Determination of Cations in Hydraulic Fracturing Flowback Water from the Marcellus Shale

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Key Words

Fracking, Capillary IC, ICS-5000$^+$, IonPac CS16, Strontium, Barium, Ion Chromatography

Goal

Quantify cations in Marcellus Shale hydraulic fracturing flowback water using ion chromatography.

Introduction

Hydraulic fracturing (also known as "fracking") has been used in the U.S. to enhance the recovery of natural gas and oil for over half a century. It has experienced profound growth within the last decade due to advances in horizontal drilling technology, which have enabled it to be used to extract petroleum from shale that had previously been uneconomical.[1] Encouraged by the success of fracking in the U.S., other countries, such as China and the U.K, are considering using this technology to increase domestic production and thus decrease their reliance on foreign fuel.[2,3] Hydraulic fracturing consists of drilling a well vertically down several thousand feet to a layer of hydrocarbon-rich shale and then horizontally for up to a mile or more. Fracturing fluid is then injected under high pressure through perforations in the horizontal well casing to fracture the adjacent shale, releasing the natural gas and oil that are trapped there.[4] Hydraulic fracturing fluid is composed of liquid that is approximately 99% water with the remainder consisting of chemical additives. Sand is added to this fluid to act as a proppant to keep open the cracks that are formed, thereby facilitating the recovery of oil and gas. This recovery is assisted by additives such as friction reducers, scale inhibitors, anti-bacterial agents, gelling agents, and corrosion inhibitors.[5] Following a fracturing event, the pressure is released and the fracking fluid that returns to the surface is referred to as flowback, which is pumped into lined storage ponds prior to subsequent recycling or disposal (Figure 1).

Figure 1. A hydraulic fracturing wastewater holding pond.[4]

Hydraulic fracturing requires large quantities of water because each well may be fractured multiple times and each fracturing event can require hundreds of thousands of gallons of fluid. This large consumption puts great stress on the local water resources, particularly in arid regions, making recycling an increasingly attractive option compared to disposing of wastewater by pumping it into disposal wells.[6] As noted in Technical Note 139, flowback wastewater contains a high concentration of anions, primarily chloride, but also a considerable amount of bromide, in addition to organic acids, all of which can impact treatment or reuse.[7] If wastewater is reused, each successive fracturing event will require adjusting the blend of additives to take into account their altered performance in the presence of the increasingly higher concentration of salts and metals that have been mobilized from the shale. Cations such as calcium, barium, and strontium are especially important because they contribute to scaling problems in water pumps, pipes, etc. resulting in poor performance of recycled water for future fracturing events.[8] Knowing the composition of anions and cations in flowback wastewater can also be used to adjust the treatment plan if surface water discharge is the final goal.

The high levels of dissolved solids (salts) in wastewater can be a challenge to ion chromatography (IC) analysis because the sample can exceed the column capacity, resulting in poor chromatography and inaccurate quantification. Even if the high ion concentrations do not overload a column, the analyte of interest may exceed its linear calibration range. Dilution is the primary strategy to overcome these issues. The Thermo Scientific™ Dionex™ AS-AP Sample Conductivity and pH Accessory can measure sample conductivity and trigger automatic sample dilution. This approach is described in Technical Note 138.[9] Technical Note 139 applies this strategy to the determination of anions in fracking flowback wastewater.[7]

The low flow rate of capillary IC systems (10–30 µL/min) allows these systems to be left on and always ready for analysis. As a result, less equilibration and calibration are required, in addition to low eluent consumption and waste generation (14–43 mL/d). With the increased mass sensitivity of capillary IC systems, results comparable to those of standard bore systems can be achieved with only 0.4 µL of sample injected.

