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Hydraulic fracturing wastewater analysis

Reagent-Free Ion Chromatography

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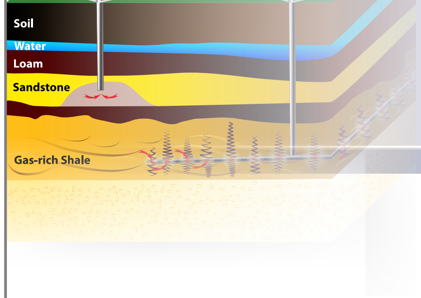

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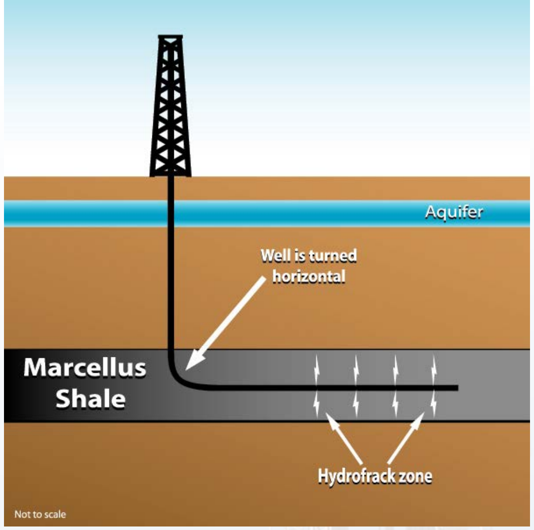
What is Hydraulic Fracturing?



Hard-to-reach natural gas and oil from deep underground deposits can be extracted through a process called hydraulic fracturing, or fracking. This process extracts natural gas and oil by drilling a well into bedrock (primarily shale) and then injecting fluid under high pressure causing cracks to form, thereby releasing trapped hydrocarbons that can then be captured. Fracking fluid contains approximately 85% water and 13% sand (proppant), the latter to prop open cracks, which facilitates the flow of oil and gas. The remainder consists of chemical additives such as friction reducers, anti-bacterial agents, and corrosion inhibitors.

There are two types of hydraulic fracturing wastewater: flowback and produced. Flowback water refers to fluid that returns to the surface upon completion of hydraulic fracturing. Produced water refers to the fluid that returns to the surface once the well starts producing natural gas and oil. Flowback is primarily composed of chemicals originally found in the fracking fluid, while produced water consists of the liquid that was resident in the shale layer. Both types of water mobilize compounds from the subsurface environment including anions, cations, metals, and radioisotopes that can be up to 20X the concentration of seawater. There are concerns that, if not properly handled, wastewater produced by hydraulic fracturing may compromise ground and surface waters, eventually leading to the contamination of drinking water sources. Many of the compounds present in this water 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. State level regulations that could be put in place would require companies to disclose the details of their fracking process including chemicals used, pumped water amounts, and drilling locations.

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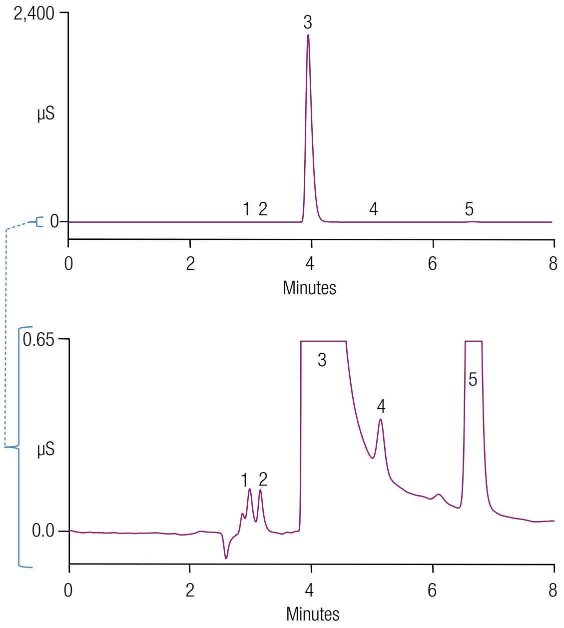
Anion Determinations by Ion Chromatography

