

Determination of Anions in Fracking Flowback Water From the Marcellus Shale Using Automated Dilution and Ion Chromatography

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Key Words

Dionex AS-AP Autosampler, Dionex IonPac AS18, Hydraulic Fracturing, In-line Conductivity

Goal

Demonstrate the use of in-line conductivity measurement to trigger automated dilution prior to separation and quantification of inorganic ions and organic acids in Marcellus Shale fracking flowback samples using ion chromatography.

Introduction

The rapid increase in U.S. natural gas production in recent years has been propelled by the extensive use of hydraulic fracturing (also known as fracking). This process extracts natural gas by drilling into bedrock (primarily shale) and then injecting fluid under high pressure causing cracks in bedrock, thereby releasing trapped gas that can be captured.¹ Fracking fluid contains approximately 85% water and 13% sand (proppant), the latter to prop open cracks, which facilitates the flow of gas. The remainder consists of chemical additives such as friction reducers, anti-bacterial agents, and corrosion inhibitors.²

Fracking has been in use since the 1940s primarily for oil extraction, however recent refinements to this process have enabled the exploitation of energy resources that had previously been inaccessible.³ While fracking provides financial benefits to both local and national economies, it has not been without controversy. Inadvertent spills or the dumping of fracking flowback (fracking solution that returns to the surface via the well bore) into unlined collection ponds can contaminate ground water.⁴

Additionally, high levels of chloride and bromide found in fracking wastewater can result in effluent discharged by wastewater treatment facilities that exceed the levels allowed in the facility's discharge permits.⁵ Chlorination or ozonation, as part of the purification process, can produce disinfection byproducts (DBP) such as bromate, chlorate, and haloacetic acids. These DBPs are carcinogens or interfere with human development and, consequently, are regulated by the U.S. Environmental Protection Agency's National Primary Drinking Water Regulations.



Organic acids, such as acetate and formate, are added to fracking fluid to adjust the pH.⁶ The pH of fracking fluid is maintained within a narrow range to ensure the effectiveness of surfactant additives that facilitate the penetration of fracking solution into bedrock. These organic acids can act as a carbon source to promote the growth of anaerobic bacteria, resulting in the production of corrosive and toxic hydrogen sulfide. Additionally, because not all of the fracking solution is recovered, bacteria can grow within the interstitial cracks following a fracking event and block gas flow over the long term, inhibiting well production. Thus, the concentration of organic acids should be closely monitored.

The high levels of dissolved salts leached from bedrock are a challenge to analyzing fracking flowback solutions. Injection of high ionic strength solutions can exceed the capacity of columns used in ion chromatography, resulting in poor chromatography, peak suppression (i.e., poor recovery), and inaccurate reporting. Additionally, high concentrations may exceed the linear calibration range for a particular analyte. These samples require dilution prior to injection, which results in an additional

sample preparation step and the possibility of errors. To minimize errors and reduce labor costs, there are a number of options available to automate the determination of the need for and then the loading of less sample:

- The AutoDilution feature of Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software. If a chromatogram has an analyte peak height or area that exceeds a pre-set limit, a smaller amount of sample is re-injected using either a:
 - a. Partial loop
 - b. Smaller loop
 - c. Vial to vial dilution using a Thermo Scientific Dionex AS-AP Autosampler
- Measurement of sample conductivity prior to injection. This can be done a) manually, which is tedious, labor intensive, and prone to error, or b) automatically, using the Thermo Scientific Dionex AS-AP Sample Conductivity and pH Accessory. If the conductivity exceeds a specified amount, Chromeleon CDS can trigger the loading of less sample as per a–c above.

