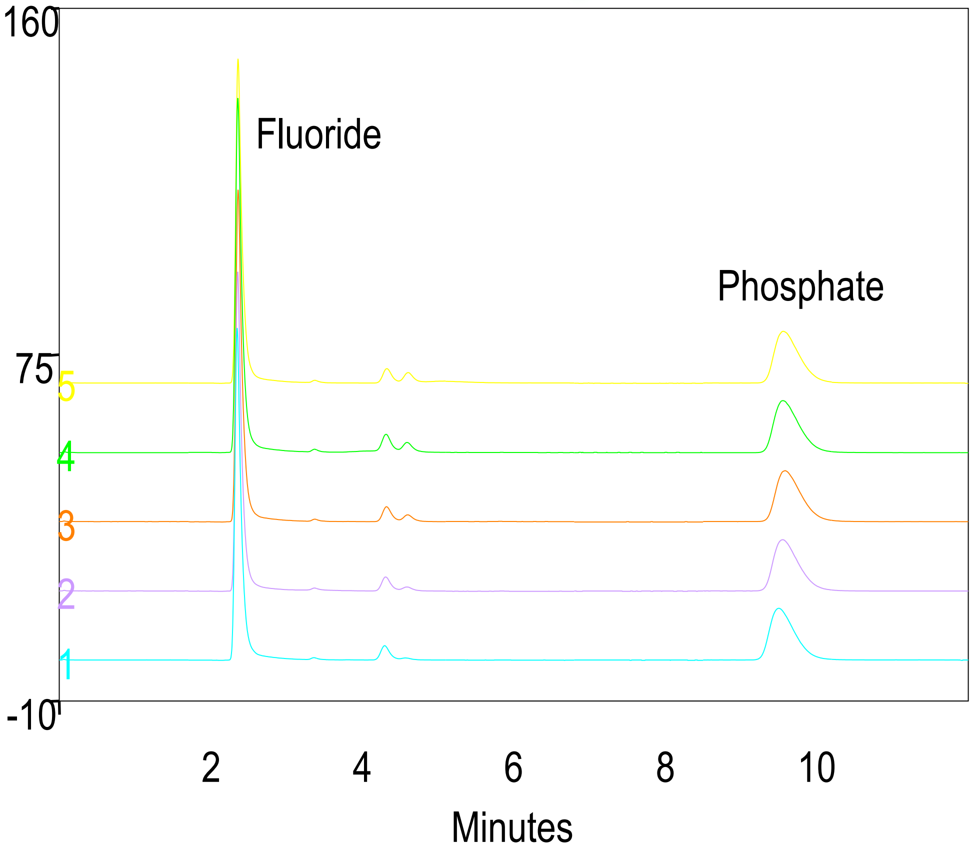
Anions in Toluene by Combustion Ion Chromatography



Column:	Dionex IonPac AS11-HC
Eluent:	25 mM KOH
Eluent Source:	Thermo Scientific Dionex EG40 Eluent Generator
Flow Rate:	1.3 mL/min
Detection:	Cond., Dionex ASRS ULTRA Suppressor, recycle 35 °C
Inj. Volume:	200 µL
Sample Prep:	Combustion w/Mitsubishi AQF-100 system 80 µL combusted 3.5 mL trap solution

Peaks:			
	1. Fluroride	0.96	mg/L
	2. Chloride	0.50	
	3. S-Sulfate	0.77	
	4. Phosphate (int. std)	0.50	

Overlay of Fluoride in Polymer



Column:	Dionex IonPac AS11-HC
Eluent :	25 mm KOH
Eluent Source:	Dionex EG40 Eluent Generator
Flow Rate:	1.3 mL/min
Inj. Volume:	100 µL
Detection:	Cond., Dionex ASRS ULTRA Suppressor, recycle
	35 °C
Sample Prep:	Combustion w/Mitsubishi AQF-100 system

Run #	Wt. of polymer (g)	F(mg/L)
1	.051	965
2	.048	976
3	.051	973
4	.055	953
5	.048	977

Challenges of CIC Technique

- CIC is a powerful technique that can measure halogen and sulfur content in a variety of matrices over a broad range of concentrations
- The strength of CIC is also it’s weakness since many samples challenge the technique itself due to:
  - The sample matrix itself may have inherent difficulties
    - Measuring fluoride or chloride in a sulfonated polymer
    - Fluoride, chloride, and sulfur in a sample containing a bromophosphate fire retardants
  - The concentration of various elements of interest in the sample
    - Low fluoride and high chloride
    - High bromide or sulfur and low fluoride where is H_2O_2 required and the unreacted H_2O_2 masks, interferes or coelutes with the fluoride peak

Challenges of CIC Technique

- Increasing the sensitivity of the ion chromatograph and thereby the MDL of the technique can be improved in several ways
  - Increase injection loop volume (200-500 µL)
    - As injection loop increases, the water dip increases and can cause problems with resolving the fluoride peak
  - Increase the final concentration of the anion being measured by either increased sample size of sample or absorbing replicate combustions of sample
    - Increased sample size is limited to ~100 mg of sample
    - Replicate combustions of sample increases time of analysis
    - Neither approach addresses the problems and difficulties with H_2O_2 coelution

