Hydraulic Fracturing Flowback Water Analysis Using In-line Conductivity, Automated Dilution, and Ion Chromatography

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Overview

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

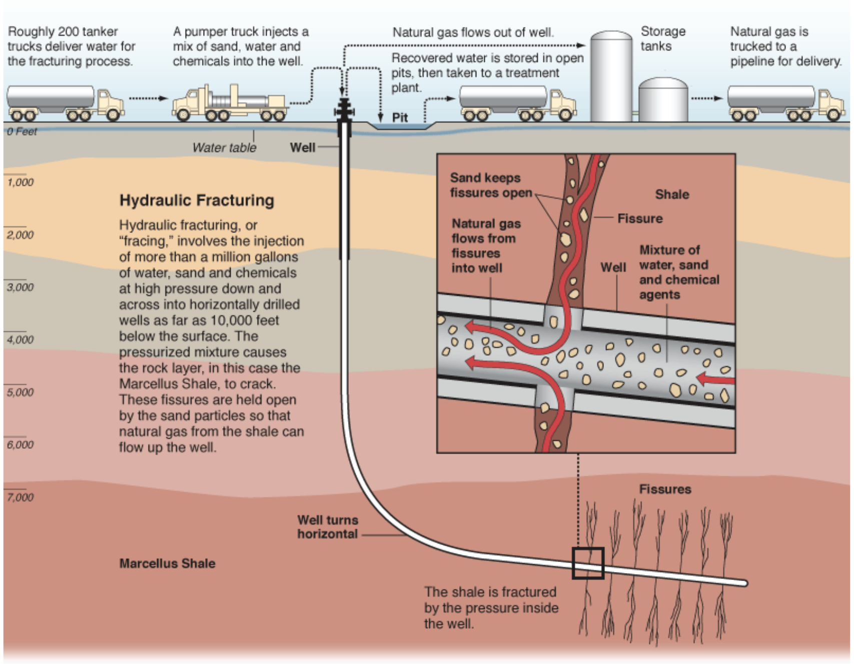
Methods: The conductivity of samples was measured in-line and, if a preset limit was exceeded, an automated dilution was performed. The diluted samples were then injected onto an ion chromatography system, the ions separated, and then quantified by comparison to standard curve values.

Results: Automated 100-fold dilutions of wastewater samples permitted accurate and consistent analyte quantification. The concentration of ions was low in the initial fraction, but most jumped approximately 10-fold afterwards and then steadily increased. Chloride, sodium, and calcium were the dominant analytes followed by strontium, magnesium, bromide, potassium, barium, and ammonium, with relatively low concentrations of organic acids, sulfate, fluoride, and lithium.

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 props 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] This process is depicted in Figure 1.

FIGURE 1. Overview of the hydraulic fracturing process.[3]



Graphic by Al Granberg

Following a fracturing event, the fracturing fluid withdrawn from the well is termed flowback and consists of the original fluid plus additional components that have been mobilized from the shale layer such as salts, metals, and radioisotopes. 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 2 and are described in greater detail in Technical Note 138.[4]

Methods

Sample Preparation

Fracking flowback wastewater from the Marcellus Shale (F1–10) were collected from successively later times during the fracking process and were filtered with 0.2 μm filters prior to analysis.

Equipment and Data Analysis

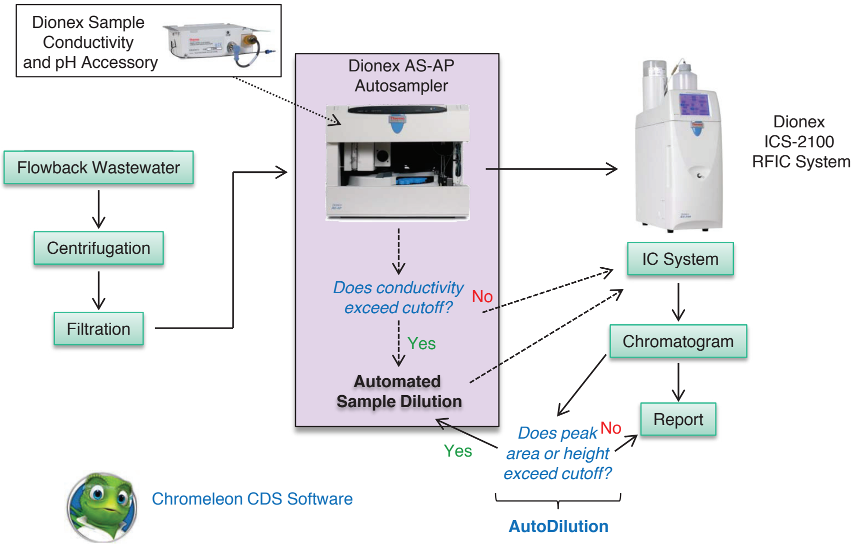
Thermo Scientific™ Dionex™ ICS-2100 Integrated Reagent-Free™ Ion Chromatography (RFIC™) system and Thermo Scientific™ Dionex™ ICS-5000$^+$ HPIC™ system
Dionex AS-AP Autosampler
Dionex AS-AP Sample Conductivity and pH Accessory
Dionex Chromeleon CDS software