These options are depicted in Figure 1 and are described in greater detail in Technical Note 138.⁷

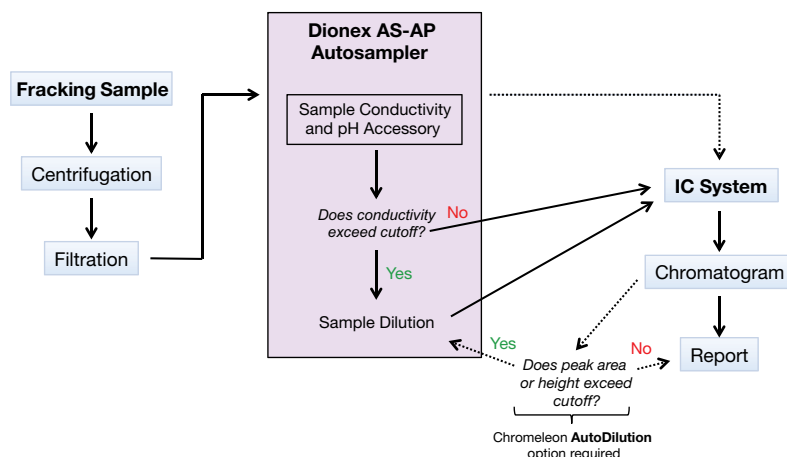


Figure 1. Automated sample analysis options available using the Dionex AS-AP Autosampler and Chromeleon software.

This Technical Note describes the analysis of fracking flowback solutions using ion chromatography following in-line determination of sample conductivity and automated dilution of high ionic strength samples.

Equipment

- Thermo Scientific™ Dionex™ ICS-2100 Integrated Reagent-Free™ IC (RFIC™) System with an additional 10-port valve (P/N 069473)
- Dionex AS-AP Autosampler
 - Dionex AS-AP Sample Conductivity and pH Accessory (P/N 074923) with the included pH electrode port plug and seal installed
- Chromeleon CDS, version 6.8 (release 6.80 DU11c or later) or 7 (release 7.1 SR1 or later)

Reagents and Standards

- 18 MΩ-cm resistivity degassed deionized (DI) water
- Thermo Scientific Dionex 1000 μS conductivity standard (P/N 080172)
- Ultra Scientific 1000 mg/L Certified IC Standards or Fisher Scientific reagents, ACS grade

Samples

Fracking flowback solutions from the Marcellus Shale (F1–10) were collected from successively later times during the fracking process.

Conditions

Chromatographic

Columns:	Thermo Scientific™ Dionex™ IonPac™ AG18/AS18, 4 mm
Eluent Source:	Thermo Scientific Dionex EGC III KOH Cartridge
Eluent:	23 mM or 39 mM KOH
Flow Rate:	1.0 mL/min
Column Temp.	30 °C
Inj. Volume:	25 μL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor*, recycle mode, 57 mA (23 mM KOH); 97 mA (39 mM KOH)
Background Conductance:	< 2 μS
Noise:	< 3 nS
System Backpressure:	2100 psi

* Equivalent or improved results can be obtained using the Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor.

Dionex AS-AP Autosampler Dilution

Syringe:	1 mL
Buffer Line Volume:	1.2 mL
Wash Solution:	18 MΩ-cm resistivity degassed DI water from autosampler wash liquid reservoir
Vials:	10 mL
Dilution Volumes:	20 μL sample into 1980 μL DI water
Draw/Dispense Speed:	50/25 μL/sec (water) 10/5 (sample)
Mix by Shake Iterations:	10
Carousel Speed:	30,000 encoder counts (maximum, default)

Dionex AS-AP Sample Conductivity and pH Accessory

Volume Drawn:	600 μL
Draw/Dispense Speed:	20/10 μL/sec

Part numbers of the consumables used in this document are listed in Table 1.

Table 1. Consumables list.

Product Name	Description	Part Number
Dionex EGC III KOH cartridge	Eluent generator cartridge	074532
Thermo Scientific Dionex CR-ATC column	Continuously regenerated anion trap column	060477
Dionex IonPac AS18 column	Separation column, 4 mm i.d.	060549
Dionex IonPac AG18 column	Guard column, 4 mm i.d.	060551
Thermo Scientific™ Dionex™ AERS™ 500 suppressor	Suppressor cartridge, 4 mm i.d. columns	082540
Dionex AS-AP Autosampler vials	Polystyrene vials with caps and blue septa, 10 mL, package of 100	074228

Sample and Standard Preparation

Samples were centrifuged at $10,000 \times g$, 10 min to pellet solid particles, which facilitated filtration. The resultant supernatant was filtered with a $0.2 \mu\text{m}$ polyethersulfone (PES) syringe filter. Samples were diluted as required with degassed 18 M Ω -cm resistivity DI water.

