



Thermo Scientific Solutions



# Hydraulic fracturing

**Analytical solutions for a healthier, cleaner  
and safer planet**

- Inorganic ion testing
- Organic contaminant testing
- Radiation monitoring
- Water chemistry analysis

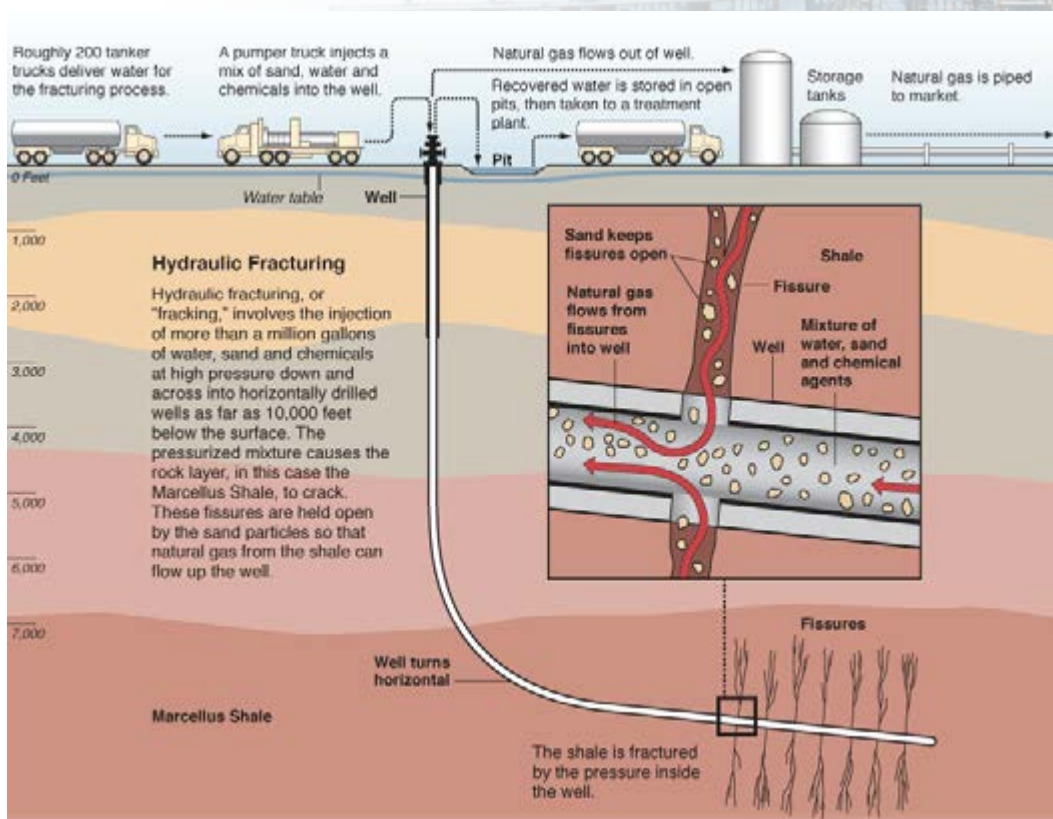
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# Hydraulic fracturing

Worldwide demand for additional energy sources has driven the growth of shale oil and gas extraction technology. But as hydraulic fracturing (HF) or fracking has burgeoned, so has speculation about its environmental impact. The chemicals used in the process can include hazardous compounds and the wastewater it produces may contain high levels of salts, metals, and occasional traces of radioactive isotopes from the subsurface environment.

