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

![Chromatogram graph showing peak analysis for different ions: Chloride, Sulfate, Nitrate, and Fluoride.](image)

- **Injection**: 66
  - Chloride
  - Sulfate
  - Nitrate
  - Fluoride
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

Flowback Wastewater ➔ Centrifugation ➔ Filtration ➔ Thermo Scientific Dionex AS-AP Autosampler ➔ Automated Sample Dilution ➔ IC System ➔ Chromatogram ➔ Report

Does peak area or height exceed cutoff?

Thermo Scientific™ Dionex™
ICS-2100 Integrated Reagent-Free™ Ion Chromatography (RFIC™) System

Thermo Scientific™ Dionex™ Chromeleon™ CDS Software
Automated Analysis: In-line Conductivity

Flowback Wastewater → Centrifugation → Filtration

Thermo Scientific Dionex AS-AP Autosampler

Does conductivity exceed cutoff?

Yes → Automated Sample Dilution

No → IC System

IC System → Chromatogram → Report

Dionex ICS-2100 RFIC System

Chromeleon CDS Software
Analysis of Anions in Automatically Diluted Fracking Flowback Wastewater

Peaks:

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

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

Measured | Undiluted
--- | ---
Acetate | < 0.05 mg/L, < 5
Formate | < 0.05, < 5
Chloride | 940.0, 94,000
Sulfate | 0.12, 12
Bromide | 8.90, 890
Analysis of Cations in Automatically Diluted Fracking Flowback Wastewater

Peaks:

1. Lithium: Measured < 0.05 mg/L, Undiluted < 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

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
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: 1. Bromate A 15 µg/L 15 B
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!
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-µg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimension Ion Chromatography and Suppressed Conductivity Detection