Preconcentration Technique

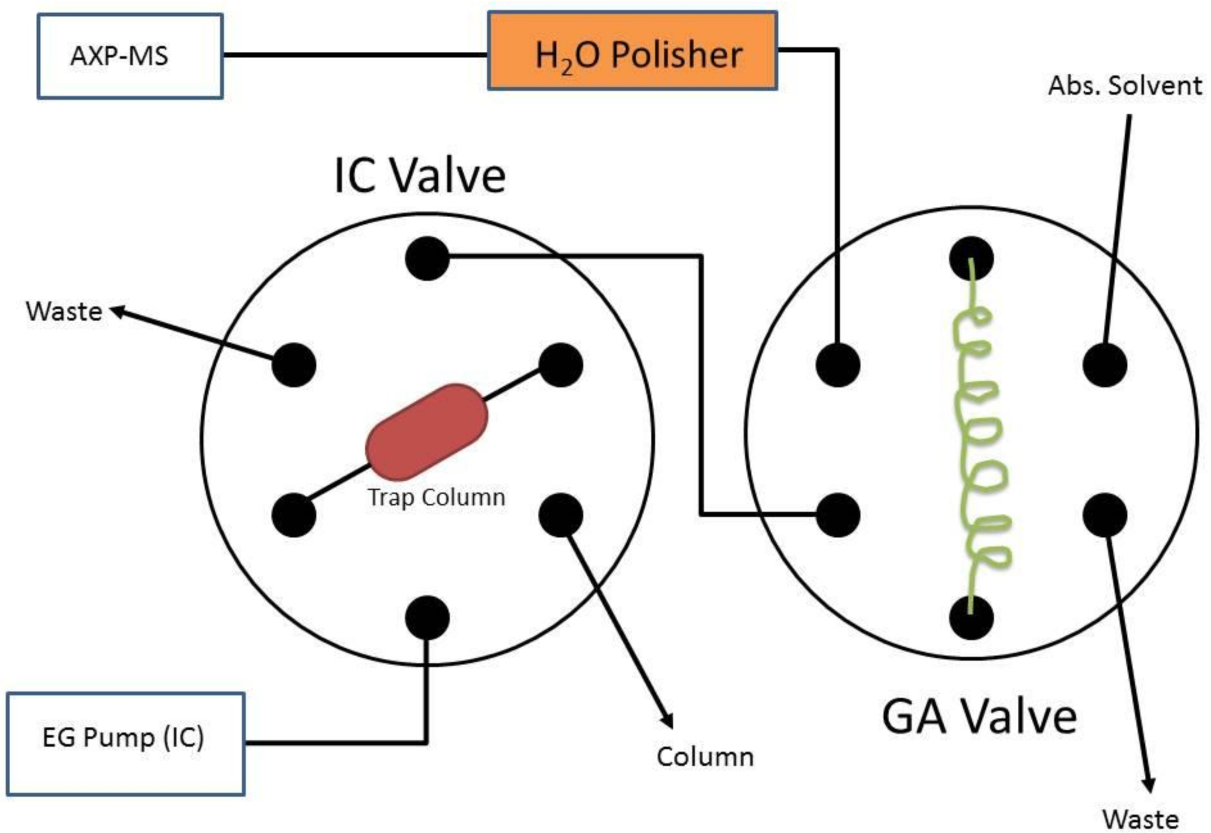
- One approach in chromatography is to use trap columns to increase the absolute amount of anions on column
- The technique is commonly referred
  - Preconcentration – when the trap column is being used to concentration the anions of interest
  - Matrix elimination – when the trap column is being used to trap the anions of interest while washing or removing the anions that are causing problems with the analysis such as H_2O_2

Preconcentration with a Thermo Scientific Dionex ICS-2100 System

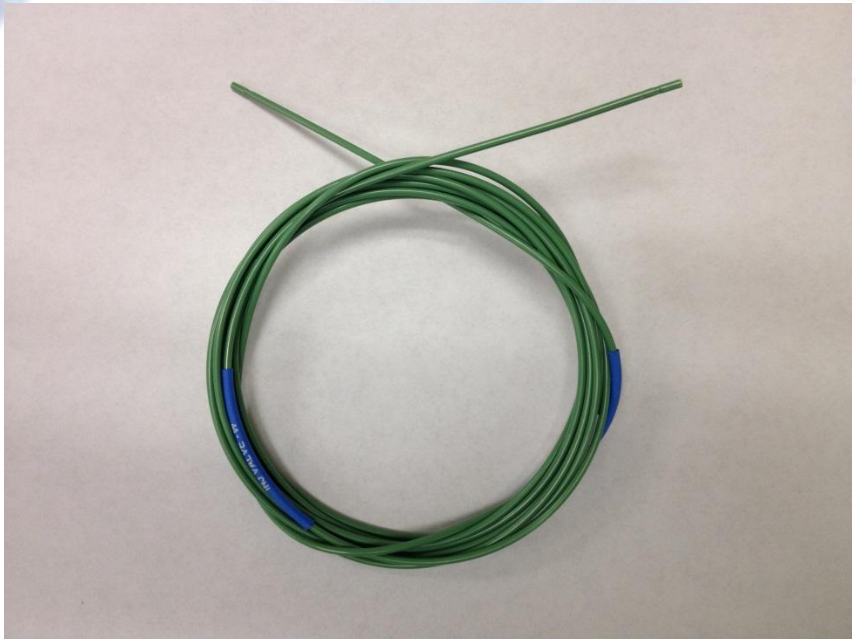
- Equipment used:
  - Mitsubishi AQF-2100H
  - Dionex ICS-2100 system with RFIC
  - Dionex IonPac AG18 and Dionex IonPac AS18 columns
  - 1.0 mL sample loop (Mitsubishi GA-210)
  - Dionex IonPac UTAC-ALP1 Ultra Trace Anion Concentrator column - extremely low pressure
  - Thermo Scientific Dionex AXP-MS Metering Pump