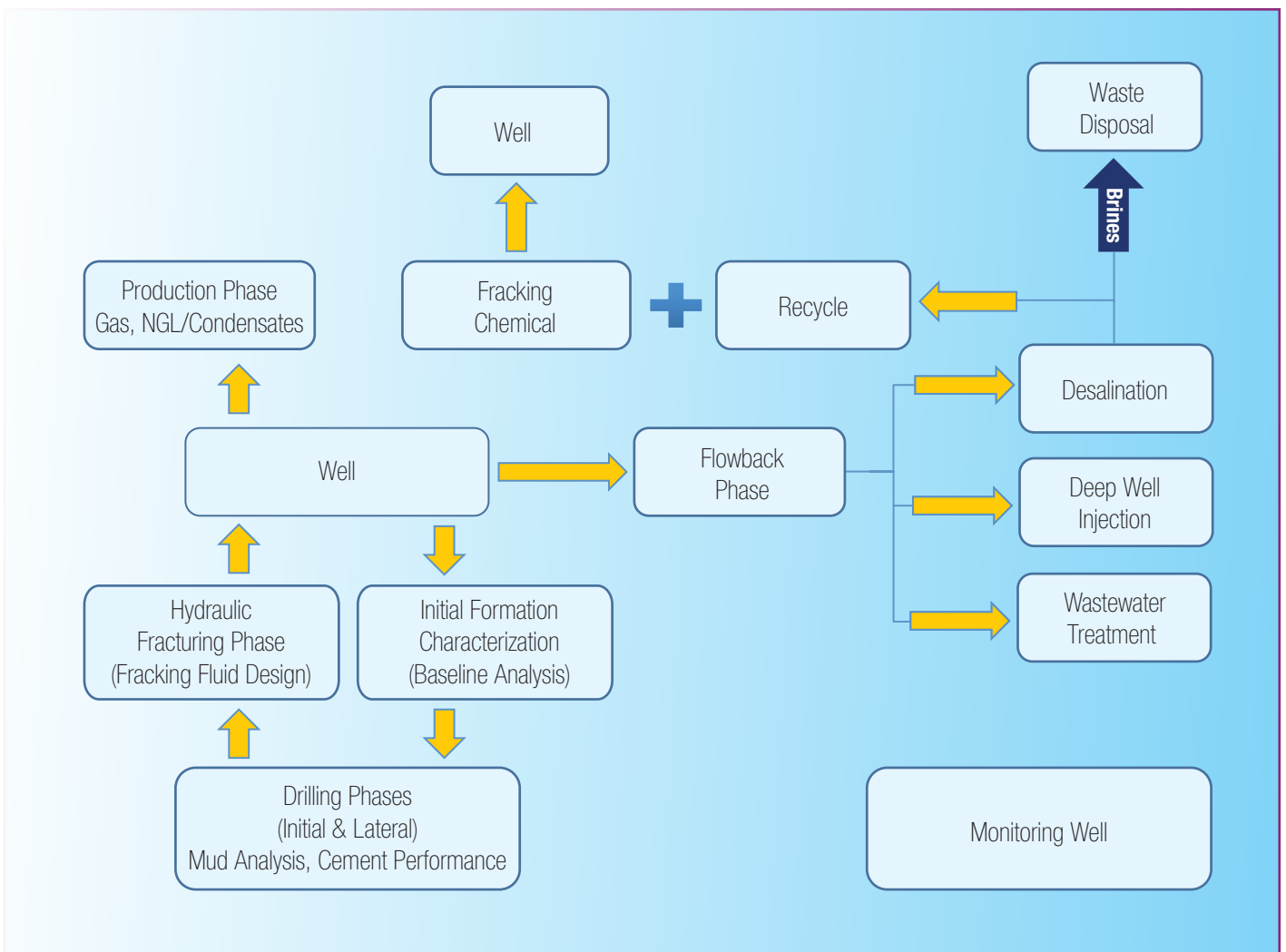
These concerns have led both citizens and government officials to question whether fracking could compromise ground and surface water, contaminate drinking water sources, and degrade air and soil quality. Accordingly, federal and state governments have accelerated their efforts to ensure that companies are conducting fracking both safely and responsibly.

Thermo Fisher Scientific supports oil and gas exploration companies, federal, state and local agencies, water treatment companies, and drinking and wastewater treatment facilities, providing them with a broad range of products, to which minimize the environmental impact of fracking. Our technologies range from radiation monitoring and ion chemical analysis to data management software and instrumentation.



