



## **Filtration, Automated Dilution, and Matrix Elimination in High Brine Samples Using Ion Chromatography**

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# High Brine Samples

- Brine = Salt concentration of 3.5% to 26%
- Sources
  - Industrial
    - Chlor-alkali process
    - Refrigeration
  - Petrochemical
    - Extraction wastewater
  - Food and Beverage
    - Preservation
  - Environmental
    - Seawater desalination plants
    - Estuary water research

# Challenges of High Salt Sample Analysis

- **Particulates**
  - High salt samples have high particulate levels
  - Clog columns and electrolytic devices
    - Reduced lifetime and performance
- **High ionic concentrations**
  - Exceed column capacity or linear calibration range
    - Reduced column lifetime
- **Disparate ionic concentrations**
  - Closely eluting ions difficult to quantify

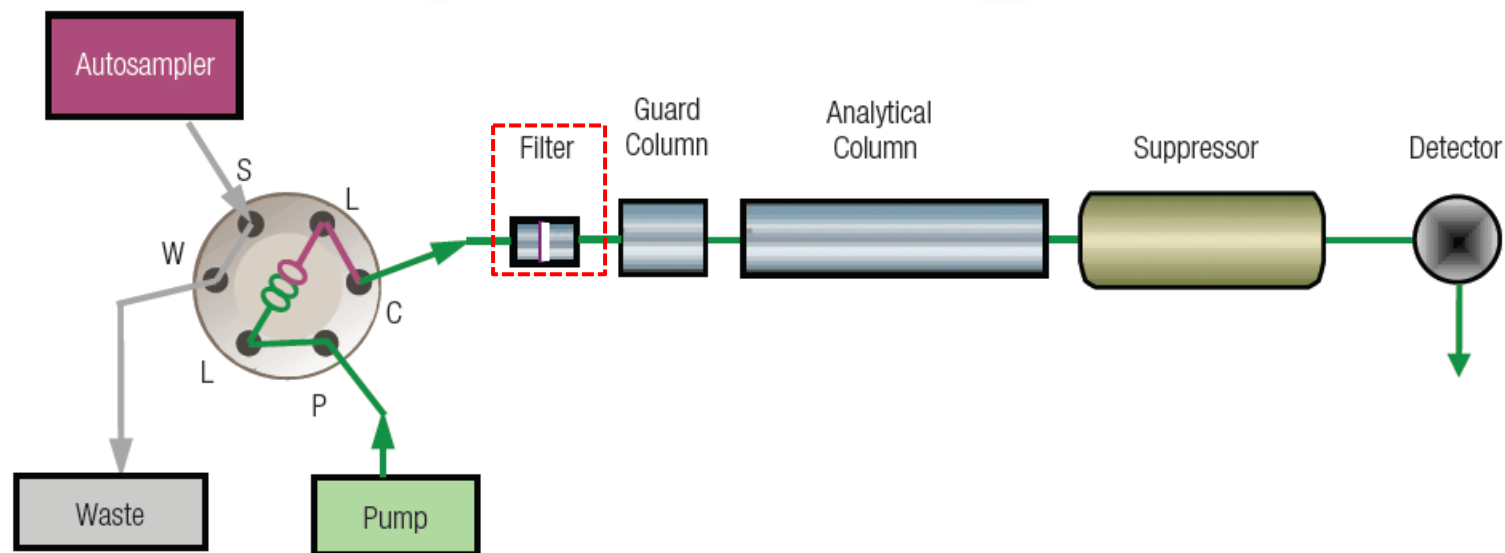
# Particulates: Sample Filtration

- Offline
  - Syringe
  - Tedious, can clog quickly, costly
- Inline
  - Simple, reliable, reproducible, and cost effective