It is important to use 18 M Ω -cm resistivity, DI water for eluent and autosampler flush solutions to avoid system contamination, decreased sensitivity, and poor calibration. Degassing the DI water by vacuum filtration prior to use is a good laboratory practice.

Standards were prepared by diluting Certified IC Standard stock solutions or by dissolving ACS grade reagents with DI water.

Instrument Setup and Installation

Install, hydrate, and condition the Dionex EGC III KOH eluent generator cartridge. This cartridge requires at least 2000 psi of backpressure for optimal operation. Install and hydrate the Dionex CR-ATC trap column and the Dionex AERS 500 Anion Electrolytically Regenerated Suppressor. Figure 2 outlines the flow path of the standard Dionex ICS-2100 system setup with a Dionex AS-AP Autosampler. Hydrate the devices and finish the system setup according to the product manuals and the Dionex ICS-2100 Operator's Manual.^{8–12} Install and condition the column using the conditions described in that column's Quality Assurance Report (QAR) for 30 min prior to installing them in-line with the suppressor. If total system backpressure is < 2000 psi, install one or more backpressure coils between the Dionex CR-ATC Continuously Regenerating Anion Trap Column and the injection valve to increase the system pressure to 2000–3000 psi.

Install the Dionex AS-AP Sample Conductivity and pH Accessory in the Dionex AS-AP Autosampler as outlined in the Accessory Setup and Operation Guide.¹³ Figure 3 depicts the setup required for Push mode with this accessory.

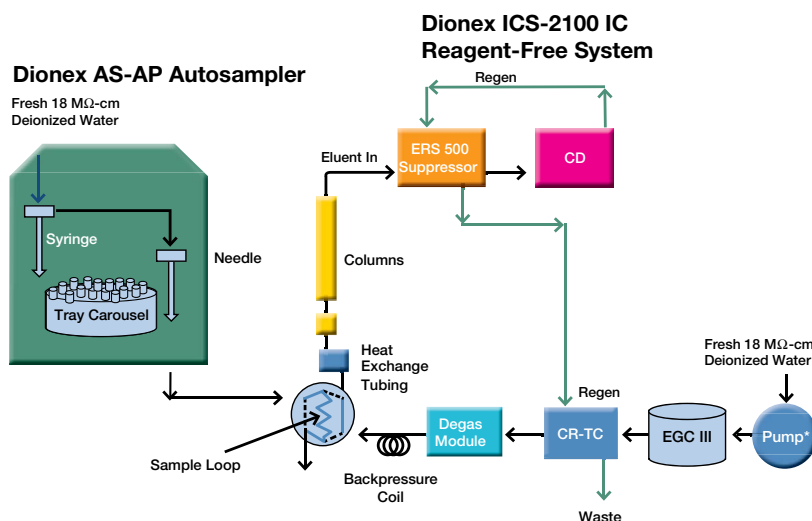


Figure 2. Flow diagram for the Dionex ICS-2100 IC Reagent-Free System with 10-port valve.