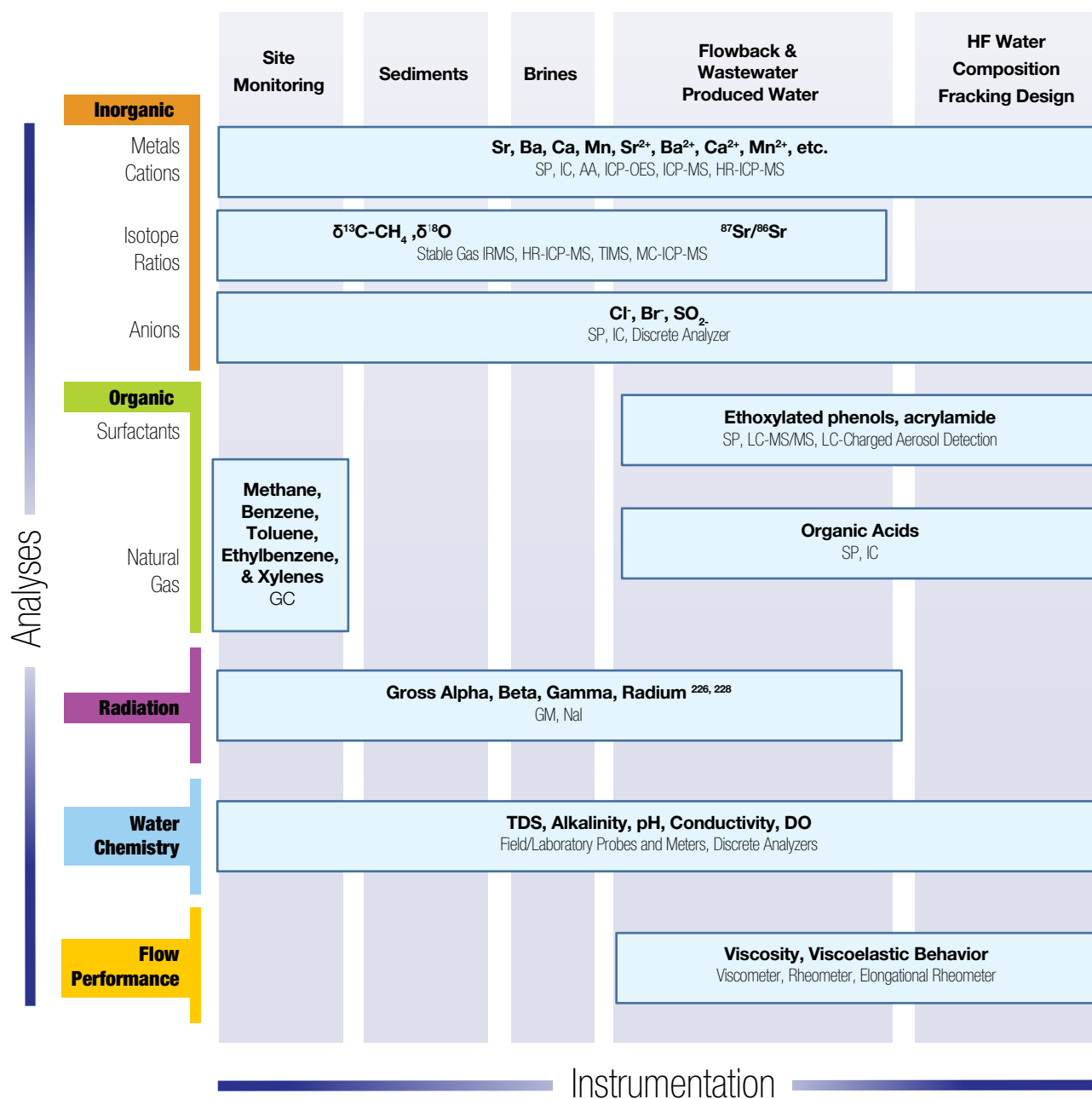
Al Granberg (<http://algranberg.com/>), "Hydraulic Fracturing" published by ProPublica (<http://www.propublica.org/special/hydraulic-fracturing-national>). Creative Commons BY-NC-ND 3.0 US.