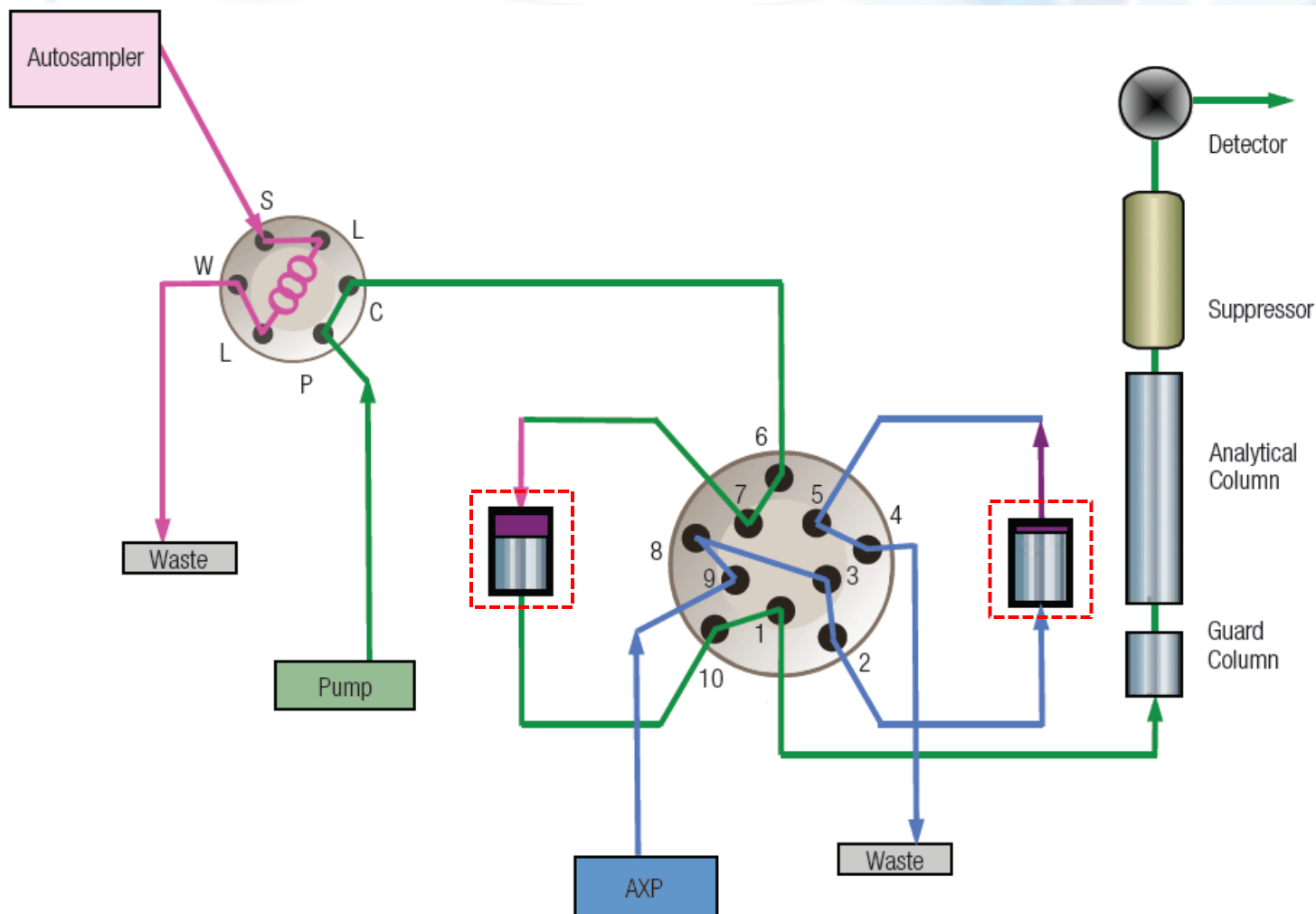
Inline high-pressure filter assembly

# Inline High-Pressure Filtration: Single Filter

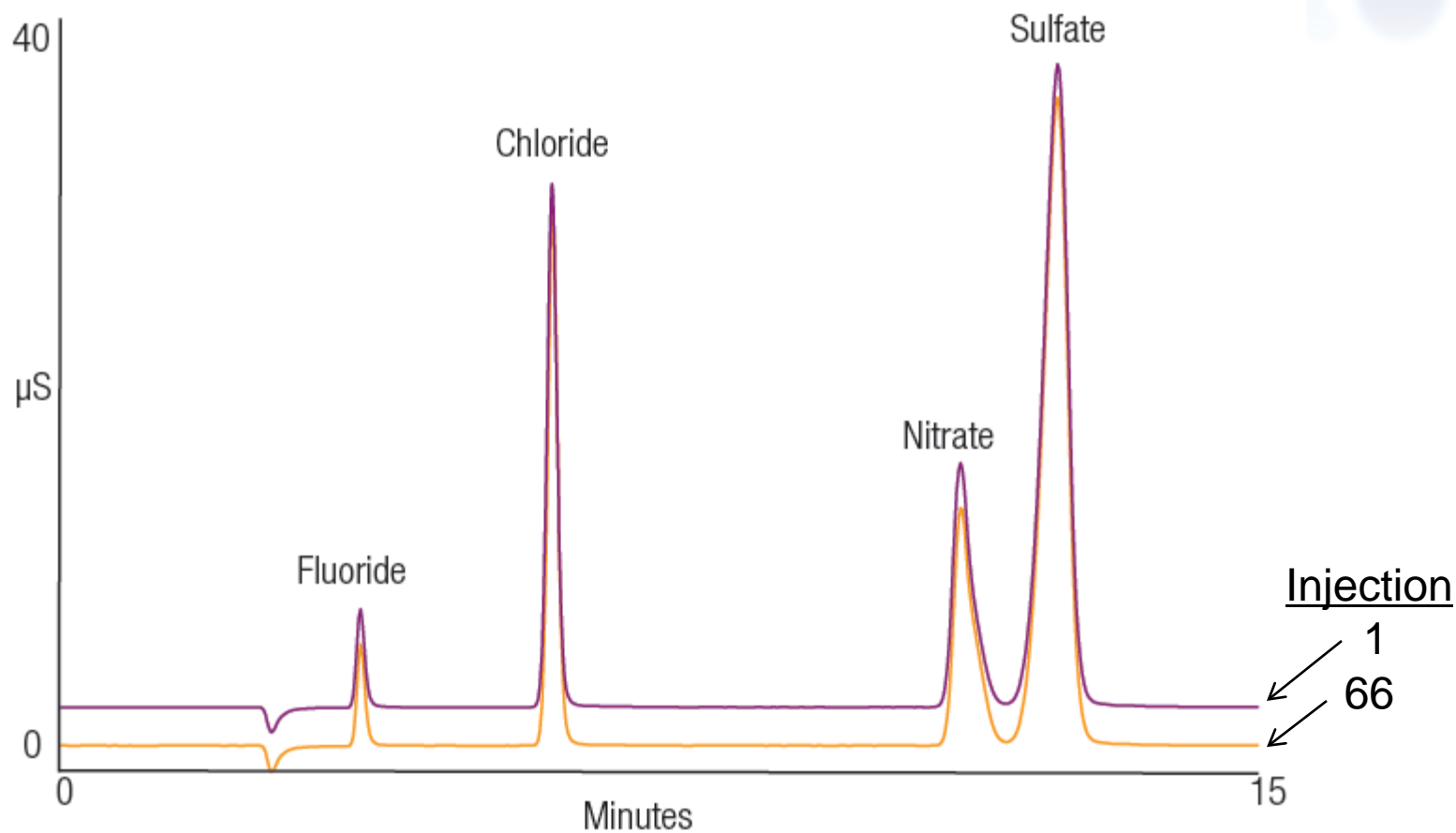


# Inline High-Pressure Filtration: Dual Filters

- Dual filters allow back flushing

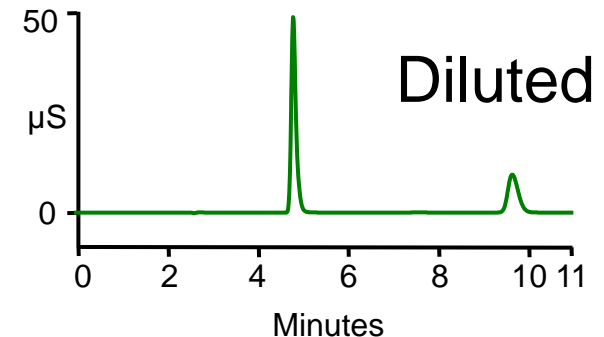
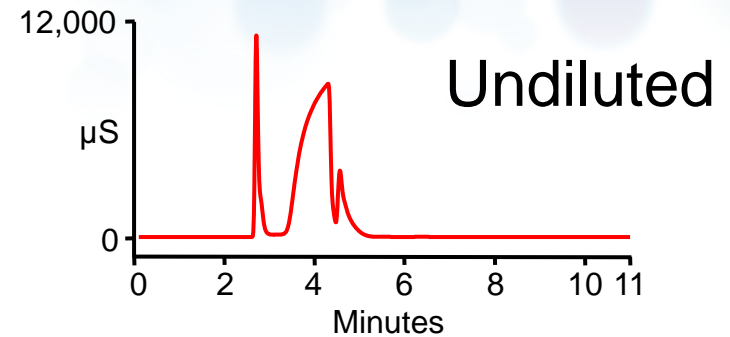