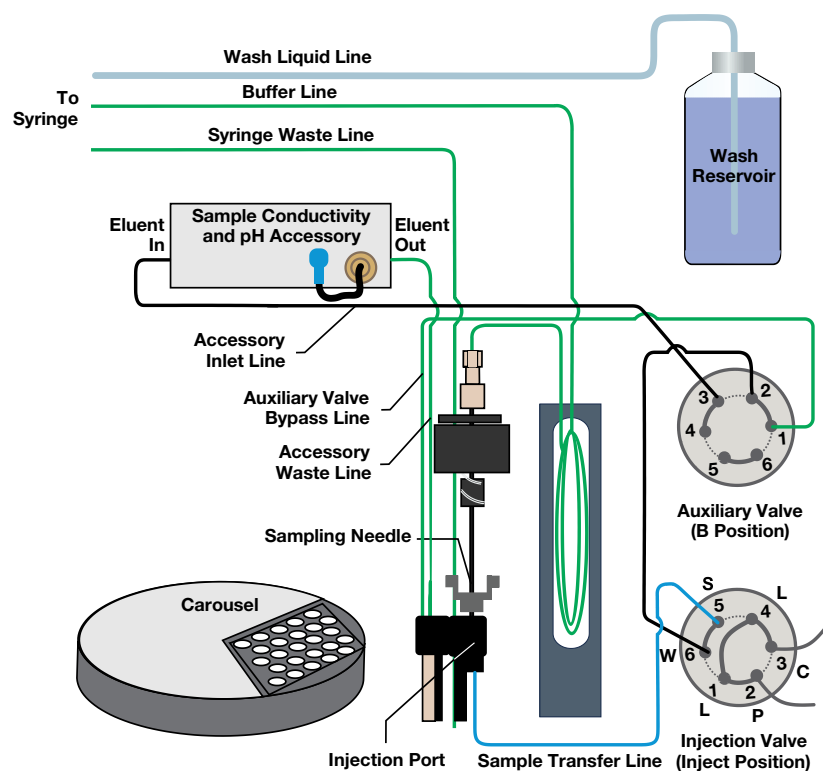


Figure 3. Dionex AS-AP plumbing schematic for Push Mode with a Sample Conductivity and pH Accessory.

For the experiments presented here, the 10-port valve of the Dionex ICS-2100 system was used as the auxiliary valve. Alternatively, if the optional high-pressure valves are installed in the Dionex AS-AP Autosampler, they can be used to divert sample to the Dionex AS-AP Sample Conductivity and pH Accessory. Install the pH electrode port plug, which reduces the amount of injected sample from 2000 to 600 μL for conductivity determination. Prior to use, the conductivity was calibrated by determining the zero point of the accessory and then measuring the conductivity of a 1000 μS standard. Chromeleon CDS was used to determine the calibration offset and slope, and calculate a cell constant. This constant, stored in the autosampler firmware, was used for subsequent measurements.

Refer to the Dionex AS-AP Sample Conductivity and pH Setup and Operation Guide and the Dionex AS-AP Autosampler Operator's Manual for more information.^{12, 13}

Chromeleon CDS Method Setup

Use the Chromeleon CDS Program Wizard to create a method that will trigger an automatic dilution when a specified conductivity value is exceeded. For the data presented here, an automated dilution of 1:100 was triggered when the conductivity measured exceeded 1500 μS . This option is currently only available in Chromeleon CDS version 6.80 DU11c or later; it will be available in an upcoming release of Chromeleon 7 CDS. See Technical Note 138 for additional details on setup and configuring the software.⁷

Results and Discussion

In-Line Conductivity Measurement and Sample Analysis

Because fracking flowback waters are known to contain high ion concentrations, the IC system was configured so that, prior to sample injection, the conductivity of samples was determined in-line using the Dionex AS-AP Sample Conductivity and pH Accessory. All of the samples analyzed had conductivity > 1500 μS , which resulted in an automatic 100-fold dilution by the Dionex AS-AP Autosampler prior to injection onto the Dionex IonPac AS18 column set. As exemplified by the chromatogram in Figure 4, chloride was the predominant anion present in all of the fracking solutions analyzed (and at its highest concentration in this fraction), while bromide was the second most abundant at ~100-fold lower concentration. The bottom portion of Figure 4 displays an expanded view of the upper chromatogram and shows that low levels of sulfate and the organic acids acetate and formate were also detected.

Columns: Dionex IonPac AG18/AS18, 4 mm
 Eluent Source: Dionex EGC III KOH cartridge
 Eluent: 39 mM KOH
 Flow Rate: 1 mL/min
 Inj. Volume: 25 μL
 Col. Temp.: 30 $^{\circ}\text{C}$
 Detection: Suppressed conductivity, Dionex ASRS 300 Suppressor, recycle mode
 Sample: 100-fold 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