This Application Note describes the quantification of cations in hydraulic fracturing flowback water from the Marcellus Shale using the Thermo Scientific™ Dionex™ ICS-5000$^+$ Reagent-Free™ High-Pressure™ Ion Chromatography (HPIC™) system with the Thermo Scientific™ Dionex™ IonPac™ CS16 standard bore (5 mm i.d.) and capillary (0.5 mm i.d.) columns. Runs were optimized to elute all of the cations with baseline resolution within 32 min. Aliquots of flowback water taken from earlier to later recovery times showed a gradual increase in cation concentrations after an initial large increase, consistent with increased mobilization of dissolved solids when fluid was in contact with shale for longer periods of time.

Equipment

Standard Bore

- Dionex ICS-5000$^+$ Reagent-Free HPIC system* including:
  - SP Single Pump or DP Double Pump
  - EG Eluent Generator module
  - DC Detector/Chromatography module with CD Conductivity Detector
- Thermo Scientific Dionex EGC III Methanesulfonic Acid (MSA) Eluent Generator Cartridge (P/N 074535)
- Thermo Scientific Dionex CR-CTC II Continuously Regenerated Cation Trap Column (P/N 066262)
- Injection Loop, 25 µL

Capillary

- Dionex ICS-5000$^+$ Reagent-Free HPIC system* including:
  - SP Single Pump or DP Double Pump
  - EG Eluent Generator module
  - DC Detector/Chromatography module with Thermo Scientific™ Dionex™ IC Cube™ and CD Conductivity Detector
- Thermo Scientific Dionex EGC-MSA Eluent Generator Cartridge (P/N 072077)
- Dionex CR-CTC II Continuously Regenerated Cation Trap Column (P/N 072079)
- Injection Loop, 0.4 µL

*This application can be performed on any Dionex ICS system capable of eluent generation.

Autosampler and Software

- Thermo Scientific Dionex AS-AP Autosampler with a 250 µL Sample Syringe (P/N 074306) and 1200 µL Buffer Line Assembly (P/N 074989)
- Vial Kit, 10 mL, Polystyrene with Caps and Blue Septa (P/N 074228)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2

Reagents and Standards

- Deionized (DI) water, Type I reagent grade, 18 M -cm resistance or better
- Ultra Scientific (North Kingstown, RI) standards
  - 1000 mg/L Lithium P/N ICC-104
  - 1000 mg/L Sodium P/N ICC-107
  - 1000 mg/L Ammonium P/N ICC-101
  - 1000 mg/L Potassium P/N ICC-106
  - 1000 mg/L Magnesium P/N ICC-105
  - 1000 mg/L Calcium P/N ICC-103
- Strontium Chloride Hexahydrate, ACS Grade (Sigma-Aldrich P/N 255521)
- Barium Chloride Dihydrate, ACS Grade (Mallinckrodt P/N 3756)

Samples

Fracking flowback water fractions from the Marcellus Shale (F1–F10).

Conditions

Standard Bore

Columns:	Dionex IonPac CG16 Guard, 5 × 50 mm (P/N 057574) Dionex IonPac CS16 Separation, 5 × 250 mm (P/N 079805)
Eluent Source:	Dionex EGC III MSA cartridge (P/N 074535)
Gradient:	20–30 mM MSA (0–10 min), 30–55 mM MSA (10–18 min), 55 mM MSA (18–32 min), 20 mM MSA (32–38 min)
Flow Rate:	1 mL/min
Column Temp.:	40 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CERS™ 500 Cation Electrolytic Suppressor (P/N 082542), recycle mode, 161 mA
Background Conductance:	< 0.2 µS
Noise:	< 1 nS
System Backpressure:	2150 psi

Capillary

Columns:	Dionex IonPac CG16 Guard, 0.5 × 50 mm (P/N 075402) Dionex IonPac CS16 Separation, 0.5 × 250 mm (P/N 075401)
Eluent Source:	Dionex EGC-MSA cartridge (P/N 072077)
Gradient:	20 mM MSA (0–10 min), 20–55 mM MSA (10–18 min), 55 mM MSA (18–34 min), 20 mM MSA (34–40 min)
Flow Rate:	0.01 mL/min
Column Temp.:	40 °C
Inj. Volume:	0.4 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CCES™ 300 Cation Capillary Electrolytic Suppressor (P/N 072053), recycle mode, 11 mA
Background Conductance:	< 0.3 µS
Noise:	< 1 nS
System Backpressure:	1100 psi

Preparation of Standards

Strontium Stock Solution, 1000 mg/L

Accurately weigh 0.3043 g of strontium chloride hexahydrate, transfer solid to 100 mL volumetric flask, and fill to the mark with DI water.