# Consistent Chromatography with Filter Back Flushing



# High Ionic Concentrations

- Exceed column capacity
  - Poor chromatography
  - Peak suppression
  - Inaccurate reporting
- Exceed linear calibration range
  - Analyte-specific
  - Inaccurate results
- Decrease column lifetime





# High Ionic Concentrations: Dilution

## Manual Analysis

- Post-run
  - Determine concentration from chromatogram peak area
    - Exceed limit → dilute → re-run sample
- Pre-run
  - Manual conductivity measurement
    - Exceed limit → dilute → run sample
- Tedious
- Dilution prone to errors

# High Ionic Concentrations: Dilution

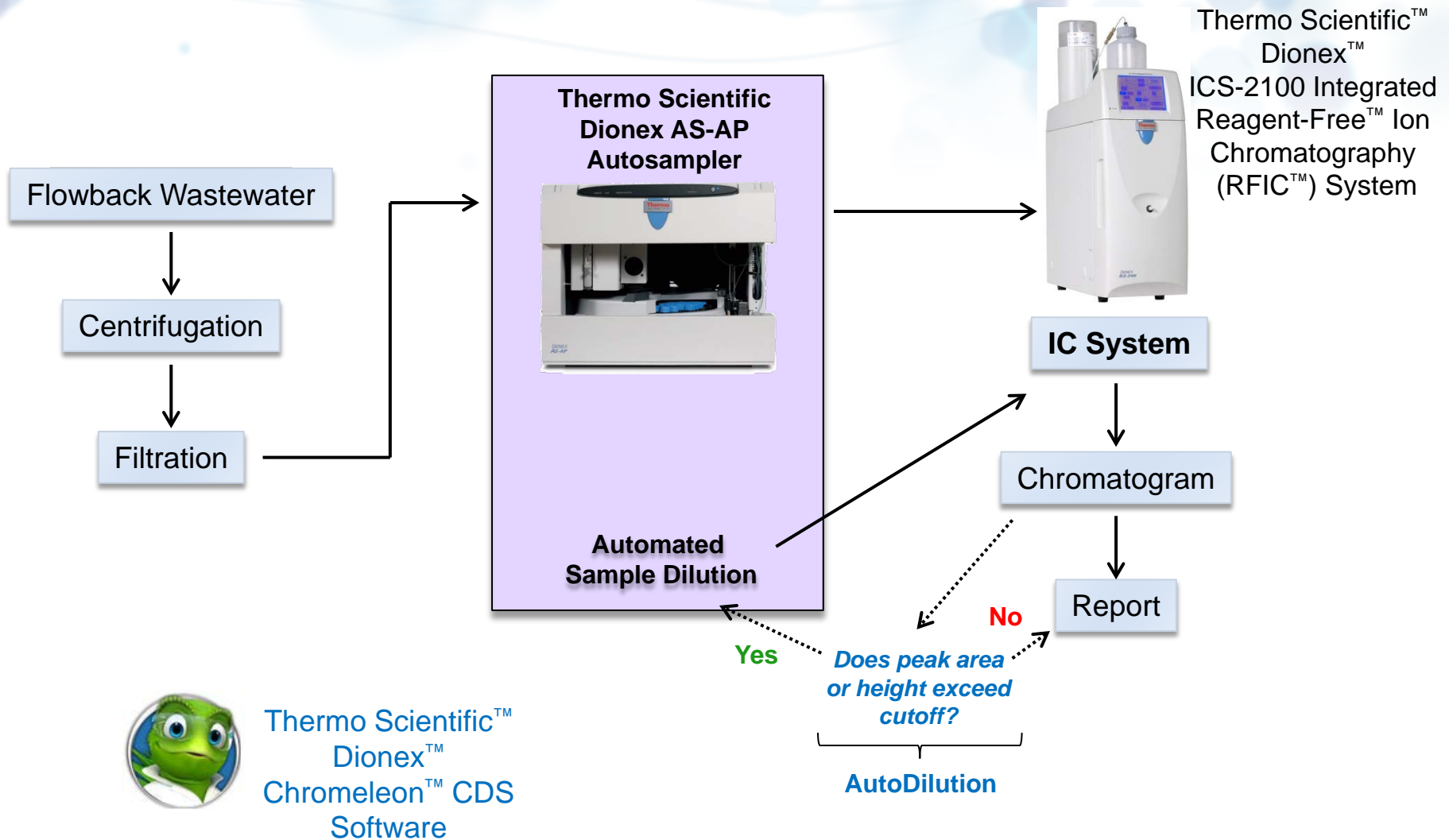
## Automated Analysis

- “AutoDilution”
  - Post-run analysis using ion chromatograph software
  - Exceeding peak height or area -> rerun with less sample loaded
- In-line Conductivity
  - Conductivity measured prior to loading sample onto column
  - Exceeding upper limit -> less sample loaded