Conditions

Columns: Thermo Scientific™ Dionex™ IonPac™ AG18/AS18, 4 mm i.d. columns
Dionex IonPac CG16/CS16, 0.5 mm i.d. columns
Eluent Source: Thermo Scientific Dionex EGC 500 KOH cartridge (4 mm)
Thermo Scientific Dionex EGC-MSA cartridge (capillary)
Detection: Suppressed conductivity, recycle mode
Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor
Thermo Scientific™ Dionex™ CCES 300 Cation Capillary Electrolytic Suppressor

See Technical Note 139 for additional method details.[5]

FIGURE 2. Automated sample analysis options available using the Dionex AS-AP Autosampler and Chromeleon CDS software.

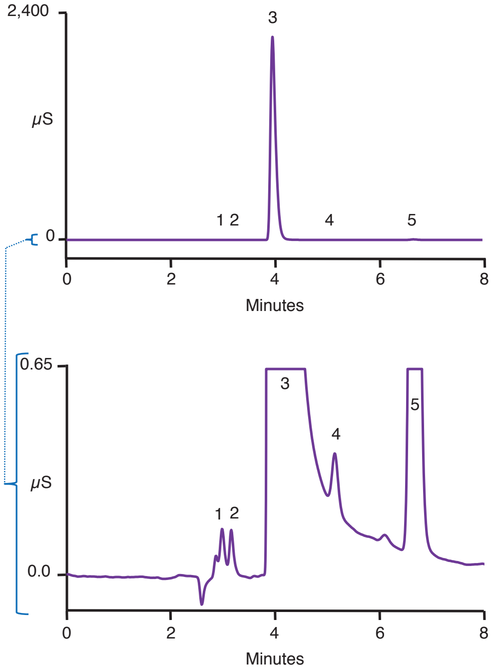


Results

In-Line Conductivity Measurement and Sample Analysis

Because fracking flowback wastewaters 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 IC column set. As exemplified by the chromatogram in Figure 3, 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 3 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.

FIGURE 3. Determination of inorganic anions and organic acids in flowback wastewater (F10).



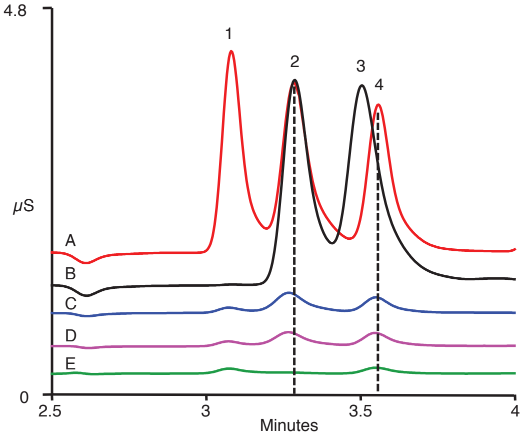
Column: Dionex IonPac AG18/AS18 column , 4 mm i.d.
Eluent Source: Thermo Scientific Dionex EGC III KOH cartridge
Eluent: 39 mM KOH
Flow Rate: 1 mL/min
Inj. Volume: 25 µL
Col. Temp.: 30 ˚C
Detection: Suppressed conductivity, Dionex ASRS 300 Anion Self-Regenerating Suppressor, recycle mode
Sample: 100-fold 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

To obtain better separation of the early eluting peaks, the eluent concentration was reduced from 39 to 23 mM KOH. As shown in Figure 4, 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 a peak appears at a slightly earlier retention time, which is predominately propionate (based on the retention time of this analyte when spiked in), but may also contain some formate. In fractions two to ten, fluoride is also present at low, but detectable concentrations.

FIGURE 4. Comparison of early eluting inorganic anions and organic acids in flowback wastewater.