Barium Stock Solution, 1000 mg/L

Accurately weigh 0.1779 g of barium chloride dihydrate, transfer solid to 100 mL volumetric flask, and fill to the mark with DI water.

Working Standard Solutions

Prepare working standard solutions for the low and high range concentrations by diluting the 1000 mg/L stock solutions with DI water to the highest concentration used for each set and then diluting as appropriate to obtain the concentrations indicated below. Store standard solutions at 4 °C when not in use.

Low concentration range:

	Concentration (mg/L)						
Ammonium	0.025	0.05	0.1	0.25	0.5	1.0	2.5
Barium	0.25	0.5	1.0	2.5	5.0	10	25
Lithium	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Potassium	0.05	0.1	0.2	0.5	1.0	2.0	5.0
Strontium	0.25	0.5	1.0	2.5	5.0	10	25

High concentration range:

	Concentration (mg/L)						
Calcium	2	4	10	25	50	100	200
Magnesium	1	2	5	12.5	25	50	100
Sodium	5	10	25	62.5	125	250	500

Sample Preparation

Samples were centrifuged at 10,000 × g, for 10 min to pellet particulates. The resultant supernatant was filtered with a 0.2 µm polyethersulfone (PES) syringe filter. Samples were then diluted 100-fold with 18 M -cm resistivity degassed DI water. While the data presented here were from samples diluted manually, this process can be automated using the Dionex AS-AP Autosampler as described in Technical Note 138.[9]

It is important to use 18 M -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 practice.

Results and Discussion

Method Optimization

Initial runs produced baseline separation of all standards using isocratic conditions (Figures 2 and 3), but in order to shorten run times, a gradient method was developed. In flowback water, sodium is typically present at ~200-fold higher concentration than ammonium, which is the next eluting cation. The large sodium peak shoulder that can result was more pronounced with the capillary system due to slight differences in sweep-out efficiencies and the larger relative sample volume injected compared to the standard bore system. To enhance the separation of the early eluting peaks and reduce the impact of the large sodium peak shoulder on quantification when using this system, MSA was held constant at 20 mM over the first 10 min. With the standard bore system, adequate separation was achieved using a gradient from 20 mM to 30 mM MSA over this same period, resulting in a 2 min reduction in run time. The concentration was then increased to 55 mM and maintained at this level until barium (the most tightly bound cation) eluted, which was within 35 min. Using an isocratic condition of 30 mM MSA, a considerably longer run time of approximately 60 minutes was required to elute barium (upper chromatograms in Figures 2 and 3). All of the peaks from the gradient runs showed baseline resolution (R_s > 1.5) with the lowest being for calcium at 3.0 (standard bore) and 4.5 (capillary).

Column:	Dionex IonPac CG16/CS16 columns, 5 mm i.d.
Eluent Source:	Dionex EGC III MSA cartridge
Eluent (A):	30 mM MSA
Gradient (B):	20–30 mM MSA (0–10 min) 30–55 mM MSA (10–18 min) 55 mM MSA (18–32 min) 20 mM MSA (32–38 min)
Flow Rate:	1 mL/min
Inj. Volume:	25 µL
Col. Temp.:	40 °C
Detection:	Suppressed conductivity, Dionex CERS 500 Suppressor, recycle mode
Sample:	Mix of standards