## Injection of Less Sample

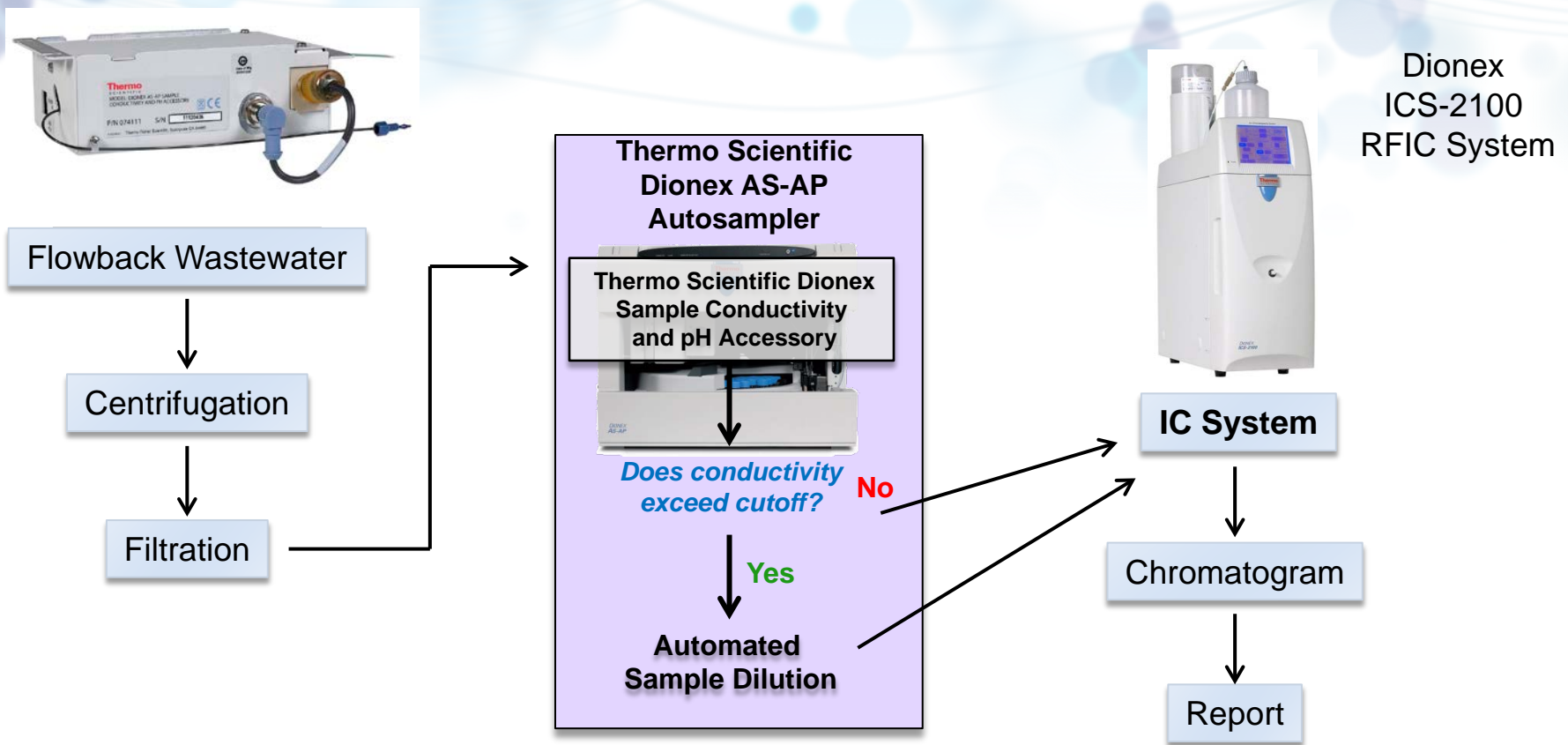
- Smaller sample loop
- Partial loop
- Automated sample dilution

# Automated Analysis: AutoDilution



Thermo Scientific™  
Dionex™  
Chromeleon™ CDS  
Software

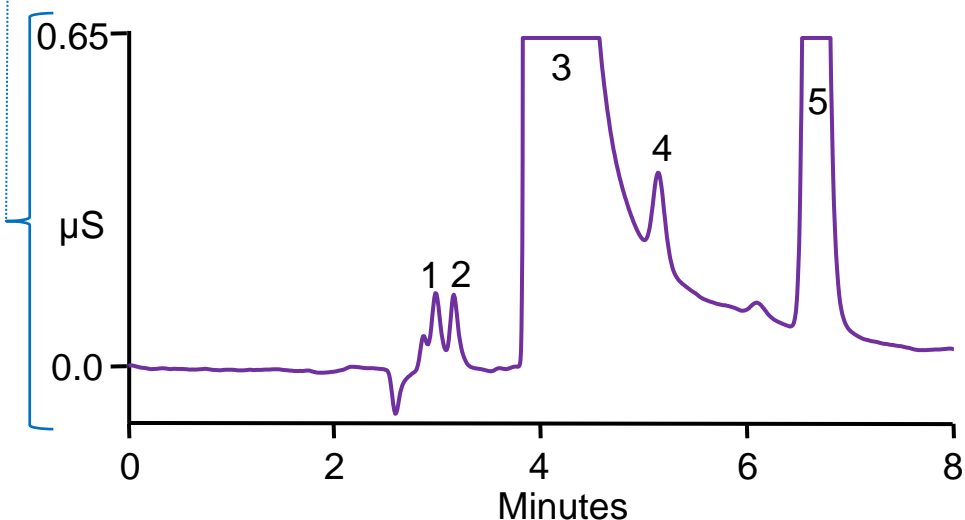
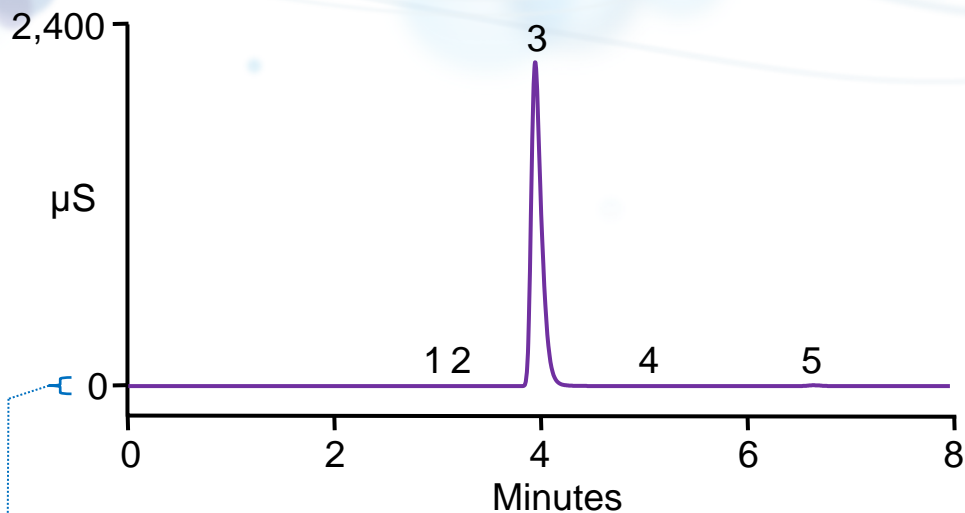
# Automated Analysis: In-line Conductivity