Preconcentration with a Dionex ICS-2100 System

Flow diagram of a preconcnetration system

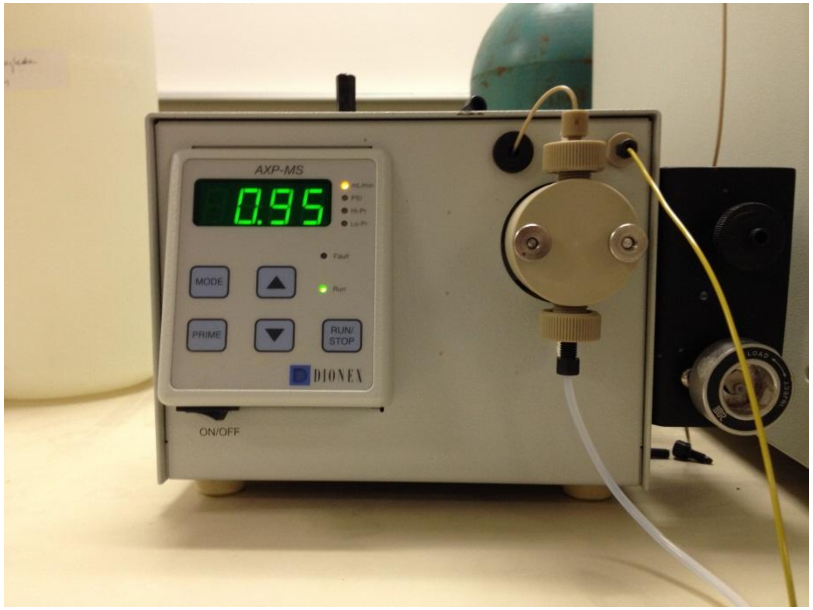


Preconcentration with a Dionex ICS-2100 System



1.0 mL sample loop
(~ 6 feet green tubing)

Dionex AXP-MS Metering Pump



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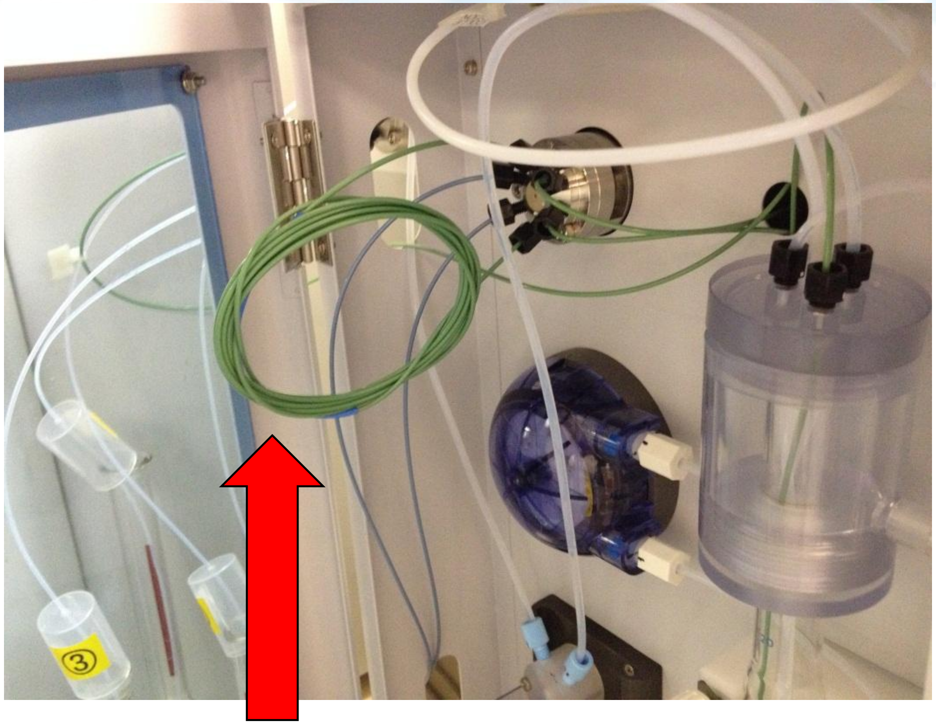
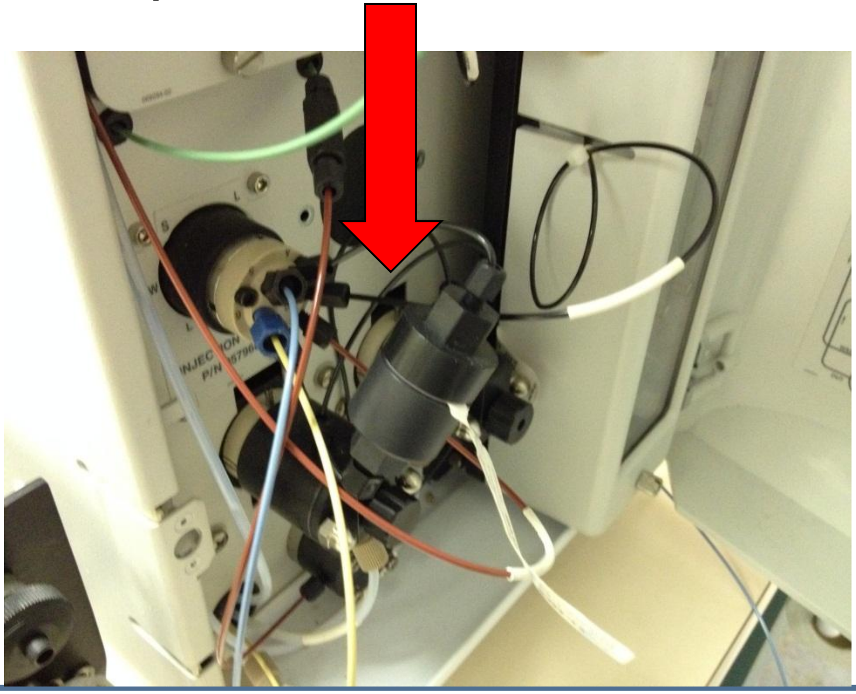
Preconcentration with a Dionex ICS-2100 System