# Workflow



Water workflow pre- and post-fracking. The analysis requirements depend on the water's future use and its potential environmental impact.

# Hydraulic fracturing monitoring



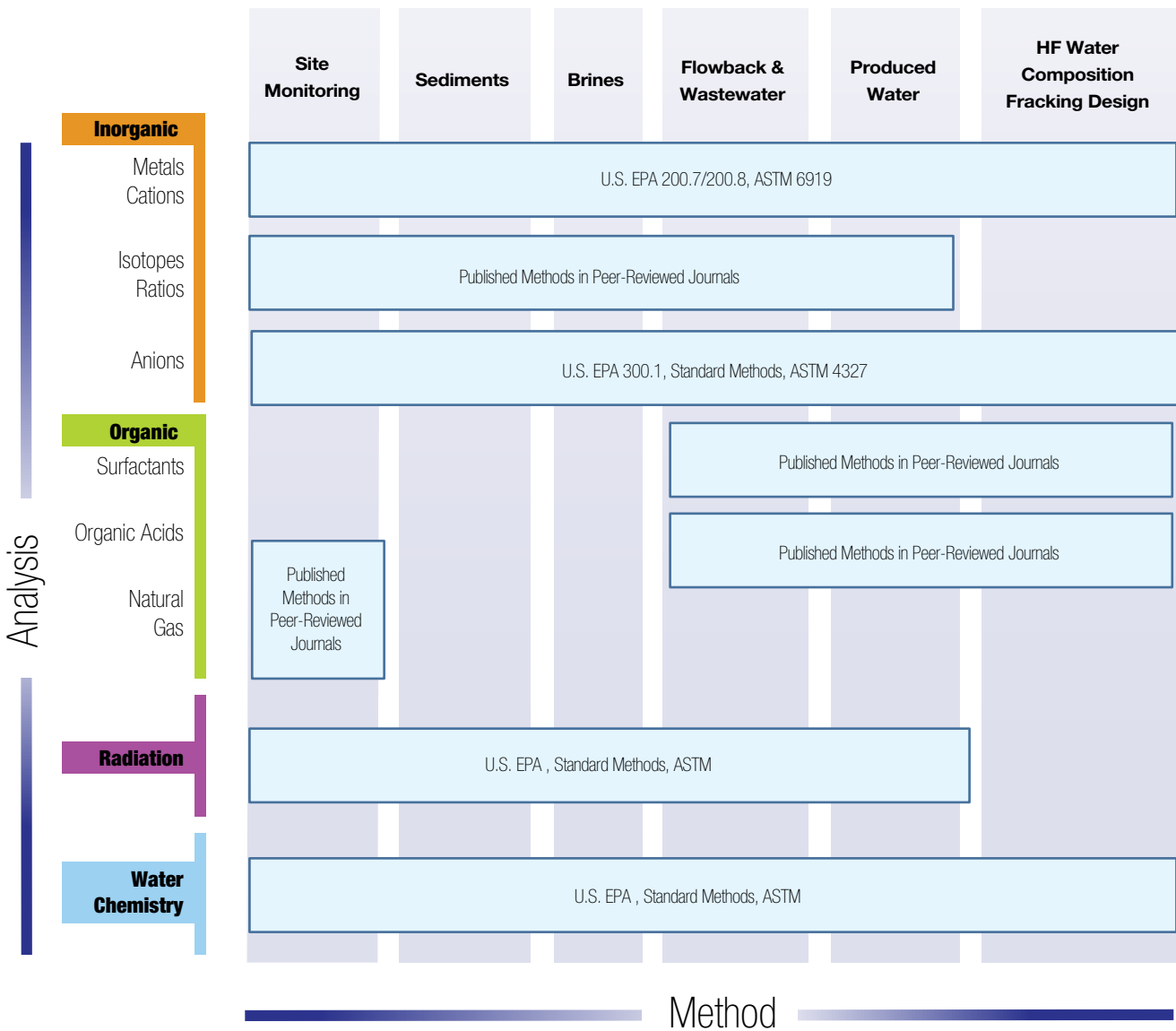
## Technology Legend:

IC ion chromatography  
 AA atomic absorption  
 ICP inductively coupled plasma  
 OES optical emission spectroscopy  
 MS mass spectrometry

HR high-resolution  
 IRMS isotope-ratio MS  
 TIMS thermal ionization MS  
 MC multicollector  
 LC liquid chromatography  
 GC gas chromatography

GM Geiger-Müller  
 TDS total dissolved solids  
 SP sample prep  
 DO dissolved oxygen  
 DA discrete analyzer

# Available methods



The broad range of analytes involved in the fracking process requires many analytical methods. Most methods are well known and have been validated by regulatory agencies. Additional methods are also available in the published literature all of which help provide information for efficient and safe shale gas operation.

# Metals and cation analysis

## AA, ICP-OES, and ICP-MS instruments

Environmental agencies are concerned with metal concentrations in flowback and produced waters and the potential implications for rivers and drinking water supplies. Conversely, drilling companies carefully monitor the produced water so they can determine the correct additives that maintain optimum performance during drilling and extraction. Thus, in addition to the environmental toxicity of certain metals, excess amounts of barium, calcium, iron, silica,

calcium, and magnesium are known to cause scaling within fracking processes. ICP-OES and ICP-MS are crucial techniques for monitoring metal contaminants in flowback and produced waters. Both allow a simultaneous determination of a wide assortment of metals from a single sample.

Cations cause scaling and lead to poor performance of water flow, resulting in increased costs of operation.



Thermo Scientific™ iCAP™ Q series ICP-MS and iCAP 7000 series ICP-OES analyzers.



# Isotope ratio analysis

## HR-ICP-MS, TIMS, and MC-ICP-MS instruments

Identifying the geochemical fingerprints of fracking waters has important implications for assessing hydrocarbon resource recovery, environmental impacts, and wastewater treatment and disposal. In many cases, the exploration of unconventional shale gas takes place in areas with historical oil and gas production, and the chemical distinction between conventional oil and gas wastewater and flowback water is not always clear. The distinct signature for produced waters has important implications for forensic evaluations of released waters, because of the limited use of artificial tracers that could definitively identify fluids from flowback water. Additionally, the continued use of proprietary chemicals has led to public concerns with the flowback water process. These concerns could be partially mitigated if novel techniques existed to definitively distinguish flowback water in the environment.

Novel diagnostic elemental and isotopic signatures (B/Cl, Li/Cl,  $\delta^{11}\text{B}$ , and  $\delta^7\text{Li}$ ) useful for characterizing and distinguishing different sources of fracking waters have been developed. In recent studies, produced water samples have shown that B/Cl ( $>0.001$ ), Li/Cl ( $>0.002$ ), and isotope ratios of  $\delta^{11}\text{B}$  (25–31%) and  $\delta^7\text{Li}$  (6–10%) from the Marcellus and Fayetteville black shale formations were distinct, in most cases, from produced waters sampled from conventional oil and gas wells. In addition, it has been proposed that boron isotope geochemistry can be used to quantify small fractions (~0.1%) of flowback water in contaminated fresh water. This is likely to be universally applied to trace flowback waters in other shale basins.



Thermo Scientific™ TRITON™ Plus Multicollector Thermal Ionization Mass Spectrometer (TIMS).

# Anion and cation analysis

## IC and discrete analysis systems

Fracking flowback and produced water, which contains ions mobilized from the subsurface environment, could contaminate surface waters if it were to leak from holding facilities or if it was not properly treated prior to discharge.