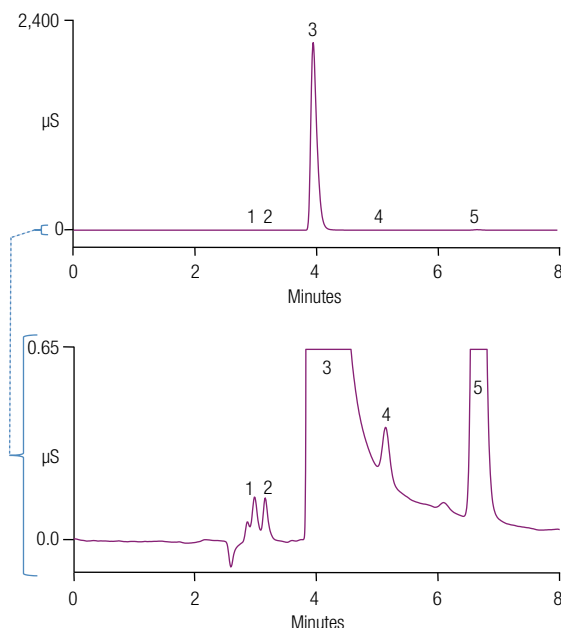


Figure 4. Determination of inorganic anions and organic acids in fracking flowback (F10).

To obtain better separation of the early eluting peaks, the eluent concentration was reduced from 39 to 23 mM KOH. As shown in Figure 5, the first fracking flowback water sample (F1) contained levels of acetate that were considerably higher than in subsequent fractions. Samples two to ten had a peak that corresponded to formate but in fraction 1 (F1) a peak appears at a slightly earlier retention time. If formate is present in F1, it is a minor constituent. This peak is likely due to propionate, which elutes at an almost identical time to the peak seen here under the conditions used. Propionate is not resolved from formate when both of these analytes are present. In fractions two to ten, fluoride is also present at low, but detectable concentrations.

Column: Dionex IonPac AG18/AS18, 4 mm
 Eluent: 23 mM KOH
 Flow Rate: 1 mL/min
 Inj. Volume: 25 μ L
 Col. Temp.: 30 $^{\circ}$ C
 Detection: Suppressed conductivity, Dionex ASRS 300 Suppressor, recycle mode
 Sample: A. Standard
 B–E. 100-fold fracking flowback F1, F2, F5, and F10, filtered, 0.2 μ m

Peaks:
 1. Fluoride 0.5 mg/L
 2. Acetate 2.5
 3. Propionate/Formate –
 4. Formate 1.0

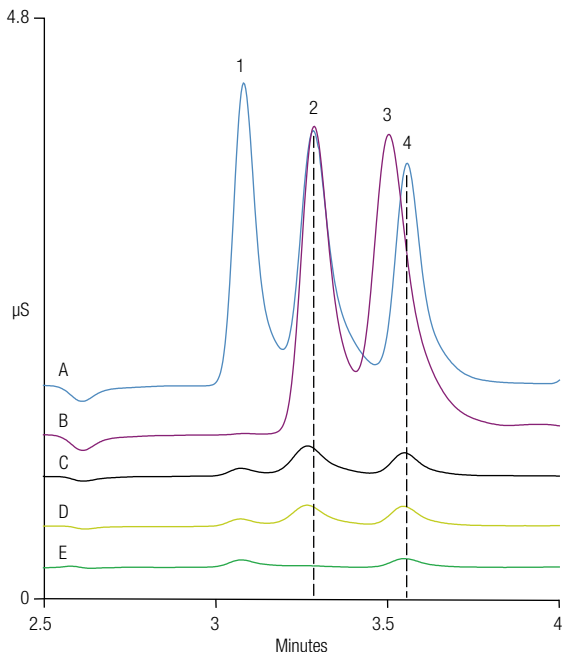


Figure 5. Comparison of early eluting inorganic anion and organic acids in fracking flowback water.

Chloride Standard Curve Determination

One concern with using concentrated samples is that the conductivity measured for an analyte will be outside of the linear quantification range. For the wastewater samples analyzed in this Technical Note, the primary analyte for which this situation might arise is chloride. To confirm that the concentrations of diluted samples were within the linear range for chloride, a standard curve was generated. As can be seen in Figure 6, the standard curve obtained was linear from 1–2000 mg/L with an r^2 of 1.00 and %RSD of 1.12. This result indicates that even a sample solution containing 200,000 mg/L of chloride, if diluted 1:100, would still fall within the range for which an accurate calculation of concentration can be obtained for this analyte.