Fracking flowback water can mobilize anions from the subsurface environment that could have a negative impact on surface waters if it was to leak from holding facilities or is not properly treated. Significant concentrations of chloride and bromide can be found in wastewaters, which are a concern to drinking water utilities since the former can interfere with treatment, while the latter can form toxic disinfection-by-products (DBPs) during water treatment. During the drinking water purification process, chlorination is used to disinfect water to kill bacteria, viruses, and other potentially harmful organisms. In this process, chloride and bromide react with naturally occurring organic matter to form a wide variety of DBPs including trihalomethanes and haloacetic acids. If ozonation is used, chloride and bromide react with ozone to produce chlorite and bromate which 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 Method 300.1 uses IC with suppressed conductivity for the determination of inorganic DBPs including bromate and chlorite. EPA Method 302 uses Two Dimensional Ion Chromatography (2D-IC) and suppressed conductivity specifically for bromate detection. 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.



Determination of inorganic anions and organic acids in fracking flowback.

Columns:	Thermo Scientific™ Dionex™ IonPac™ Dionex IonPac AG18/AS18, 4 mm
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 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

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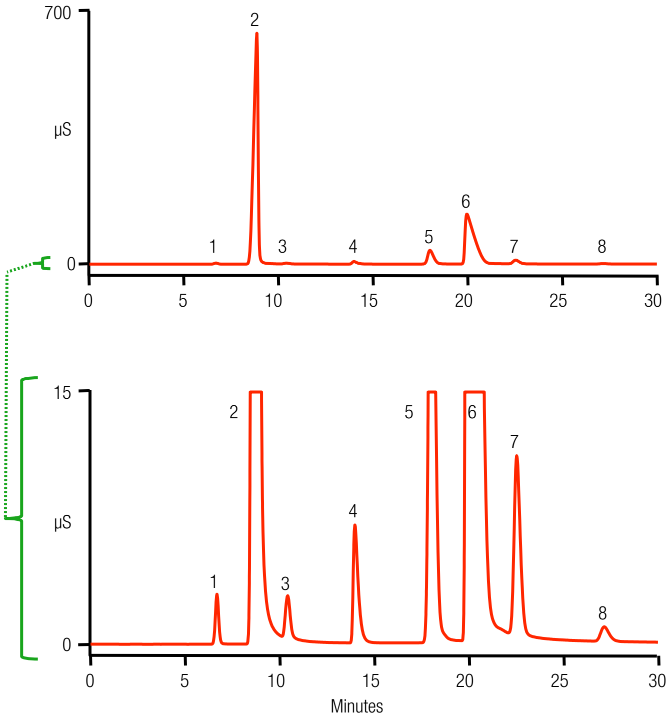
Cation Determinations by Ion Chromatography

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 subsurface environment. The levels of calcium, barium, and strontium are especially important to determine as they contribute to scaling problems in water pumps, pipes, etc. resulting in poor performance of water recycled for future fracturing events. Knowing the composition of both anions and cations in flowback wastewater can also be used to adjust the treatment plan if surface water discharge is the final goal.



Determination of cations in fracking flowback water using capillary IC.