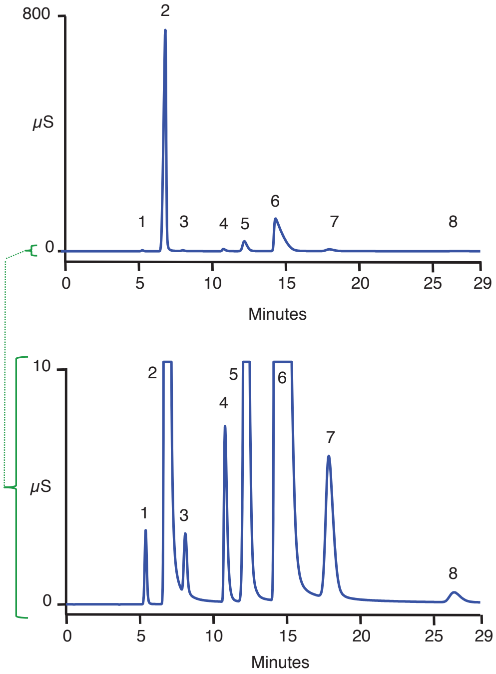
Column: Dionex IonPac AG18/AS18 column, 4 mm i.d.
Eluent: 23 mM KOH
Flow Rate: 1 mL/min
Inj. Volume: 25 µL
Col. Temp.: 30 ˚C
Detection: Suppressed conductivity, Dionex ASRS 300 Anion Self-Regenerating Suppressor, recycle mode
Sample: A. Standard
B–E. 100-fold fracking flowback F1,F2, F5, and F10, filtered, 0.2 µm

Peaks:

	A
1. Fluoride	0.5 mg/L
2. Acetate	2.5
3. Propionate/ Formate	--
4. Formate	1.0

For cation analysis samples were diluted 100-fold, in a manner similar to that described for anion analysis, and then separated on a Dionex IonPac CS16 capillary column. As can be seen in Figure 5, sodium was the predominant species at 30,000 mg/L, followed by calcium at 12,000 mg/L. Strontium and magnesium were the next most abundant, followed by potassium, barium, and lithium, in order of decreasing concentration.

FIGURE 5. Determination of cations in flowback wastewater (F4).



Column: Dionex IonPac CG16/CS16 columns, 0.5 mm i.d.
Eluent Source: Dionex EGC-MSA cartridge
Eluent: 30 mM MSA
Flow Rate: 0.01 mL/min
Inj. Volume: 0.4 μL
Col. Temp.: 40 °C
Detection: Suppressed conductivity, Dionex CCES 300 Cation Capillary Electrolytic Suppressor, recycle mode
Sample: 100-fold fracking flowback, filtered, 0.2 μm

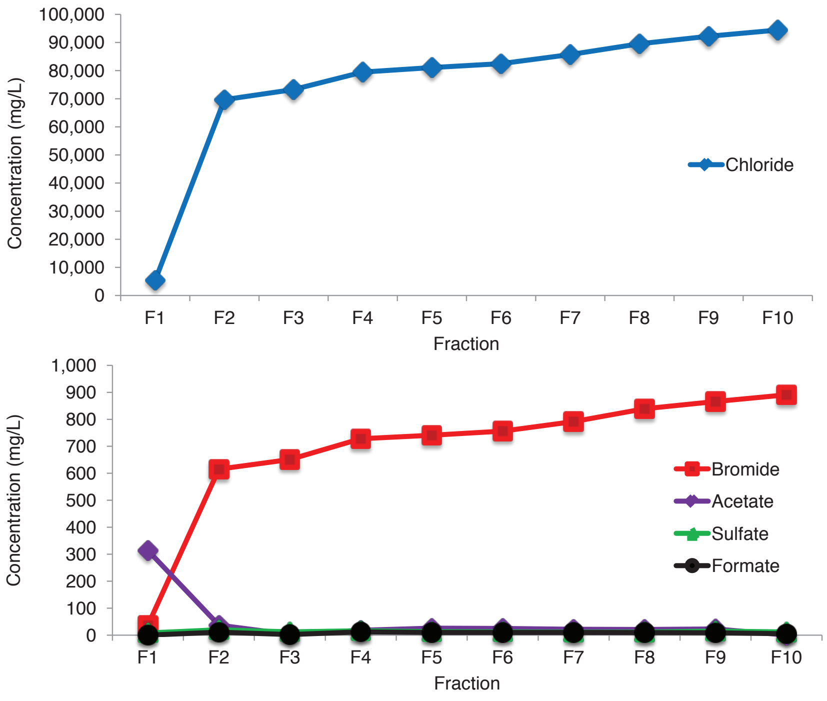
Peaks:

	Measured	Undiluted
1. Lithium	0.33 mg/L	33
2. Sodium	300.0	30,000
3. Ammonium	1.5	150
4. Potassium	5.8	580
5. Magnesium	13.0	1,300
6. Calcium	120.0	12,000
7. Strontium	14.0	1,400
8. Barium	2.2	220

Changes in the Concentrations of Ions in Flowback Wastewater

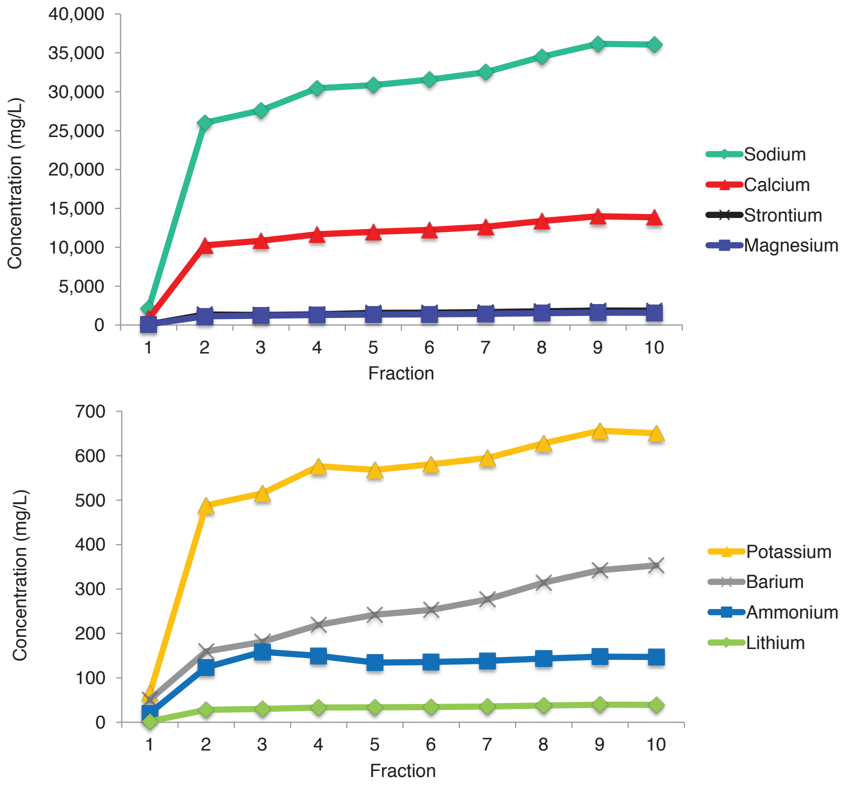
Following a fracturing event, the level of ions in the flowback water, as it returns to the surface, varies due to the variable depths at which the fracking fluid was present. In Figures 6 and 7, fractions 1 – 10 correspond to samples taken from an even distribution of aliquots of 1 – 140,000 gallons of wastewater recovered. As can be seen in Figure 6, 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.

FIGURE 6. Concentration change of anions in fracking flowback wastewater.



Cations had a similar trend in concentration increase to that of anions. As can be seen in Figure 7, sodium was the predominant species, followed by calcium. Strontium and magnesium were the next most abundant, followed by potassium, barium, ammonium, and lithium, in order of decreasing concentration.

FIGURE 7. Concentration change of cations in fracking flowback wastewater.



Conclusion

This poster demonstrates that by using the Dionex AS-AP Sample Conductivity and pH Accessory in combination with Chromeleon CDS, samples containing high levels of ions, 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.

References

1. *Water and Hydraulic Fracturing: A White Paper from the American Water Works Association;* American Water Works Association: Denver, CO, 2013. [Online] http://www.awwa.org/fracturing (accessed Feb 11, 2014).
2. Bomgardner, M. Cleaner Fracking. C&EN, 2012, 90(142), 13–16.
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4. Thermo Scientific Technical Note 138: Accurate and Precise Automated Dilution and In-line Conductivity Measurement Using the AS-AP Autosampler Prior to Analysis by Ion Chromatography, Sunnyvale, CA, 2013. [Online] http://www.dionex.com/en-us/webdocs/114807-TN138-Autosampler-IC-Automated-Dilution-TN70764_E.pdf (accessed Feb 11, 2014).
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