Chromleon CDS  
Software

Dionex  
ICS-2100  
RFIC System

# Analysis of Anions in Automatically Diluted Fracking Flowback Wastewater

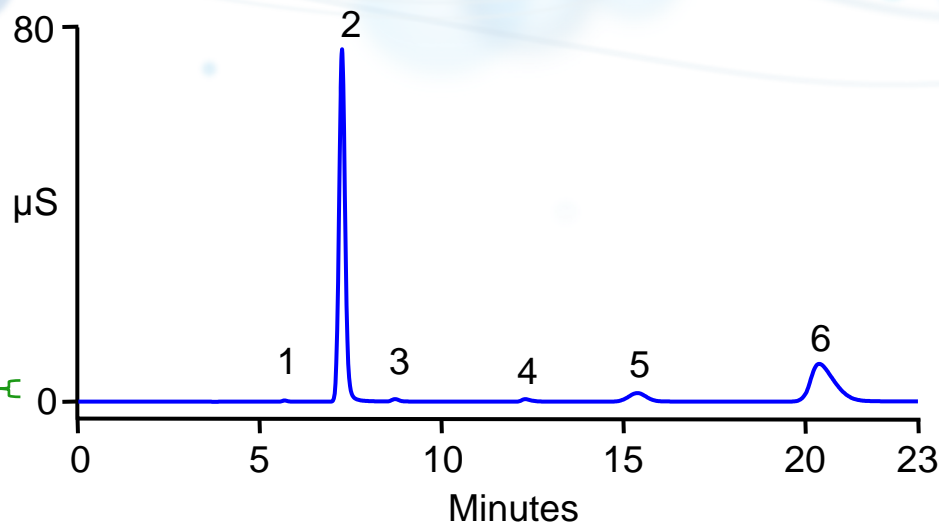


Column: Thermo Scientific™ Dionex™ IonPac™ AG18/AS18 columns , 4 mm  
 Eluent Source: Thermo Scientific Dionex EGC III KOH Eluent Generated cartridge  
 Eluent: 39 mM KOH  
 Flow Rate: 1 mL/min  
 Inj. Volume: 25 μL  
 Col. Temp.: 30 °C  
 Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, recycle mode

Sample: **100-fold** diluted fracking flowback, filtered, 0.2 μm

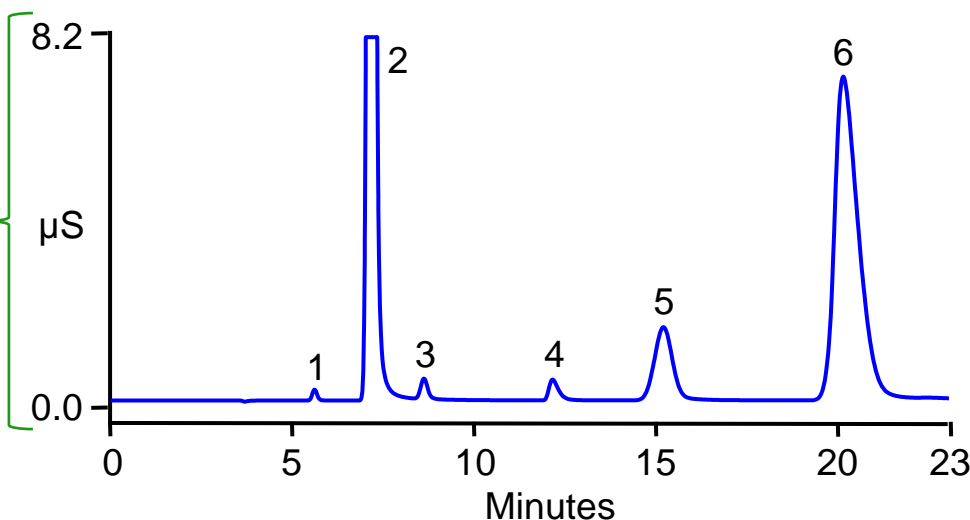
Peaks:	Measured	Undiluted
1. Acetate	< 0.05 mg/L	< 5
2. Formate	< 0.05	< 5
3. Chloride	940.0	94,000
4. Sulfate	0.12	12
5. Bromide	8.90	890

# Analysis of Cations in Automatically Diluted Fracking Flowback Wastewater



Column: Dionex IonPac CG16/CS16 columns, 0.4 mm  
 Eluent: 30 mM MSA  
 Flow Rate: 0.01 mL/min  
 Inj. Volume: 0.4 µL  
 Col. Temp.: 40 °C  
 Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ CCES™ 300 Cation Self-Regenerating Suppressor, recycle mode

Sample: **1000-fold** diluted fracking flowback, filtered, 0.2 µm



Peaks:

	Measured	Undiluted
1. Lithium	< 0.05 mg/L	< 5
2. Sodium	28.0	28,000
3. Ammonium	0.35	350
4. Potassium	0.50	500
5. Magnesium	1.1	1,100
6. Calcium	10.0	10,000

# Disparate Ion Concentrations: Matrix Elimination

- Thermo Scientific™ Dionex™ OnGuard™ (offline) and Thermo Scientific™ Dionex™ InGuard™ (inline) Sample Preparation Cartridges
  - Isolate Analytes from Sample Matrix
    - Eliminate matrix species that are not of interest and may interfere with the analysis
    - Reduce concentration of species that are in very large concentration relative to analytes of interest
    - Trap species that reduce the life of consumables
  - Concentrate Analytes
    - Retain analyte species onto a Guard column followed by elution into a smaller volume