Column:	Dionex IonPac CG16/CS16 columns, 0.5 mm i.d.
Eluent Source:	Thermo Scientific Dionex EGC-MSA
Gradient:	20–30 mM MSA (0–10 min) 30–55 mM MSA (10–18 min) 55 mM MSA (18–30 min) 20 mM MSA (30–36 min)
Flow Rate:	0.01 mL/min
Inj. Volume:	0.4 µL
Col. Temp.:	40 °C
Detection:	Suppressed conductivity, Thermo Scientfic™ Dionex™ CCES™ 300 Cation Capillary Electrolytic Suppressor, recycle mode
Sample:	100-fold diluted flowback water, filtered, 0.2 µm

Peaks:

	Measured	Undiluted
1. Lithium	0.34 mg/L	34 mg/L
2. Sodium	320.0	32,000
3. Ammonium	1.8	180
4. Potassium	5.8	580
5. Magnesium	13.0	1,300
6. Calcium	120.0	12,000
7. Strontium	13.0	1,300
8. Barium	2.3	230

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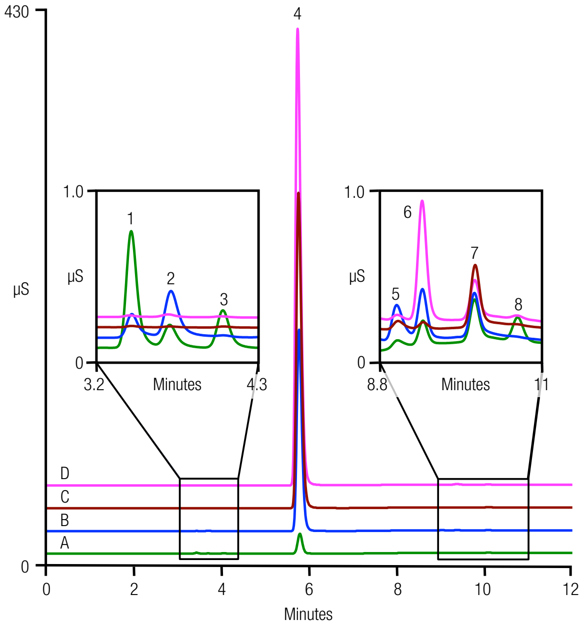
Anions and Cations in Produced Water

Column:	Dionex IonPac AG18/AS18 columns, 2 mm i.d.
Eluent Source:	Dionex EGC KOH cartridge
Gradient:	15 mM KOH (0–3 min) 15–29 mM KOH (3–4 min) 29 mM KOH (4–12 min) 15 mM KOH (12–17 min)
Flow Rate:	0.25 mL/min
Inj. Volume:	2.5 µL
Col. Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 suppressor, recycle mode
Sample:	A: Standard Produced Water, diluted, filtered, 0.2 µm B: 50-fold dil. TX C: 200-fold dil. CA D: 500-fold dil. ND

Peaks:

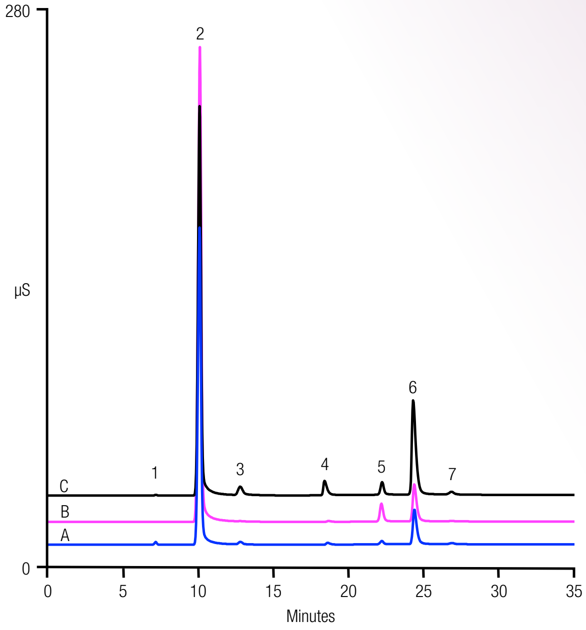
	A	B	C	D
1. Fluoride	0.4 mg/L	0.078	--	--
2. Acetate	0.4	0.88	0.020	0.048
3. Formate	0.4	0.070	0.057	0.058
4. Chloride	16	160	260	380
5. Carbonate	--	--	--	--
6. Bromide	0.4	0.66	0.13	1.7
7. Sulfate	0.4	0.39	0.54	0.36
8. Nitrate	0.4	--	--	--