Significant concentrations of chloride and bromide can be found in wastewaters. These chemicals are a concern to drinking water utilities because the former can interfere with treatment, while the latter can form toxic disinfection byproducts (DBPs) during water treatment. Another anion of importance is sulfate, which is regulated as a secondary contaminant. The reduction of sulfate to hydrogen sulfide is highly toxic causing corrosion and affecting the aesthetic character of water by creating an unpleasant odor.

If wastewater is reused, each successive fracturing event requires adjusting the blend of additives to account for their altered performance in the presence of increasingly higher concentrations of salts and metals that have been mobilized from the subsurface environment. The levels of calcium, barium, and strontium are especially important to measure as they contribute to scaling problems in water pumps, pipes, and other pieces of equipment resulting in poor performance of water recycled for future fracturing events. Information about the composition of both anions and cations in fracking wastewater can also be used to adjust the treatment plan if surface water discharge is the final goal. Both IC and automated discrete analyzers can perform ionic elements by anion and cation analysis.



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Thermo Scientific™ Dionex™ ICS series ion chromatography systems.

IC can also be used for organic acid analysis. The organic acids formate and acetate are 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.



Thermo Scientific™ Gallery™ Automated Photometric Analyzer.



Thermo Scientific™ Gallery™ Plus Automated Photometric Analyzer.



Thermo Scientific™ Aquakem™ Photometric Analyzer.



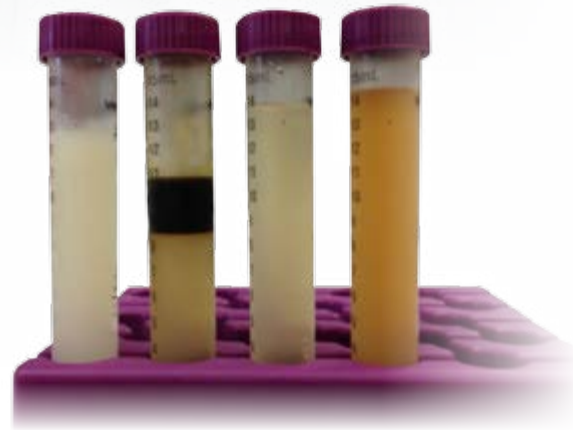
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# Water chemistry: Titration

## Titration for fracking design and water samples

General chemistry measurements such as pH are important for both environmental impact analysis as well as optimizing fracturing fluids. For example, pH maintains the effectiveness of other components, such as cross-linkers, and needs to be monitored and maintained neutral to prevent excess precipitation of mineral salts and scale formation. Hardness and alkalinity provide general information on the water chemistry.



Hydraulic fracturing flowback and produced wastewater samples.

The METTLER TOLEDO titration system and liquid handler combined with two Dionex IC systems and our Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System Software.

## Sample preparation



### Matrix interference removal (metals, anions, cations, and hydrophobic compounds)

Fracking wastewater samples, such as those depicted above, may require removal of certain components prior to analysis. These samples can be pretreated to remove matrix interferences such as metals, anions, cations, and hydrophobic compounds.



Thermo Scientific™ Dionex™ InGuard™ Cartridges.



Thermo Scientific™ Dionex™ IonPac™ Guard Columns.



Thermo Scientific™ Dionex™ OnGuard™ II Cartridges.



Thermo Scientific™ Dionex™ SolEx™ SPE Cartridges.

# Water chemistry: Parameter Analysis

## Electrochemistry and colorimetry benchtop, online, and handheld instruments

With rising transportation costs and scarcity of water in shale rock regions, the fracking industry is transitioning toward water recycling. The industry has made investments in various technologies, including localized electrocoagulation and centralized traditional water treatment to recycle flowback and produced waters. Both of these processes require basic water chemistry measurements to validate the effectiveness of the recycling process and to characterize the water quality. Accurate characterization is also required for custody transfer of water among the recyclers, transporters, and drillers. The primary water chemistry parameters needed in water recycling are: pH, total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), and sometimes chlorine or ozone when oxidation is utilized. These measurements are performed either online for process validation or in the laboratory or field for water characterization measurements. For more than 50 years, water professionals all over the world have relied upon our liquid sensing and analysis instruments to measure critical water parameters, making Thermo Scientific water chemistry analyzers trusted tools in the lab, online, and in the field.