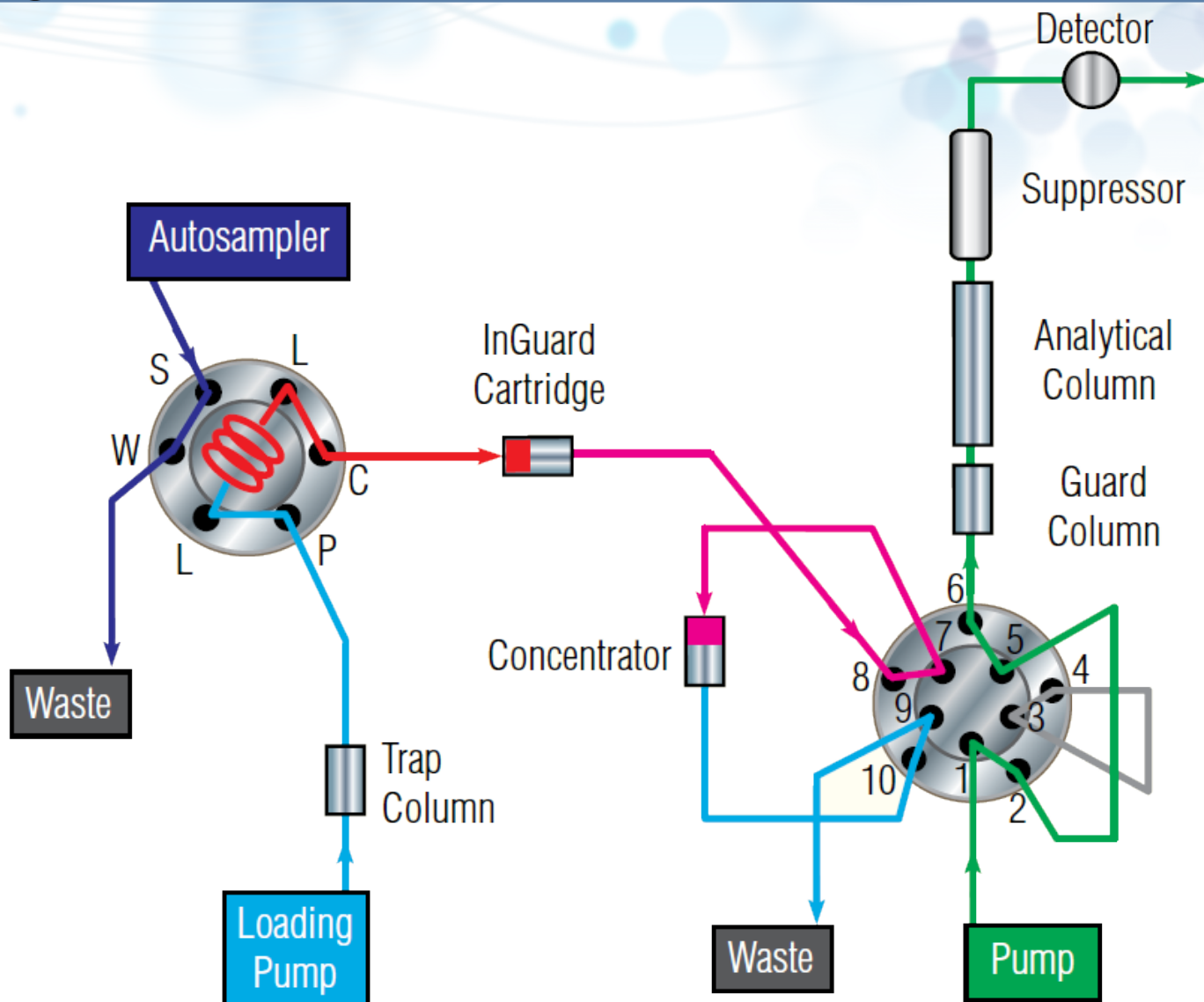
# Dionex InGuard Sample Pretreatment Cartridges

- Automated sample pretreatment cartridges to remove matrix interferences
  - Can be used multiple times
  - Some cartridges can also be regenerated
- Removes matrix interferences such as cations, transition metals, anions, or hydrophobic substances

