The Importance of Anion and Organic Acid Determinations in Fracking Wastewater by Ion Chromatography

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Executive Summary

Hydraulic Fracturing is a process that extracts natural gas and oil from underground rock formations. There are environmental concerns that hydraulic fracturing may affect groundwater and wastewater causing contamination of drinking water sources. Ion Chromatography is a viable technique to monitor anions and organic acids that are found in fracking flowback waters. These analytes can 1) alter the viscosity of the fracturing water -affecting the hydraulic fracturing process and 2) harm the quality of ground and surface waters–potential sources for drinking water.

Keywords

Fracking, Hydraulic Fracturing, Flowback, Anions, Organic Acids, Wastewater, Ion Chromatography

What is Hydraulic Fracturing?

Hard-to-reach natural gas and oil from deep underground rocks can be extracted through a process called hydraulic fracturing, or fracking. In the process of fracking, a wellbore is drilled into reservoir rock formations, as shown in Figure 1.

Fracking utilizes many chemicals containing hazardous compounds and millions of gallons of water under pressure to extract the natural gas or oil.

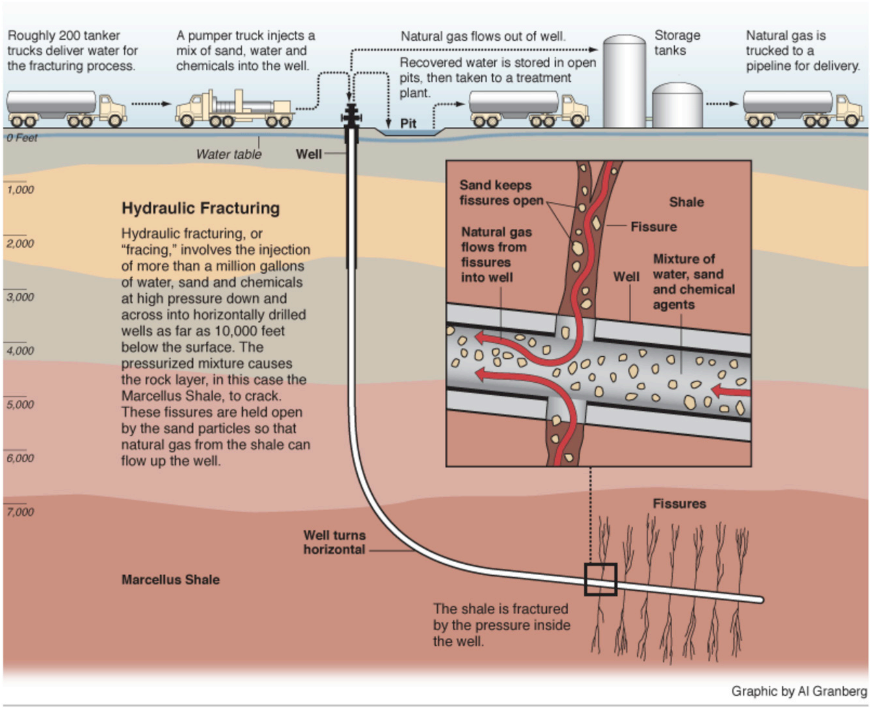

Figure 1: The process of hydraulic fracturing.[2]

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What Concerns Have Been Expressed About Hydraulic Fracturing?

There are concerns that hydraulic fracturing may compromise groundwater and wastewater, eventually leading to the contamination of drinking water sources. For example, flowback water is the main source of wastewater from gas drilling. Flowback water is a carrier of contaminants that are subject to discharge or storage regulations. Fracturing fluid has been excluded from the EPA's jurisdiction due to its exemption by the U.S. Congress in the Safe Drinking Water Act of 2005. However in June 2011, the EPA decided to examine claims of water pollution related to hydraulic fracturing in several U.S. states including Pennsylvania, Texas, and California. These regulations will require companies to disclose the details around their fracking process including chemicals used, pumped water amounts, and drilling locations.