### Field



Thermo Scientific™ Orion™ AQ3700 AQUafast™ Colorimeter.



Thermo Scientific™ Orion Star™ A321 Waterproof pH Portable Meter.

### Lab



Thermo Scientific™ Orion Star A2115 Benchtop pH Meter Kit.

### Online



Thermo Scientific™ AquaPro™ Multi-Input Intelligent Analyzer with Thermo Scientific™ AquaSensors™ DataStick™ pH Measurement System.



Thermo Scientific™ Orion AquaMate 8000 UV-Vis Spectrophotometer.

# Radioisotope analysis

## Radiation testing products

Increased shale gas extraction has led to concerns about the toxicity and radioactivity of produced water from a mixture of fracturing fluids and deep saline formation waters that may discharge to the environment. Geologic formations that are now subject to hydraulic fracturing often contain naturally occurring radionuclides, commonly referred to as NORMs (naturally occurring radioactive materials), typically consisting of uranium, thorium, radium, and lead-210. When NORMs are concentrated by fracking activities, these are classified as TENORM (technologically enhanced naturally occurring radioactive material).



Thermo Scientific™ Shielded RIIDEye™ Analyzer Kit, which includes a RIIDEye identifier with a 2 × 2 NaI detector, lead shield with top sliding door, and a 0.5 L Marinelli sample beaker with patented easy-lift lid.



Thermo Scientific™ RIIDEye™ X and RIIDEye M Handheld Radioisotope Identifiers.

# Viscosity measurements

## Rheological analysis

The rheology of hydraulic fracturing fluids affects the penetration and fracturing of the geological formation as well as the transport, suspension stability deposition of proppants, and the flowback after placement. Viscosity is crucial to achieving easier penetration into tightly packed shales for optimal fracking processes. Viscoelasticity is the key factor for the transport and stabilization of the proppants.

The rheological properties are part of the data, which is fed into the mathematical simulation of the fracking process. The better the quality of the rheological data, the closer the simulation to reality. This requires rheological tests to be performed under formation conditions including high pressures and temperatures. When the fracking is finally performed, the fracking fluid has to be tested frequently on site to guarantee that its flow properties stay at the calculated optimum.



Thermo Scientific™ HAAKE™ Viscotester™ IQ Rheometer.



Thermo Scientific™ HAAKE™ MARS™ Rotational Rheometer.

# Chemical imaging analysis

## Raman imaging microscope

Identify minerals and assess thermal maturity of carbonaceous materials such as kerogen in oil shale using Raman imaging analysis. Raman spectroscopy has proven to be an information-rich, nondestructive analytical technique that can be used for the exploration of new shale oil deposits. Raman microscopes can identify regions of interest and visually assess chemical composition and distribution quickly.



Thermo Scientific™ DXR™ xi Raman Imaging Microscope.



# Analysis of natural gas in water

## GC and GC/MS instruments

The extraction of shale gas has led to increased concerns about methane, ethane, and propane contamination of groundwater resources. These concerns are based on 1) fluid (water and gas) flow and discharge to shallow aquifers due to the high pressure of the injected fracturing fluids in the gas wells; 2) the potential explosion and asphyxiation hazard of natural gas; and 3) the large number of private wells in rural areas that rely on shallow groundwater for household and agricultural use.

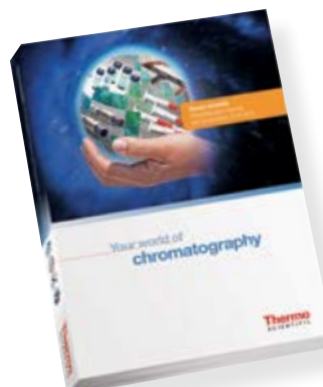


Thermo Scientific™ TRACE™ 1310 Gas Chromatograph with the Thermo Scientific™ TriPlus™ 300 Headspace Autosampler.