Column:	Dionex IonPac CG16/CS16 columns, 0.5 mm i.d.
Eluent Source:	Dionex EGC-MSA (capillary) cartridge
Gradient:	20–30 mM MSA (0–10 min) 30–55 mM MSA (10–18 min) 55 mM MSA (18–34 min) 20 mM MSA (34–40 min)
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Col. Temp.:	40 °C
IC Cube Temp.:	15 °C
Detection:	Suppressed conductivity, Dionex CCES 300 Cation Capillary Electrolytic Suppressor, recycle mode
Sample:	Produced Water, diluted, filtered, 0.2 µm A: 50-fold dil. TX B: 200-fold dil. CA C: 1000-fold dil. ND

Peaks:

	A	B	C
1. Lithium	0.2 mg/L	--	0.049
2. Sodium	86	140	92.0
3. Ammonium	1.0	0.088	3.7
4. Potassium	1.3	0.64	6.2
5. Magnesium	0.48	2.7	1.6
6. Calcium	10.0	11.0	21.0
7. Strontium	0.25	--	0.53



**Download Application Note 1105:
Determination of Anion and Cations in Produced Water from Hydraulic Fracturing**

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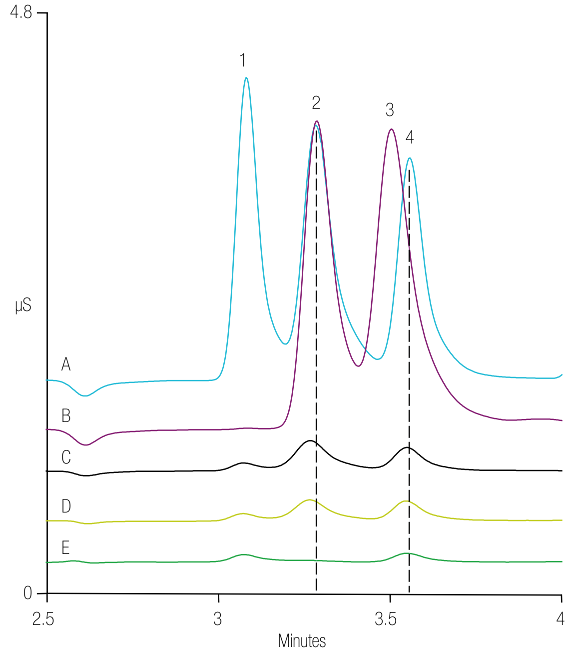
Organic Acid Determinations by Ion Chromatography

The organic acids formate and acetate are also commonly found in fracking wastewaters. These organic acids are added to control pH, but can also be sources of carbon for bacterial growth. 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 mm
Eluent:	23 mM KOH
Flow Rate:	1 mL/min
Inj. Volume:	25 µL
Col. Temp.:	30 °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 µm

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



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

Download the White Paper: The Importance of Anion and Organic Acid Determinations in Fracking Wastewater by Ion Chromatography

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Dionex OnGuard II Cartridges

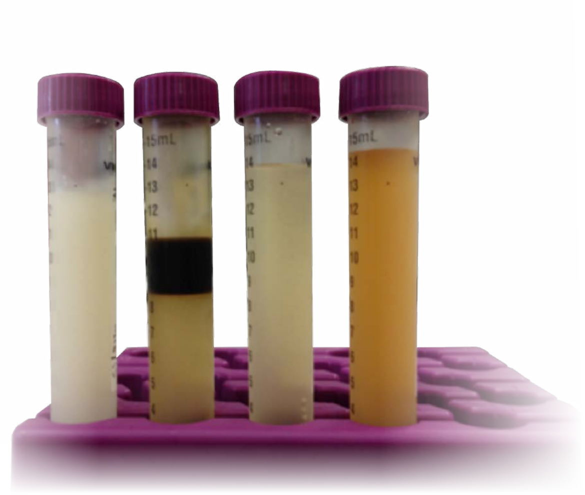
Fracking wastewater samples, such as those depicted in the image below, may require removal of components that could interfere with analysis. These samples can be pretreated to remove matrix interferences like metals, anions, cations, and hydrophobic compounds using the Thermo Scientific™ Dionex™ OnGuard™ II line of disposable cartridges. By removing interferences, the OnGuard cartridges can facilitate trace-level determinations in matrices such as fracking wastewater. The OnGuard II RP cartridge specifically would be ideal for fracking wastewater as it removes hydrophobic substances such as hydrocarbons and surfactants.