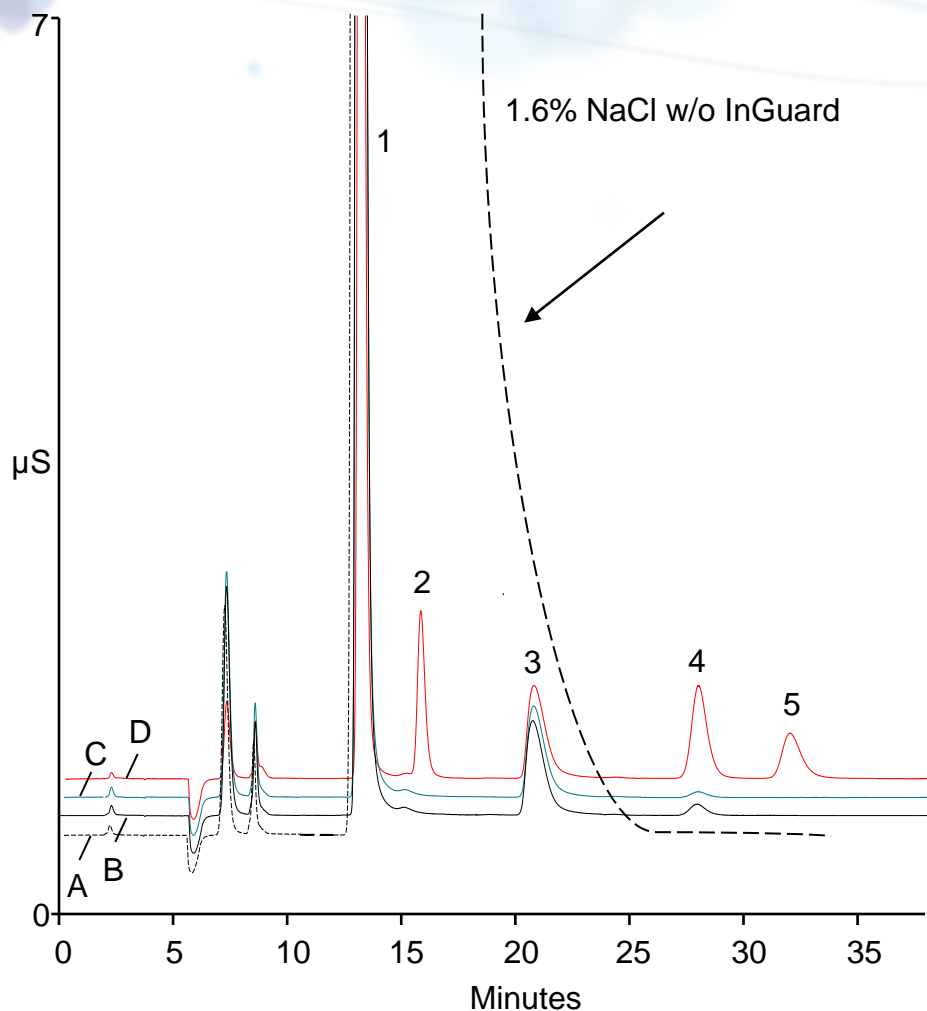




# Inline Matrix Elimination Using a Dionex InGuard Cartridge



# Removal of High Chloride Using InGuard Ag/Na



Column: Dionex IonPac AG16/AS16 columns, 4 mm i.d.  
 Concentrator: TAC-LP1 concentrator column  
 Eluent: 23 mM KOH  
 Flow Rate: 1 mL/min  
 Inj. Volume: 100 µL  
 Col. Temp.: 30 °C  
 Detection: Suppressed conductivity, Dionex ASRS 300 Anionic Self-Regenerating Suppressor, external water mode

Sample Prep: InGuard Ag followed by InGuard Na

Sample Loading: Deionized water, 1 mL/min  
 Concentrator  
 Loading time: 4 min

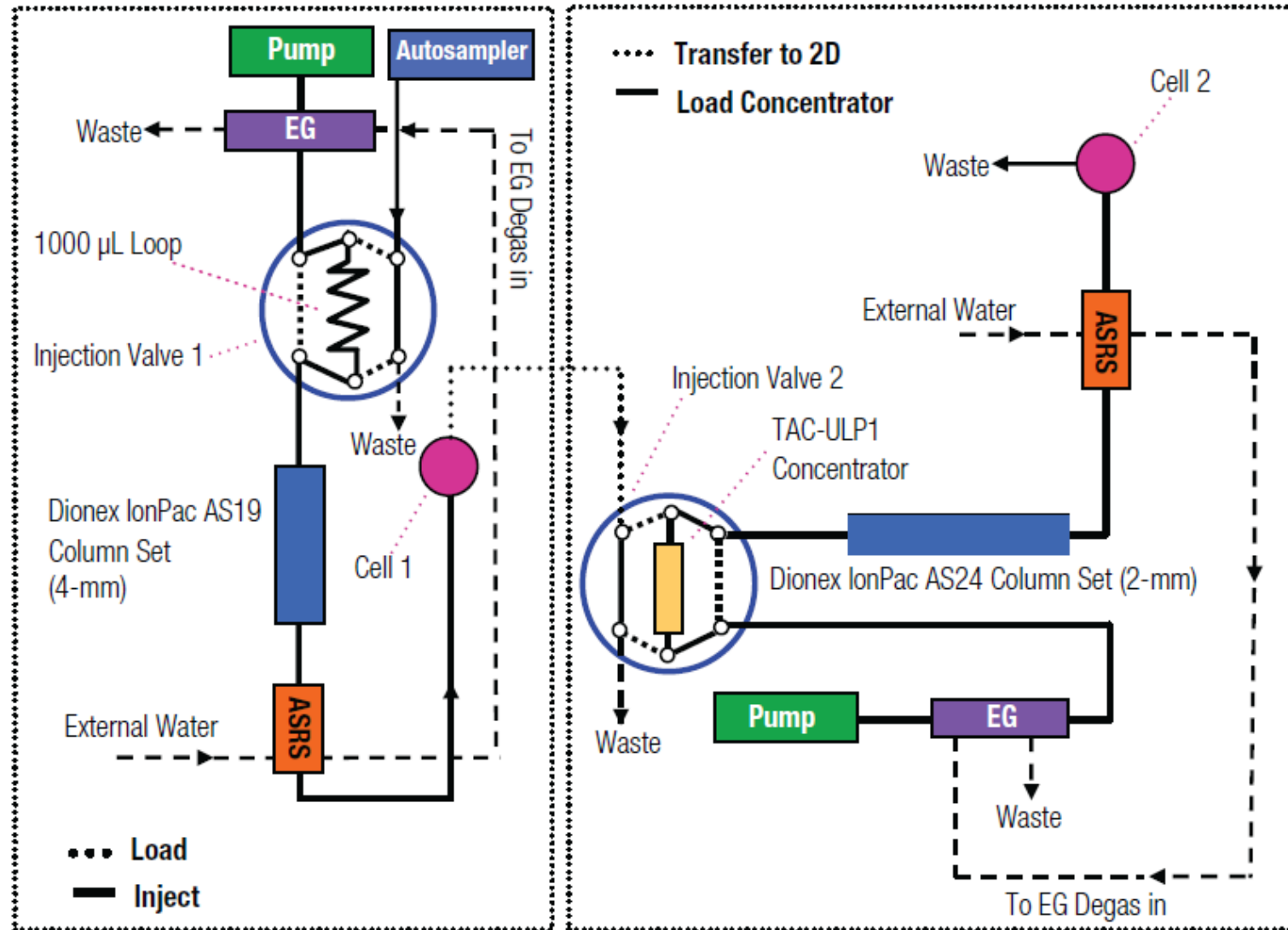
Peaks:

1. Chloride	-- mg/L
2. Nitrite	2
3. Carbonate	--
4. Nitrate	2
5. Sulfate	2

# Disparate Ion Concentrations: Matrix Elimination

- Dionex OnGuard or Dionex InGuard Cartridges
- Two-dimensional (2-D) IC
  - First dimension
    - Separate analyte of interest from matrix ions
      - Transfer to concentrator column
  - Second dimension
    - Resolve analyte from ions surrounding peak of interest
  - Interfering matrix components are transferred to waste
  - Samples can be injected directly without need for pretreatment cartridges or dilution