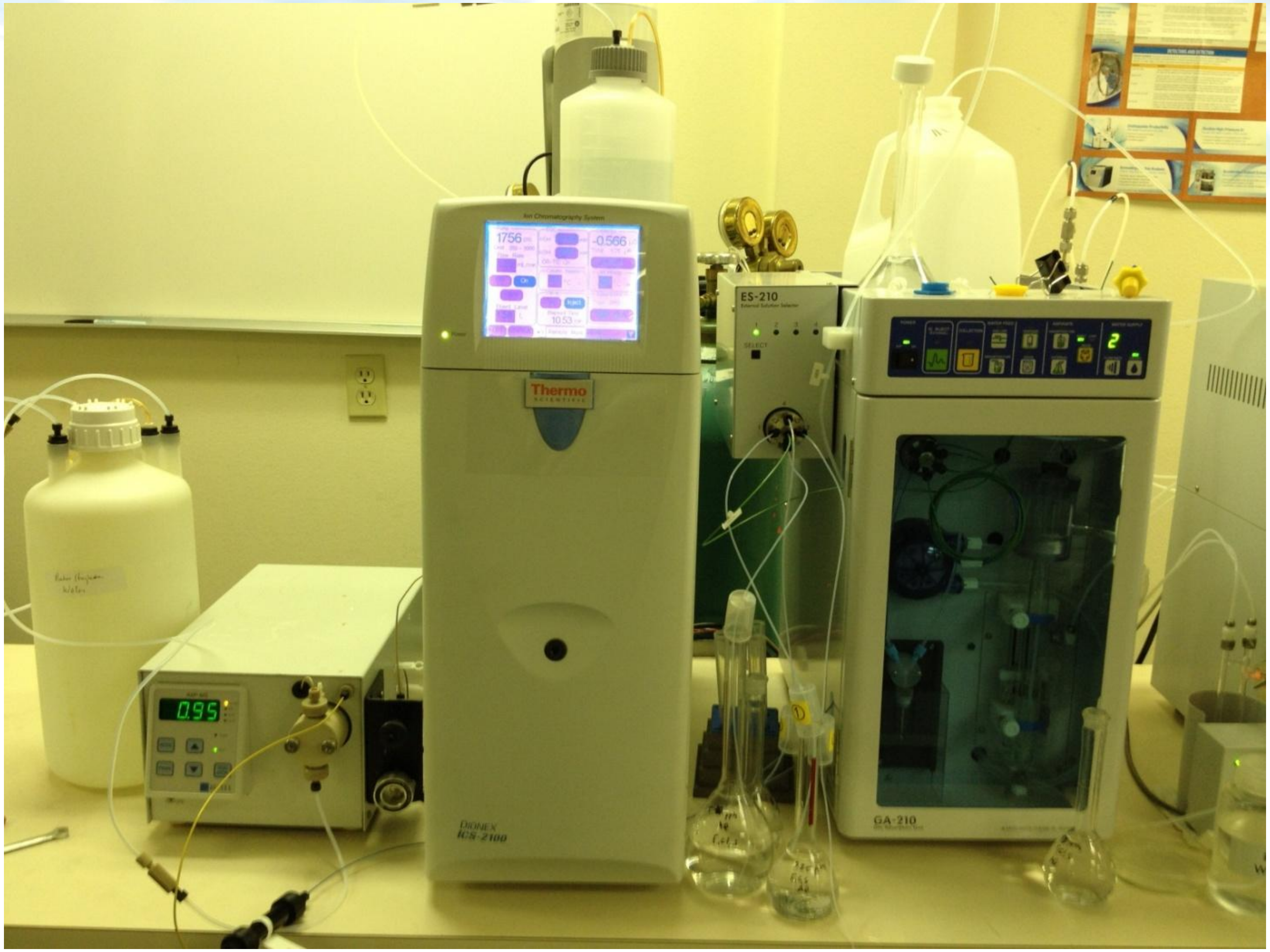


1.0 mL sample loop installed

Dionex IonPac UTAC-ALP1 trap column installed



Preconcentration with a Dionex ICS-2100 System



Dionex ICS-2100 preconcentration system with a Dionex AXP-MS pump