White Paper 70784

Bromide Analysis for Hydraulic Fracturing

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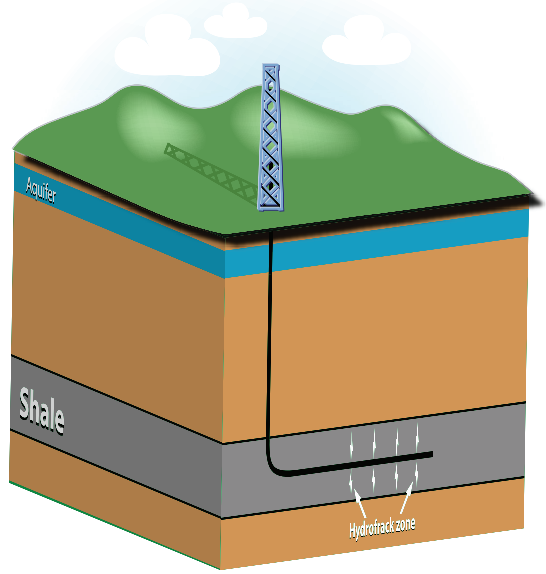
Executive Summary
During the hydraulic fracturing process, salts (anions and cations), metals, and radio isotopes within the shale layers are dissolved and mobilized to the surface as flowback water. Bromide (Br^-) along with Strontium (Sr^{2+}), and Barium (Ba^{2+}) are signatures for flowback waters. Of these, bromide is of particular concern as it can lead to increased formation of brominated disinfection byproducts during drinking water disinfection.

Keywords
Marcellus Shale, Reagent-Free Ion Chromatography, EPA Method 300.1, Flowback Water



Increased Bromide Levels as a Result of Hydraulic Fracturing
Hydraulic fracturing, also known as fracking, is a process that extracts natural gas and oil from underground rock formations by injecting a solution consisting of water mixed with a sand or ceramic proppant and chemicals before injection into a well at high pressure (480 to 850 bar) to open existing fractures or initiate new fractures. The proppant props open fractures in the shale, allowing gas that has been trapped to flow out. The chemical mixtures vary depending on the subsurface environment. During the fracking process salts (anions and cations), metals, and radioisotopes within the shale layers are dissolved and mobilized to the surface in flowback water. Though present and readily detected in Marcellus Shale flowback waters, Na^+, Ca^{2+}, and Cl^- can originate from many sources. However, bromide (Br^-) along with strontium, (Sr^{2+}) and barium (Ba^{2+}) are signatures for flowback waters. Of these, Br^- is of particular concern since it can lead to increased formation of brominated disinfection by products during drinking water disinfection.[1] Brominated flowback waters can impact source drinking water sources if improperly discharged, if spilled during fracking and transport, seepage from storage tanks, and natural migration of brines to shallow aquifers. Increased brominated Disinfection By-Products (DBPs) at drinking water utilities along the Allegheny River have been linked to increased bromide discharged from waste treatment plants receiving flowback wastes. Because most treatment plants are not designed to handle increased brines, new alternatives to wastewater management have been implemented which include reuse and deep well injection.

Monitoring of Bromide in Surface, Ground-, and Flowback Waters

Though there are trends to preventing and minimizing flowback water discharges, long term monitoring of bromide will continue to be important to preserve the integrity of source drinking water. Additional liquid known as produced water — a mix of fracking fluid and groundwater — comes up with the gas for most of the life of the fractured shale well. Although the releases of produced water are at lower flow rate, the solutions are hypersaline and require disposal. Additionally, it may not always be economical to transport wastewater to deep well injection sites.

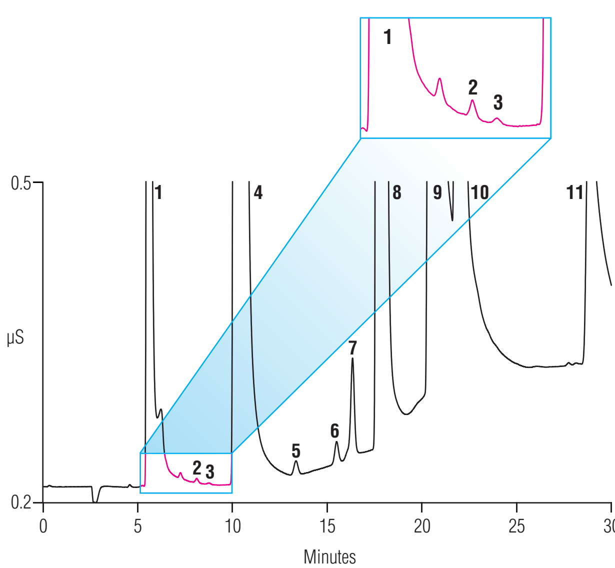
EPA methods to monitor bromide using IC with suppressed conductivity detection are well established. EPA Method 300.1 is a direct injection technique which measures bromide along with common anions. In addition, this method can be used to monitor bromate, which forms from the ozonation of bromide. A more recent and improved method is EPA Method 302, which uses Two-Dimensional Ion Chromatography (2D-IC) for bromate detection and suppressed conductivity detection. Though designed specifically for ease-of-use, 2D-IC has other advantages; it does not produce toxic colorimetric reagents, works in high salts samples, allows the use of Reagent-Free™ Ion Chromatography (RFIC™), achieves greater sensitivity for bromate, and can be easily modified by using only the first channel if only bromide analysis is required.[2]