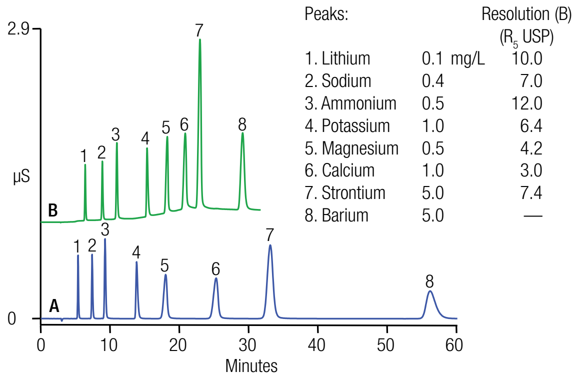

Figure 2. Separation of cations using isocratic and gradient methods with a standard bore column.

Column:	Dionex IonPac CG16/CS16 columns, 0.5 mm i.d.
Eluent Source:	Dionex EGC-MSA (capillary) cartridge
Eluent (A):	30 mM MSA
Gradient (B):	20 mM MSA (0–10 min) 20–55 mM MSA (10–18 min) 55 mM MSA (18–34 min) 20 mM MSA (34–40 min)
Flow Rate:	0.01 mL/min
Inj. Volume:	0.4 µL
Col. Temp.:	40 °C
Detection:	Suppressed conductivity, Dionex CCES 300 Suppressor, recycle mode
Sample:	Mix of standards

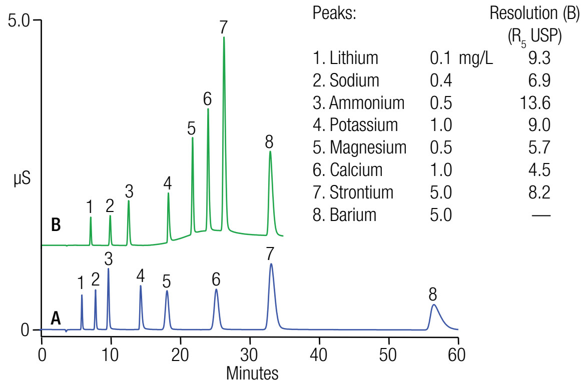

Figure 3. Separation of cations using isocratic and gradient methods with a capillary column.

The linearity of the method was determined using triplicate injections of calibration standards at seven concentrations (Table 1). Plotting peak area versus concentration demonstrated a linear relationship between concentration and peak area for the concentration ranges used with coefficient of determinations (r^2) that ranged from 1.000 to 0.9997 (Table 1). The exception was ammonium, which exhibited a quadratic fit relationship to concentration.

Table 1. Cation calibration results.

		Coefficient of Determination (r^2)*	
	Concentration (mg/L)	Standard Bore	Capillary
Lithium	0.005–0.5	0.9997	0.9998
Sodium	2.5–500	1.000	0.9999
Ammonium	0.025–2.5	1.000	0.9998
Potassium	0.05–10	0.9998	0.9999
Magnesium	0.5–100	1.000	1.000
Calcium	1.0–200	1.000	1.000
Strontium	0.25–25	1.000	0.9999
Barium	0.25–25	0.9999	1.000

*Linear fit, except for ammonium, which was quadratic.

Determination of Cation Concentrations in Fracking Flowback Water

Based on the results of anion analysis, it was known that fracking flowback water contains high ion concentrations.[7] To prevent column overloading and ensure that the analyte concentrations were in their linear range, samples were diluted 100-fold prior to injection onto the Dionex IonPac CS16 column.

The predominant cation present in the flowback water fractions was sodium (33,000 mg/L), while calcium was the second most abundant at just under one third that concentration (13,000 mg/L) (Figure 4). These were followed in concentration by magnesium, strontium, and potassium. The lower portion of Figure 4 displays a zoomed in view of the chromatogram in the upper portion, which shows that the concentrations of barium, ammonium, and lithium are less than 250 mg/L.

A capillary IC system uses considerably less water and, consequently, generates much less waste, while obtaining data using a 0.4 µL injection of sample. As shown in Figure 5, values comparable to those obtained with a standard bore column were obtained using a 0.5 mm i.d. column.