and a Dionex IonPac UTAC-LP trap column installed

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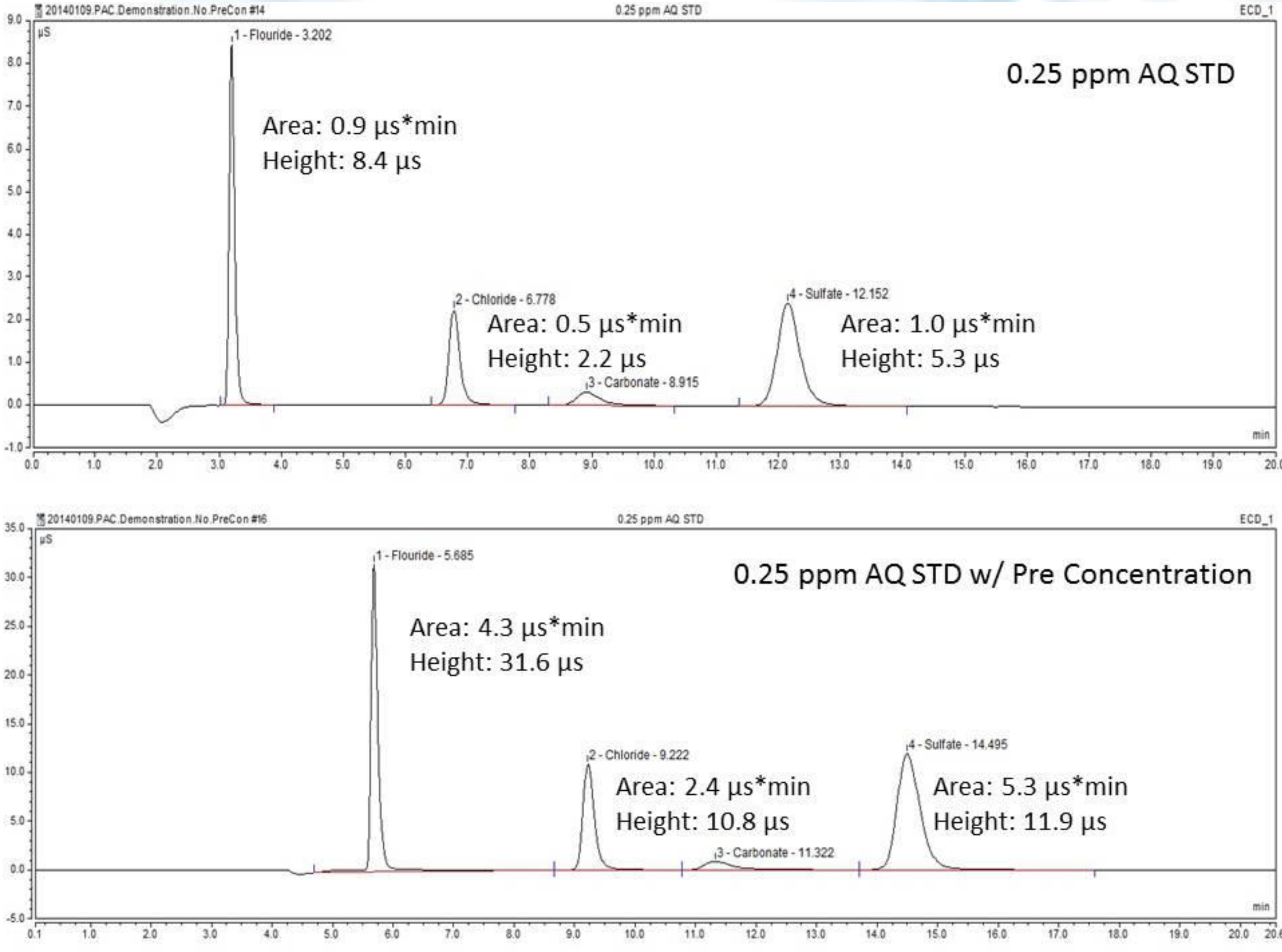
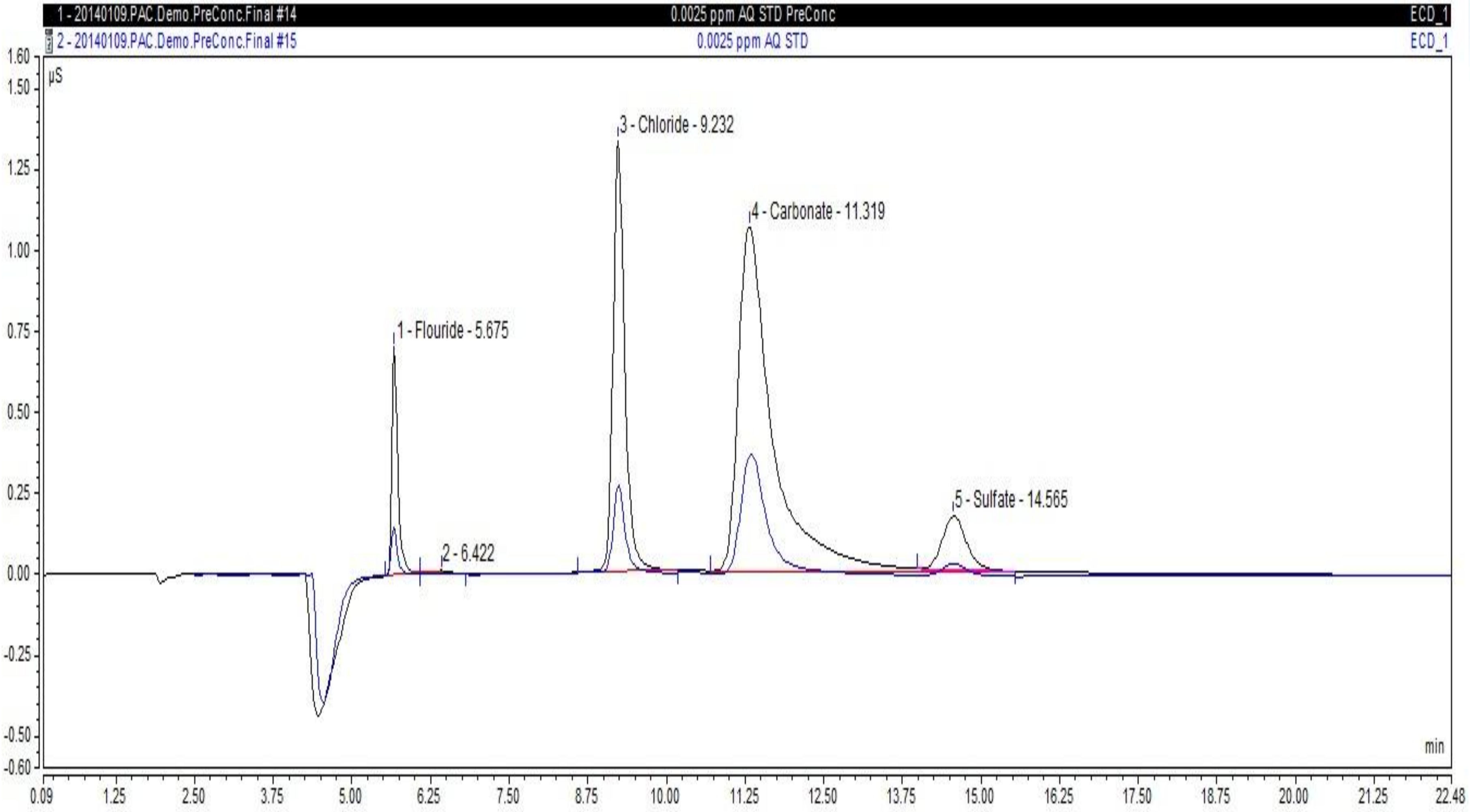
Preconcentration with a Dionex ICS-2100 System