Dionex InGuard Cartridges

The Thermo Scientific™ Dionex™ InGuard™ catridges serve the same purpose as the Dionex OnGuard II sample pretreatment cartridges. However, they are installed in-line between the Thermo Scientific DionexAS-AP Autosampler and the IC injection valve enabling the automation of the interferant elimination process.

Dionex IonPac Guard Columns

In order to prevent fracking wastewater sample contaminants from binding to an analytical column, an additional guard column can be placed prior to the analytical column. For example, the Dionex IonPac NG1Guard column can be uesed to prevent decreased retention time or peak efficiency loss of the specific analytical column being used.



Hydraulic fracturing flowback and produced wastewater samples.

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AutoDilution

Fracking wastewater samples can have analyte concentrations that exceed 150,000 mg/L. Such high concentrations necessitate loading less sample volume or diluting prior to injection to avoid exceeding column capacity and to ensure that the concentrations determined fall within the linear calibration range. The latter is particularly important when regulated methods are used, which typically prescribe a concentration range for each analyte.

Using the AutoDilution feature of Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, the need for sample dilution can be easily automated. Samples are run undiluted and then, based on the peak height or area of analytes in the resultant chromatogram, the amount of sample injected can be reduced before re-analysis using:

– A partial loop injection

– A smaller volume injection loop

– Dilution by the autosampler

Dionex AS-AP Autosampler

The Dionex AS-AP Autosampler can be used with the entire ICS product family and provides high-performance, automated sample processing for IC applications. The autosampler can be configured for simultaneous or sequential sample delivery. In simultaneous delivery mode, samples are delivered through a splitter to two injection valves for dual full-loop injections. With this configuration, you can perform two separate analyses on one sample (e.g., anions and cations). For sequential delivery, valves are configured to divert the sample stream to the appropriate injection valve for loading.

Dionex AS-AP Sample Conductivity and pH Accessory

The in-line sample conductivity and pH measurement option offers a level of automation and convenience unmatched by any other IC autosampler. The Dionex AS-AP Sample Conductivity and pH Accessory allows in-line measurement of the sample conductivity and pH prior to injection. Chromeleon CDS software triggers can then be used to modify the sample as needed prior to injection, saving time by not having to rerun samples and putting less stress on columns, extending their lifetime.

Reagent-Free Ion Chromatography

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Ion chromatography is the method of choice for anion, cation and organic acid quantification commonly found in wastewater. Reagent-Free™ Ion Chromatography (RFIC™) systems, which include the Thermo Scientific Dionex ICS-2100, Thermo Scientific™ Dionex™ ICS-4000 Capillary HPIC,™ and Thermo Scientific Dionex ICS-5000$^+$ HPIC systems, electrolytically create the precise amount of eluent required for IC applications.

Just Add Water

Eluent generation eliminates the need to handle acids and bases that are traditionally required for the preparation of IC eluents, allowing chromatographers to run a full range of gradient and isocratic separations more effectively than hand-made eluents. These systems allow for a simpler and more reliable way to deliver superior results while simultaneously saving time and labor. Furthermore, because the instrument pump seals and pistons only come into contact with deionized water, overall pump maintenance is significantly reduced.