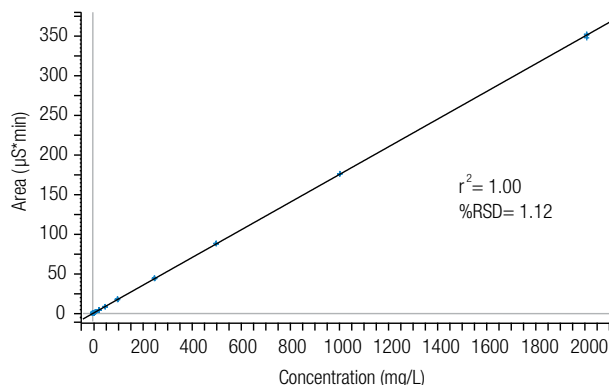


Figure 6. Chloride standard curve.

Change in Ion Concentrations During Fracking

As fracking progresses, the level of anions in flowback water changes. As can be seen in Figures 7 and 8, chloride and bromide concentrations increased ~10-fold from the first to the second fraction and then, in subsequent fractions, showed a slower, but steady increase. This result suggests that, as fracking proceeds, progressively more of these ions are dissolved into the flowback solution from the bedrock.

Conversely, the concentration of acetate decreased sharply and then remained at low levels from fraction two onwards. These elevated concentrations would increase the amount of processing required by water treatment facilities. In a similar manner, what appears to be propionate (or a mixture with formate) in the first fraction is no longer present in measureable quantities in subsequent fractions. In contrast to the other analytes quantified, the level of sulfate remained relatively constant, averaging 13 mg/L.

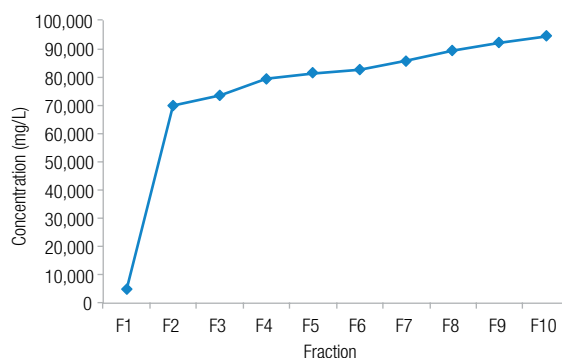


Figure 7. Concentration of chloride in fracking flowback samples.

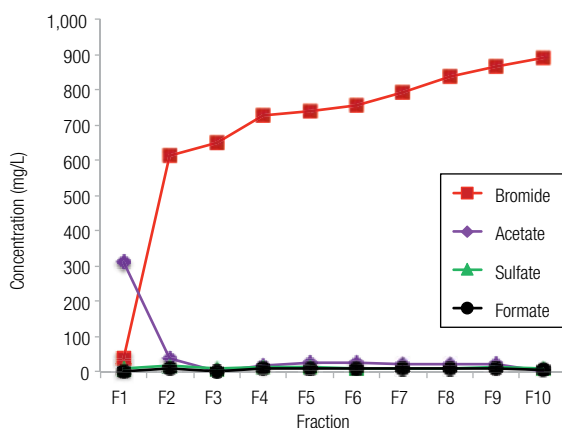


Figure 8. Concentration of inorganic anions and organic acids in fracking flowback samples.

One explanation for the apparent decrease in acetate and propionate/formate is that, at high chloride concentrations, the capacity of the column for these analytes is diminished. To investigate this possibility, acetate was added to 100-fold dilutions of fractions five and ten at a concentration 50% of that already present. As shown in Table 2, the recovery of acetate was 114 and 103%, for fractions 5 and 10, respectively. If high chloride levels had decreased the binding of acetate to the column, a lower recovery would have been expected, particularly for fraction 10, which had the highest chloride concentration. Since this was not the case, the large drop in acetate measured indicates a decrease in the amount present in fracking flowback water samples after the first fraction.

Table 2. Recovery of acetate in fracking flowback water.

Fraction	Amount Acetate Measured (µg/L)	Amount Acetate Added (µg/L)	Recovery (%)
F5	230	110	114
F10	160	80	103

Conclusion

This Technical Note demonstrates that by using the Dionex AS-AP Sample Conductivity and pH Accessory in combination with Chromeleon CDS, samples containing high levels of anions, such as fracking flowback wastewater, can be automatically diluted prior to injection if a preset conductivity maximum is exceeded. This prescreening eliminates repeat analysis, thereby reducing eluent waste, extending column life, and providing fast, accurate results.

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