In addition, flowback water mobilizes compounds from the subsurface environment, such as anions, cations, metals, and radioisotopes that can also negatively impact surface waters. Significant concentrations of chloride and bromide can be found in wastewaters due to the process of hydraulic fracturing. Elevated or fluctuating chloride, heavy metals, phosphates, and other chemicals present in sediment can directly damage aquatic ecosystems. Treatment of waste high in chloride is expensive because the chloride is not easily removed by chemical or biological processes; finally, high chloride concentrations may also increase costs for downstream water users (e.g., industrial or drinking water facilities, see below).

Though desalination removes most total dissolved solids (TDS), increased concentrations of chloride and bromide have been detected in wastewater discharges known to have received hydraulic fracturing waters. Rising concentrations of chloride and bromide are a concern to drinking water utilities since these compounds can form toxic disinfection-by-products (DBP's) during water treatment. During the drinking water process, chlorination is used to disinfect water to kill bacteria, viruses, and other potentially harmful parasites. In this process, chloride and bromide react with naturally occurring organic matter leading to the formation of a wide variety of DBP's including trihalomethanes and haloacetic acids. If ozonation is used, chloride and bromide react with ozone to produce chlorite and bromate. Both chlorite and bromate are carcinogenic and may lead to reproductive and developmental abnormalities. As a result, the National Primary Drinking Water Regulations has set maximum contaminant levels (MCLs) for both bromate and chlorite.

EPA 300.1 Determination of inorganic anions in drinking water by ion chromatography is a well established method used for ground-, surface and drinking water. This method is ideal for pre- and post-hydraulic fracturing analysis as well. The Thermo Scientific™ Dionex™ ICS-5000+, Dionex ICS-2100, Dionex ICS-1600, and Dionex ICS-1100 systems are recommended for such environmental related work. Figure 2 illustrates the separation of bromide and chloride in a fracking flowback sample using the Thermo Scientific™ Dionex™ IonPac™ AS18 column on the Dionex ICS-2100. Another anion of importance is sulfate, which is regulated as a secondary contaminant. The reduction of sulfate to hydrogen sulfide affects the aesthetic character of water by creating an unpleasant odor. The separation of sulfate is also shown in Figure 2. In addition to inorganic anions, the organic acids formate and acetate are also commonly found in fracking process waters. These organic acids are added to control pH, but are also ideal sources of carbon for bacterial growth. Acetate and formate from a flowback sample is shown in Figure 3. Bacterial growth in fracking waters can result in the production of hydrogen sulfide which is very toxic and causes increased odor and corrosion issues.

Column:	Dionex IonPac AG18/AS18, 4 × 250 mm
Eluent:	39 mM KOH
Eluent Source:	Thermo Scientific Dionex EGC III KOH cartridge
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 um

Peaks:		Total	
	1. Unknown	--	mg/L
	2. Unknown	--	
	3. Chloride	94000	
	4. Sulfate	12	
	5. Bromide	890	

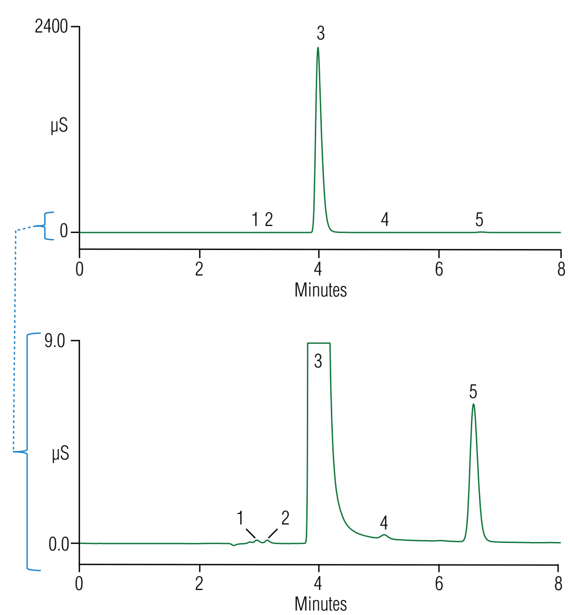

Figure 2. Fracking flowback sample analyzed using the Dionex IonPac AS18 column.