0.25 ppm (aqueous) preconcentration (1.0 mL) vs. direct inj. (200 µL)



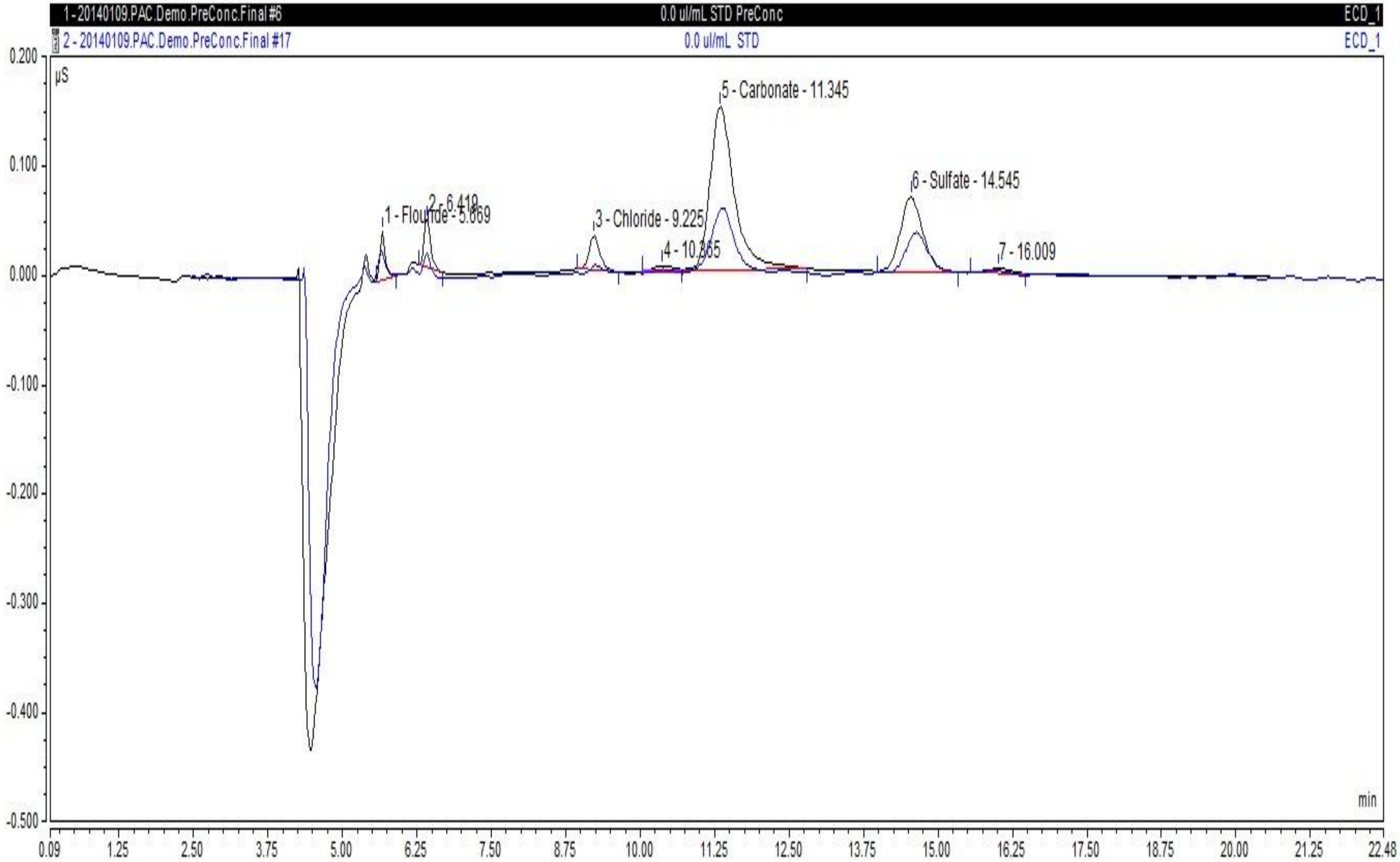
Preconcentration with a Dionex ICS-2100 System

2.5 ppb (1.0 mL) vs. direct inj. (200 µL)