Table 2 compares the concentrations determined using standard bore versus capillary configurations as a percentage, with 100% being complete agreement. As can be seen, the values obtained were in good agreement at between 92 and 109% of each other, with the all but 5 being within 5%.

Column: Dionex IonPac CG16/CS16 columns, 5 mm i.d.
Eluent Source: Dionex EGC III MSA cartridge
Gradient: 20–30 mM MSA (0–10 min)
30–55 mM MSA (10–18 min)
55 mM MSA (18–32 min)
20 mM MSA (32–38 min)
Flow Rate: 1 mL/min
Inj. Volume: 25 µL
Col. Temp.: 40 °C
Detection: Suppressed conductivity, Dionex CERS 500 Suppressor, recycle mode
Sample: 100-fold diluted flowback water, filtered, 0.2 µm

Peaks:	Measured	Undiluted
1. Lithium	0.33 mg/L	33 mg/L
2. Sodium	330.0	33,000
3. Ammonium	1.8	180
4. Potassium	5.9	590
5. Magnesium	13.0	1,300
6. Calcium	130.0	13,000
7. Strontium	14.0	1,400
8. Barium	2.1	210

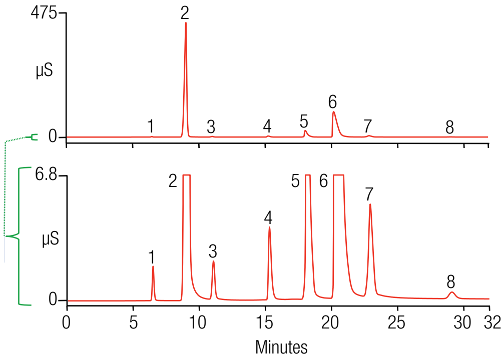

Figure 4. Determination of cations in fracking flowback water (F4) using a standard bore column.

Column: Dionex IonPac CG16/CS16 columns, 0.5 mm i.d.
Eluent Source: Dionex EGC-MSA (capillary) cartridge
Gradient: 20 mM MSA (0–10 min)
20–55 mM MSA (10–18 min)
55 mM MSA (18–34 min)
20 mM MSA (34–40 min)
Flow Rate: 0.01 mL/min
Inj. Volume: 0.4 µL
Col. Temp.: 40 °C
Detection: Suppressed conductivity, Dionex CCES 300 Suppressor, recycle mode
Sample: 100-fold diluted flowback water, filtered, 0.2 µm

Peaks:	Measured	Undiluted
1. Lithium	0.35 mg/L	35 mg/L
2. Sodium	320.0	32,000
3. Ammonium	1.8	180
4. Potassium	6.1	610
5. Magnesium	13.0	1,300
6. Calcium	130.0	13,000
7. Strontium	14.0	1,400
8. Barium	1.9	190

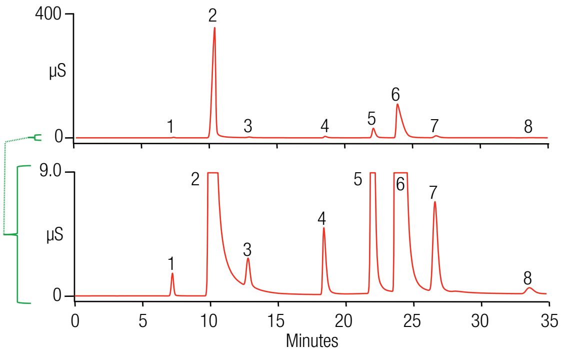

Figure 5. Determination of cations in fracking flowback water (F4) using a capillary column.

Table 2. Concordance of cation concentrations determined using capillary and standard bore IC systems.