Column: Dionex IonPac AG18/AS18, 4 × 250 mm
Eluent: 23 mM KOH
Eluent Source: Thermo Scientific Dionex EGC III KOH cartridge
Flow Rate: 1 mL/min
Inj. Volume: 25 µL
Col. Temp.: 30 °C
IC Cube Temp.: 15 °C
Detection: Suppressed conductivity, Dionex ASRS 300, Anion Self-Regenerating Suppressor, recycle mode
Sample: **A**. Standard
B. 100-fold diluted fracking water, filtered, 0.2 um

Peaks:	Total	Total	
1. Fluoride	0.5	--	mg/L
2. Acetate	2.5	310	
3. Formate	1.0	150	
4. Chlorite	5.0	--	
5. Chloride	3.0	4000	

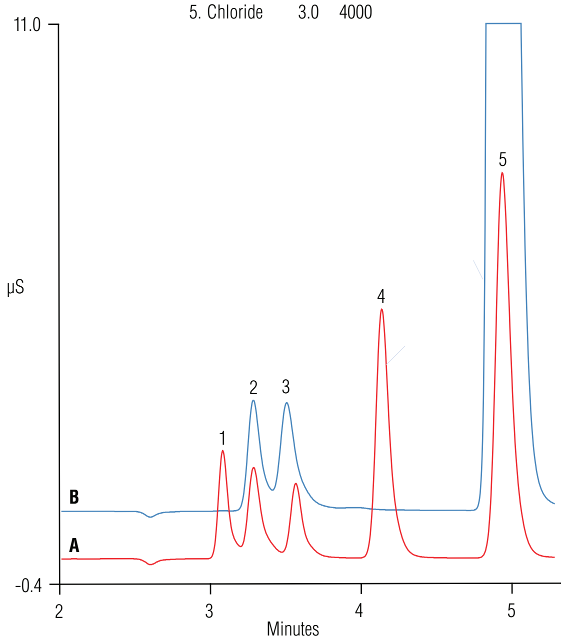

Figure 3. Fracking flowback sample analyzed using a Dionex IonPac AG18/AS18 column set.

In certain instances, longer chain organic acids can result from bacterial growth in flowback and produced waters without the generation of hydrogen sulfide, such as in waters with lower sulfate concentrations. The longer chain organic acids lower the pH and cause corrosion and the bacterial growth itself may block the shale cracks and inhibit gas flow. The analysis of longer chain organic acids in a high salt sample is shown in Figure 4. In order to avoid interference from the high chloride peak, ion exclusion chromatography using the Dionex IonPac ICE-AS6 column is used.

Column: Thermo Scientific™ Dionex™ IonPac™ ICE-AS6
Eluent: 1.0-mM heptafluorobutyric acid
Flow Rate: 1.0 mL/min
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ AMMS™ ICE Anion MicroMembrane™ Suppressor
Sample: 0.5% sodium chloride, 50 µL

Peaks:	Total	
1. Tartaric	1.0	mg/L (ppm)
2. Citric	0.5	
3. Malic	1.0	
4. Glycolic	1.0	
5. Lactic	1.0	
6. Acetic	1.0	
7. Succinic	1.0	

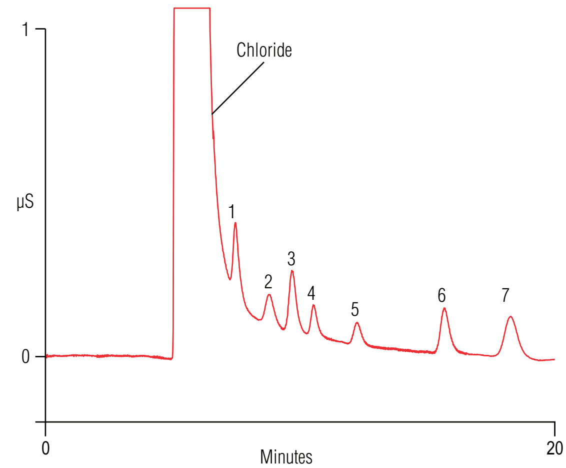

Figure 4. Separation of long chain organic acids using ion exclusion chromatography.

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