It is important to note that bromide is not toxic and therefore not regulated. It is none the less crucial for drinking water operators to know the seasonal bromide fluctuations from their source waters. The same instrumentation used for anions and bromate can be used for this purpose. This allows for a more cost efficient operation of drinking water treatment. EPA methods allow for the use of hydroxide or carbonate eluents and an RFIC system.

An RFIC system provides:

- ***Improved Sensitivity***: Hydroxide eluents are reduced to water, which have a lower background than suppressed carbonate eluent.
- ***Ease-of-Use***: Electrolytic suppression does not require the addition of sulfuric acid thereby reducing disposal costs.
- ***Simplicity***: The user only needs to add deionized water when using electrolytic eluent generation.

An RFIC system and 2D-IC are only available by using Thermo Scientific Dionex IC technology.

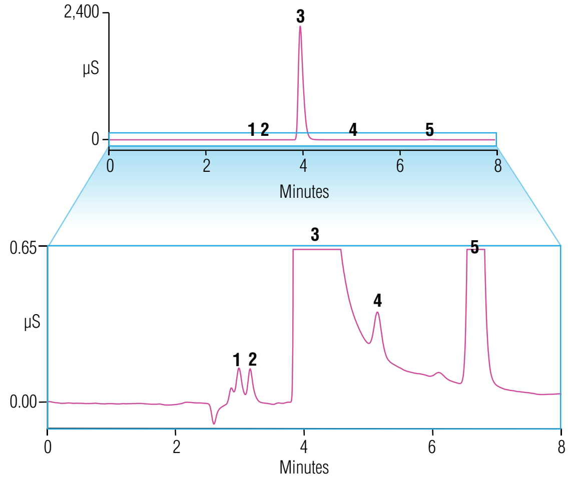


Column: Thermo Scientific™ Dionex™ IonPac™ AG19/AS19 column, 4 mm
Eluent: 10 mM KOH (0–10 min), 10–45 mM (10–25 min), 45 mM (25–30 min)
Eluent Source: Thermo Scientific Dionex EGC-KOH cartridge with Thermo Scientific Dionex CR-ATC Continuosly Regenerating Anion Trap Column
Temperature: 30 °C
Flow Rate: 1.0 mL/min
Inj. Volume: 250 µL
Detection: Thermo Scientific™ Dionex™ ASRS™ ULTRA II, Anion Self-Regenerating Suppressor, recycle mode

Peaks:

1. Fluoride		7. Bromide	
2. Chlorite	1.0 µg/L	8. Nitrate	
3. Bromate	0.5	9. Carbonate	
4. Chloride		10. Sulfate	
5. Nitrite		11. Phosphate	
6. Chlorate	1.0		

Figure 1. Simultaneous monitoring of bromide, common anions and DBP's chlorite, bromate, and chlorate using an RFIC system and suppressed conductivity detection.



Column:	Dionex IonPac AG18/AS18 columns, 4 mm
Eluent:	39 mM KOH
Eluent Source:	Dionex EGC III KOH cartridge
Flow Rate:	1.0 mL/min
Inj. Volume:	25 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS 300 Suppressor, recycle mode
Sample:	100-fold dilution of fracking flowback, filtered, 0.2 µm

Peaks:

	Total
1. Acetate	< 5 mg/L
2. Formate	< 5
3. Chloride	94,000
4. Sulfate	12
5. Bromide	890

Figure 2. Anion analysis of hydraulic fracturing flowback water from the Marcellus Shale. Note the high bromide and very high chloride levels common for flowback waters from the Marcellus Shale.

References

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2. http://www.dionex.com/en-us/webdocs/62038-Bro-IC-Bromate-Drinking-Water-11Sep2012-BR70261_E.pdf
3. Thermo Scientific. Technical Note TN 139, *Determination of Anions in Fracking Flowback Water From the Marcellus Shale Using Automated Dilution and Ion Chromatography*, Thermo Scientific TN70773_E, Sunnyvale, CA, 2013.

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