	% Concordance of Capillary vs Standard Bore IC Concentrations[a]							
Fraction	**Lithium**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**	**Strontium**	**Barium**
1	92	99	104	98	103	97	102	109
2	99	99	101	99	97	96	97	106
3	98	98	102	98	98	96	97	104
4	99	98	102	98	97	96	94	103
5	100	99	104	99	99	97	98	104
6	101	100	104	100	100	98	99	105
7	101	100	106	100	100	98	99	105
8	101	101	105	101	100	98	97	105
9	101	100	105	100	100	98	99	104
10	100	100	103	99	99	97	98	103

[a] (Capillary IC concentration/Standard bore IC concentration) × 100

Change in Cation Concentration with Volume of Fracking Flowback Water Recovered

As increasing amounts of flowback wastewater are returned to the surface, the level of ions changes. As shown in Figure 6, the concentration of the majority of cations increased approximately 10-fold from the first to the second fraction and then, in subsequent fractions, showed a slower, but steady increase. While most showed a gradual increase, barium had a more dramatic change, more than doubling (from 160 mg/L (F2) to 360 mg/L (F10)).

The observed increase in ionic content suggests that the longer fracking fluid is in contact with the shale layer, the more salt that is mobilized into the flowback water. If this wastewater is to be reused for additional fracturing events, knowledge of the ions present can be used to optimize the fracking fluid mixture. For example, the propensity of cations, such as calcium, strontium, and barium to form scale would gradually occlude the cracks that are formed or build up in pipes used to process fracking fluids reducing the efficiency of oil or gas recovery. To minimize scale formation, the amount of anti-scaling additive used would need to be increased and/or additional dilution with fresh water would be required.

Conclusion

This Application Note demonstrates that after diluting hydraulic fracturing flowback water, the concentration of cations can be accurately determined using the Dionex ICS-5000$^+$ HPIC system with a capillary or standard bore Dionex IonPac CS16 column. The chromatographic conditions were optimized so that all the cations analyzed eluted with baseline resolution within 32 min. The most abundant analyte was sodium, followed by calcium, strontium, magnesium, potassium, barium, ammonium, and lithium. Wastewater from progressively later recovery volumes showed a gradual increase in cation concentrations indicative of more extensive association with the shale layer that was targeted for hydrocarbon extraction.

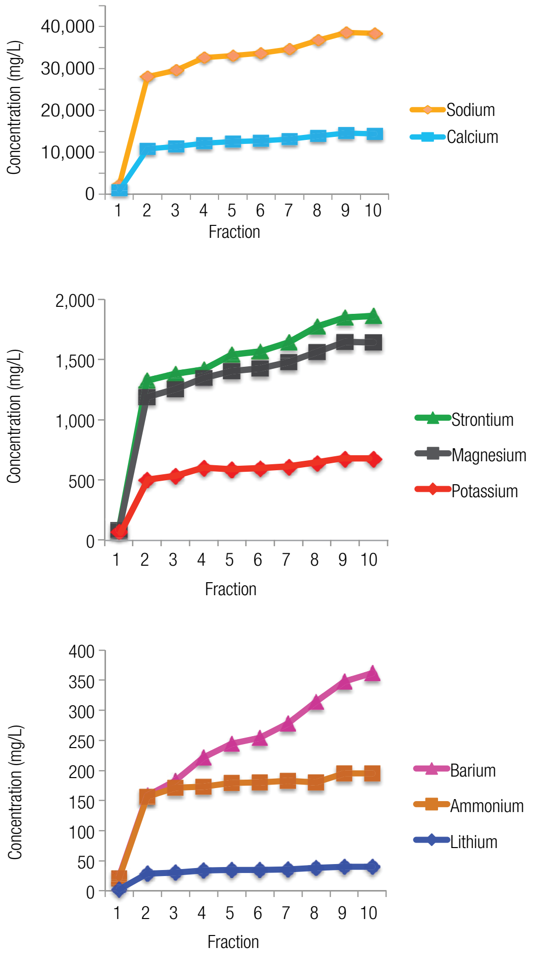

Figure 6. Cation concentrations of fracking flowback water fractions.

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