# 2-D IC System Setup

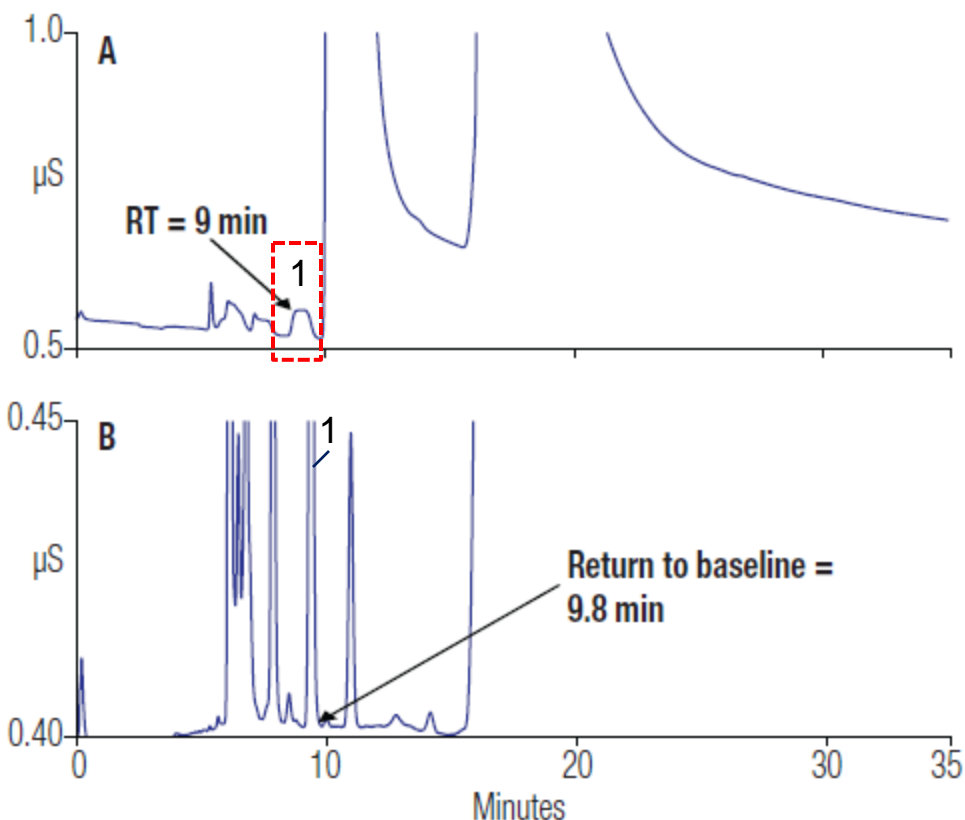


# 2-D IC System Setup

- Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ System
  - Continuous operation up to 5000 psi
  - Reagent-free eluent generation
  - Choice of capillary, microbore, and standard bore flow rates and columns
  - Dual pumps
  - Easy configuration
  - Ideal system for 2-D IC setup



# 2-D IC: First Dimension Determination of Bromate Isolation Cut Window

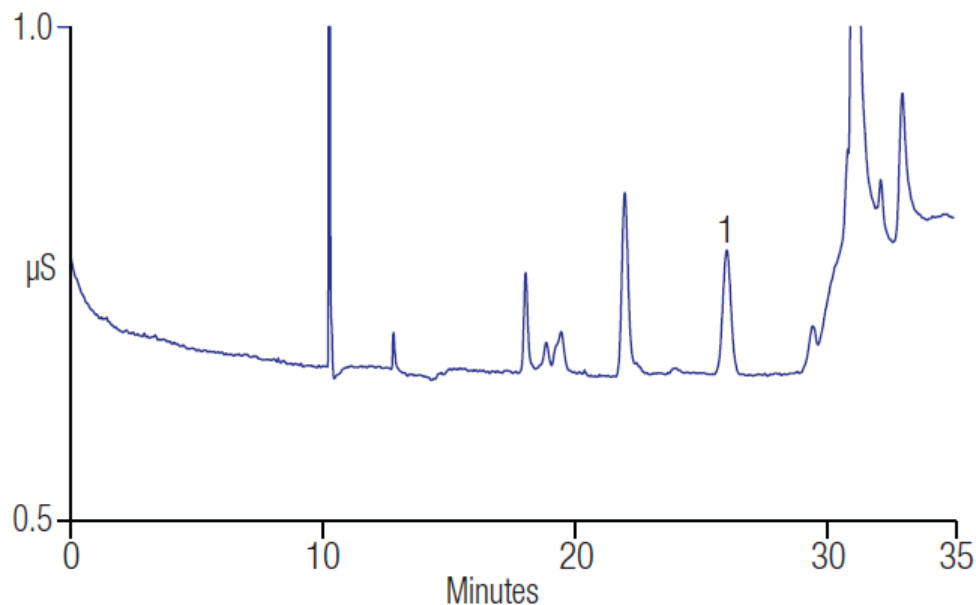


Column: Dionex IonPac AG19/AS19 columns, 4 mm i.d.  
Eluent Source: Dionex EGC II KOH cartridge  
Eluent: 10 mM KOH 0–12 min, 65 mM 12.1–35 min  
Flow Rate: 1 mL/min  
Inj. Volume: 1000 µL  
Col. Temp.: 30 °C  
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA II suppressor, external water mode

Sample: A) Laboratory synthetic sample matrix  
B) Deionized water

Peak:	A	B
1. Bromate	15 µg/L	15

# 2-D IC: Second Dimension Bromate Separation



Column: Dionex IonPac AG24/AS24 columns, 2 mm i.d.  
Eluent Source: Dionex EGC II KOH cartridge  
Eluent: 10 mM KOH 0–24 min,  
10–65 mM 24.1–35 min  
Flow Rate: 0.25 mL/min  
Cut Volume: 2 mL  
Col. Temp.: 30 °C  
Concentrator: TAC-ULP1, 5 × 23 mm  
Detection: Suppressed conductivity,  
Dionex ASRS ULTRA II  
suppressor, external water  
mode

Peak:  
1. Bromate 5.0 µg/L

# Conclusion

- Challenges for analysis of high salt matrices
  - Particulates
  - High ionic concentrations
  - Disparate analyte concentrations
- Solutions
  - Inline Filtration
    - Single, dual
  - Inline conductivity measurement and automated sample dilution
  - Matrix elimination using Dionex InGuard columns or 2-D IC



# Thank you!

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# Application and Technical Notes

- **TN 144:** Inline Filtration for Ion Chromatography
- **TN 138:** Accurate and Precise Automated Dilution and In-line Conductivity Measurement Using the AS-AP Autosampler Prior to Analysis by Ion Chromatography
- **TN 139:** Determination of Anions in Fracking Flowback Water From the Marcellus Shale Using Automated Dilution and Ion Chromatography
- **AN 187:** Determination of Sub- $\mu\text{g/L}$  Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimension Ion Chromatography and Suppressed Conductivity Detection