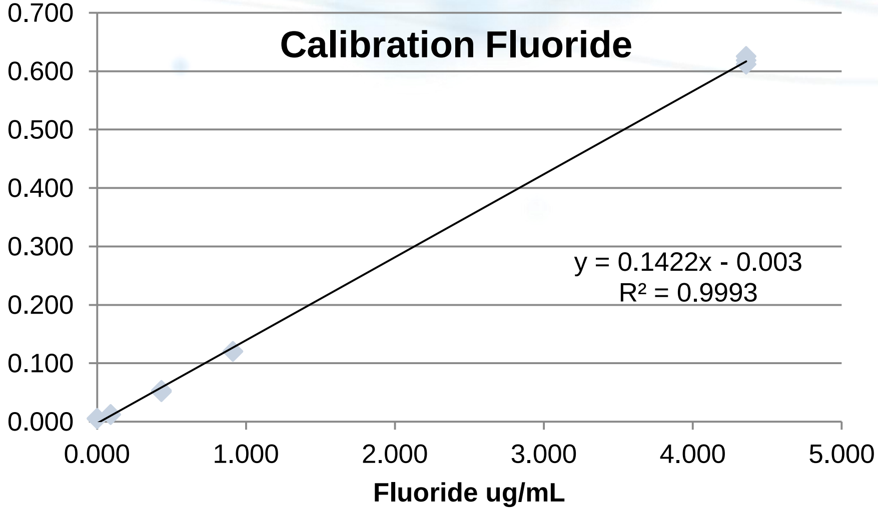
Preconcentration with a Dionex ICS-2100 System

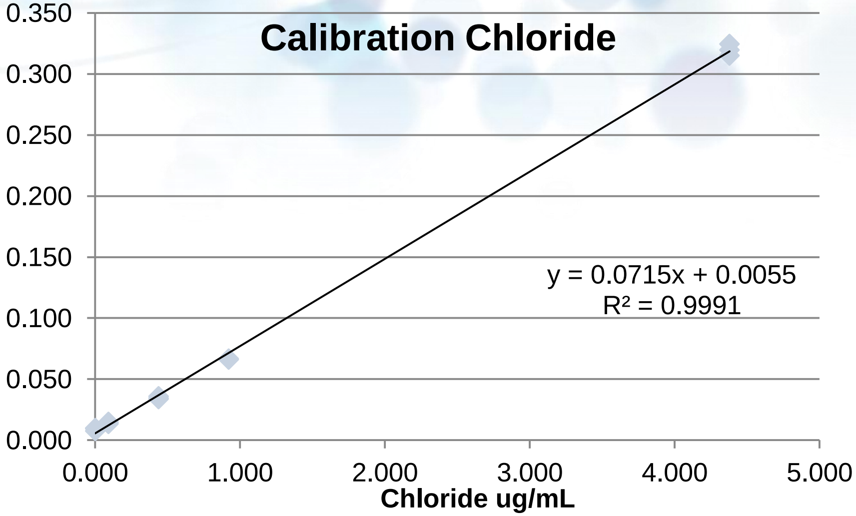
Solvent blank preconcentration (1.0 mL) vs. direct inj. (200 µL)