Chromatography Columns and Consumables Catalog 2014 – 2015 - “Your World of Chromatography”

A comprehensive portfolio of columns, accessories, vials and closures for use on GC and GC/MS and LC and LC/MS instrumentation.

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# Surfactant analysis

## LC systems with charged aerosol detection

During the hydraulic fracturing process, poor fluid recovery can result from formation capillary pressure, wetting characteristics, and unfavorable gas-water surface tension conditions. To address these interacting properties, a flowback enhancement additive, typically containing a surfactant, may be included in the fracturing fluid system. Choosing the right surfactant is critical to optimizing the flowback, although in some cases fracturing without a flowback additive may provide a better result.



Thermo Scientific™ Dionex™ Corona™ Veo™ Charged Aerosol Detector.



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A comprehensive portfolio of columns, accessories, vials and closures for use on GC and GC/MS and LC and LC/MS instrumentation.

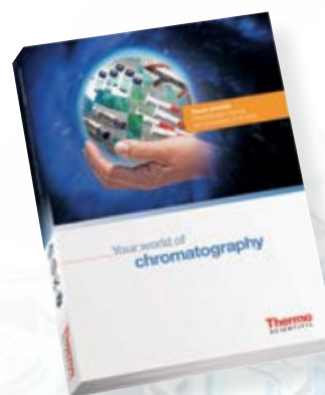
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Thermo Scientific™ Vanquish™ System with Charged Aerosol Detector.



Thermo Scientific™ Dionex™ UltiMate™ 3000 LC System.



# Fisher Scientific

## lab equipment, supplies, chemicals & field sampling products

Laboratory solutions for exploration, production,  
midstream, and water management

Fisher Scientific provides one of the largest offerings of bench-top scientific equipment, laboratory supplies, chemicals, and field sampling products to ensure maximum efficiency and accuracy for all U.S. EPA, ASTM, and API methods.

The Fisher Chemical portfolio of high-purity solvents comprises more than 600 solvents suited to a wide range of laboratory applications, from LC/MS to HPLC to GC to spectrophotometry. Manufactured in ISO 9001:2008-certified facilities, each Fisher Chemical solvent undergoes rigorous quality assurance and testing to ensure excellent lot-to-lot and bottle-to-bottle consistency.

Achieving quality results is essential—whether it is an exploration and production (E&P) application, midstream processes, or water management, Fisher Scientific has the products and support for success.



Fisher Scientific™ Basic Stirring Hotplate.



Thermo Scientific™ Orion Star™  
A212 Conductivity Benchtop Meter.



Fisher Chemical OPTIMA LC/MS Solvents.



# Applications for hydraulic fracturing

- [Application Note 1094: Determination of Cations in Hydraulic Fracturing Flowback Water from the Marcellus Shale](#)
- [Application Note 1105: Determination of Anions and Cations in Produced Water from Hydraulic Fracturing](#)
- [Application Note 10405: Rapid and Reliable Detection of Dissolved Gases in Water](#)
- [Application Note 43184: Determination of Elemental Components of Fracking Flowback Solutions from Marcellus Shale, USA, using ICP-OES](#)
- [Poster Note 71014: Hydraulic Fracturing Flowback Water Analysis Using In-line Conductivity, Automated Dilution, and Ion Chromatography](#)
- [Poster Note 90004: Analytically Monitoring the Effect of Fracturing Activity](#)
- [Technical Note 139: Determination of Anions in Fracking Flowback Water From the Marcellus Shale Using Automated Dilution and Ion Chromatography](#)
- [White Paper 70693: The Importance of Anion and Organic Acid Determinations in Fracking Wastewater by Ion Chromatography](#)
- [White Paper 70784: Bromide Analysis for Hydraulic Fracturing](#)
- [White Paper 71116: Hydraulic Fracturing Wastewaters](#)

<http://www.thermoscientific.com/en/about-us/general-landing-page/hydraulic-fracturing.html>

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