Capillary RFIC

Column size, injection volumes, and flow rates are scaled down by a factor of 10 to 100 in capillary IC. A capillary IC system can be left always ready to run samples as soon as they are prepared. A continuous mode of operation is possible because capillary IC systems consume only 15 mL of water a day, translating into 5.2 L a year.

The Dionex ICS-5000$^+$ and the Dionex ICS-4000 IC systems represent our latest innovations in capillary ion chromatography. They are also high-pressure IC (HPIC) systems, which allow continuous operation up to 5000 psi when configured as an RFIC system, permitting the use of Thermo Scientific™ Dionex™ IonPac™ 4 µm particle-size columns. These columns yield fast separations with short (150 mm) columns, or high resolution with standard length (250 mm) columns.

Learn more at www.thermoscientific.com/eluentgeneration

2-Dimensional Ion Chromatography for High Matrix Samples

2-Dimensional Ion Chromatography (2-D IC) is used for matrix diversion or matrix elimination prior to analysis of trace components in high salt wastewater samples. There are numerous advantages of the 2-D matrix diversion approach. Initial sample loading onto a 4 mm column allows a large amount of sample to be loaded due to the analytical column's high capacity. It also allows for higher selectivity of the analytes of interest relative to the matrix ions. Second, it is possible to focus the analyte peak that is partially resolved in the first dimension onto a concentrator column and then fully resolve that peak in the second dimension. Additionally, the second dimension column has a smaller cross-sectional area relative to the first dimension, which improves detection sensitivity. Lastly, the 2-D matrix diversion approach allows the potential for higher selectivity due to combining separate chemistries in two dimensions. The Dionex ICS-5000+ system's modular design with dual channel capabilities makes this an ideal system for 2-D IC applications.

A Unique Set of Column Chemistries

At the heart of our ion chromatography is a unique set of column chemistries that provide high selectivities and efficiencies with excellent peak shape and resolution. The Thermo Scientific™ Dionex™ IonPac™ polymeric columns address a variety of chromatographic separation modes including ion exchange, ion exclusion, reversed-phase ion pairing, and ion suppression. Our column chemistries are designed to solve specific applications, and we offer a variety of selectivities and capacities for simple and complex sample matrices. Additionally, our Dionex IonPac column line is available in standard bore, microbore, and capillary formats for the ultimate application flexibility.

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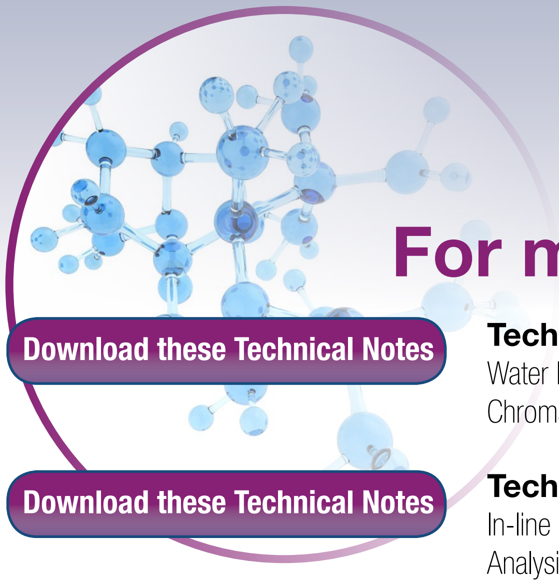

For more information

Download these Technical Notes

Technical Note 139: Determination of Anions in Fracking Flowback Water From the Marcellus Shale Using Automated Dilution and Ion Chromatography

Download these Technical Notes

Technical Note 138: Accurate and Precise Automated Dilution and In-line Conductivity Measurment Using the AS-AP Autosampler Prior to Analysis by Ion Chromatography

Download these Application Notes

Application Note 1094: Determination of Cations in Hydraulic Fracturing Flowback Water from the Marcellus Shale

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