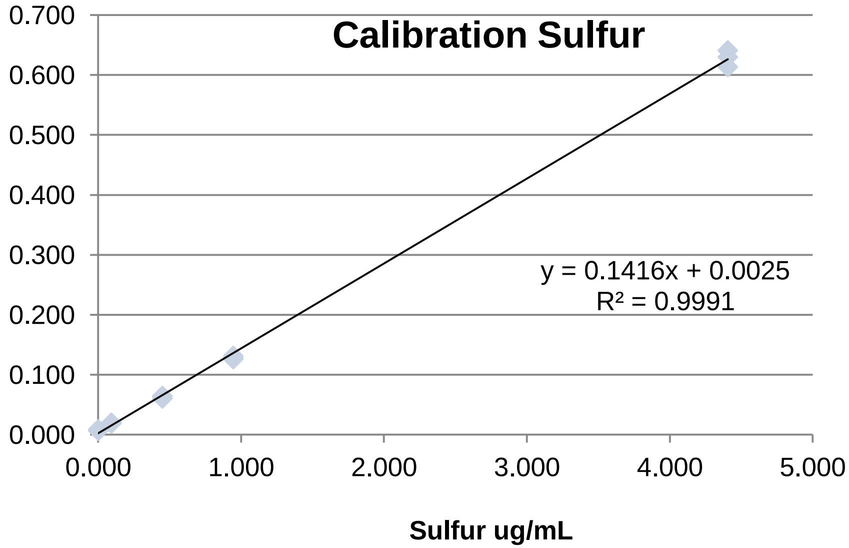


Preconcentration with a Dionex ICS-2100 System

CIC Calibration Curves – F, Cl and S







Preconcentration with a Dionex ICS-2100 System

Fluoride			
Conc	Ave Area	SD	%RSD
0.0	0.005	0.0006	10.9
0.1	0.012	0.0002	1.9
0.5	0.052	0.0013	2.5
1.0	0.120	0.0002	0.2
5.0	0.619	0.0068	1.1

Chloride			
Conc	Ave Area	SD	%RSD
0.0	0.009	0.0013	13.9
0.1	0.014	0.0008	5.6
0.5	0.035	0.0011	3.2
1.0	0.066	0.0008	1.2
5.0	0.320	0.0047	1.5

Sulfur			
Conc	Ave Area	SD	%RSD
0.0	0.008	0.0010	13.3
0.1	0.019	0.0004	2.2
0.5	0.063	0.0021	3.4
1.0	0.128	0.0026	2.0
5.0	0.628	0.0138	2.2

CIC Calibration Curves – F, Cl and S Raw Data

Preconcentration with a Dionex ICS-2100 System

Precision Data Pre-Concentration (1.0 mL Sample Loop)
Concentration in mg/kg

Sample Analysis (90 µl combusted)				
Anion	**Replicate**	**Sample-1**	**Sample-2**	**Sample-3**
Fluorine	Result-1	0.880	0.418	0.046
1 Result = 3 Replicates	Result-2	0.870	0.455	0.043
	Ave	0.875	0.437	0.045
	SD	**0.008**	**0.027**	**0.003**
	%RSD	0.878	6.146	5.849
Chlorine	Result-1	0.895	0.441	0.000
1 Result = 3 Replicates	Result-2	0.863	0.445	0.000
	Ave	0.879	0.443	0.000
	SD	**0.022**	**0.003**	**0.000**
	%RSD	2.522	0.575	—
Sulfur	Result-1	0.954	0.446	0.026
1 Result = 3 Replicates	Result-2	0.918	0.529	0.039
	Ave	0.936	0.488	0.032
	SD	**0.026**	**0.059**	**0.009**
	%RSD	2.726	12.047	26.784

Summary of Results

- The preconcentration configuration can be easily achieved with the Dionex ICS-2100 system, the Dionex AXP-MS pump, and the appropriate trapping column
- Precision of peak area
  - At concentrations of 100 ppb – 5000 ppb
    - ~ 2.0 % RSD or less
  - MDL (using MDL = SD*2.8)
    - ~ 50 ppb
- The same configuration can be used for “matrix elimination” to wash through the trap column the unreacted H_2O_2 thereby eliminating coelution issues around the fluoride peak

Hardware for CIC Preconcentration

Part Number	Description
082351	Dionex ICS-2100 Ion Chromatography System with Degas, Full Dionex EG Control, Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System, version 7, Windows Workstation
060684	Auxiliary Pump Kit AXP-MS
063475	Dionex IonPac UTAC-ULP1 Ultra Trace Anion Concentrator Column - Ultra Low Pressure (5 x 23 mm)
059604	Dionex IonPac ATC-HC Anion Trap Column (9 x 75 mm)

Thank you!

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