



# Determination of elemental components of fracking flowback solutions from Marcellus Shale, USA, using ICP-OES

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## Goal

The goal of this note is to demonstrate the use of ICP-OES as a key solution for examining fracking flowback waters.

## Introduction

The rapid increase in U.S. natural gas production in recent years has been propelled by the extensive use of hydraulic fracturing (also known as fracking). This process extracts natural gas by drilling into bedrock (primarily shale) and then injecting fluid under high pressure causing cracks in bedrock, thereby releasing trapped gas to be captured<sup>1</sup>. Fracking fluid contains approximately 85% water and 13% sand, the latter being used to prop open cracks within the bedrock, facilitating the flow of gas. The remainder consists of chemical additives such as friction reducers, anti-bacterial agents, and corrosion inhibitors<sup>2</sup>.

While fracking has been in use since the 1940s primarily for oil extraction, recent refinements to the process have enabled the exploitation of energy resources that had previously been inaccessible<sup>3</sup>. While fracking provides financial benefits to both local and national economies, it has not been without controversy. Inadvertent spills or the storage of fracking flowback solutions (fracking solution that returns to the surface via the well bore) into unlined collection ponds can contaminate ground water<sup>4</sup>. Additionally, high levels of minerals found in fracking wastewater can impact drinking water sources prior to disinfection at downstream drinking water utilities. In addition, the resulting effluent discharged by the fracking facility may exceed the allowed levels in the facility's discharge permits<sup>5</sup>.

A challenge with analyzing fracking flowback solutions is the high levels of dissolved solids as salts that are leached from bedrock. Direct analysis of these solutions can often suppress key analytes, and cause the user to need to dilute the sample such that accurate measurement for trace analytes can be impossible. Additionally, high concentrations may exceed the linear calibration range for a particular analyte. The need for a robust RF generator and full wavelength selection are key to getting accurate results.

## Instrumentation and method parameters

A Thermo Scientific™ iCAP™ 7400 ICP-OES Duo with a standard sample introduction kit was used for this analysis. The duo view plasma allows for elements expected at trace levels to be analyzed axially, for best sensitivity and for elements expected at high concentrations to be measured radially, for best dynamic range. In conjunction with this instrument, a Teledyne CETAC ASX-560 Autosampler was used. Instrument parameters used during analysis are shown in Table 1.

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. To determine method detection limits (MDL), a blank solution was analyzed with ten repeats and the standard deviation determined. This was repeated three times and the average calculated. The selected wavelengths and plasma views, as well as the determined MDLs can be found in Table 2.

**Table 1. Instrument parameters.**

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white Internal standard Tygon® orange/blue
Pump Speed	40 rpm
Nebulizer	Glass concentric
Nebulizer Gas Flow	0.65 L·min <sup>-1</sup>
Spray Chamber	Glass cyclonic
Auxiliary Gas Flow	0.7 L·min <sup>-1</sup>
Coolant Gas Flow	14 L·min <sup>-1</sup>
Center Tube	2 mm
RF Power	1350 W
Plasma View	<b>Axial</b> <b>Radial</b>
Exposure Time	UV 20 s, Vis 10 s      UV 5 s, Vis 5 s

**Table 2. Wavelengths and plasma views used and MDLs achieved.**

Element	Wavelength (nm)	Plasma view	MDL (mg·L <sup>-1</sup> )
Al	167.079	Axial	0.0001
As	189.042	Axial	0.0013
B	208.893	Axial	0.0005
Ba	234.758	Radial	0.3504
Ba	455.403	Radial	0.0003
Be	313.042	Axial	0.0001
Ca	315.887	Radial	0.1203
Cd	228.802	Axial	0.0001
Co	228.616	Axial	0.0004
Cr	267.716	Axial	0.0005
Cu	324.754	Axial	0.0002
Fe	259.940	Radial	0.0281
K	769.896	Radial	0.0453
Mg	279.079	Radial	0.1406
Mn	259.373	Axial	0.0001
Mo	202.030	Axial	0.0001
Ni	231.604	Axial	0.0004
P	213.618	Axial	0.0007
Pb	220.253	Axial	0.0016
S	182.034	Axial	0.0012
Sb	206.833	Axial	0.0044
Se	196.090	Axial	0.0024
Si	212.412	Axial	0.0024
Sn	189.989	Axial	0.0005
Ti	323.482	Axial	0.0005
Tl	190.856	Axial	0.0013
V	311.071	Axial	0.0005
Zn	202.548	Axial	0.0004

## Sample preparation

Fracking flowback solutions from the Marcellus Shale (F1–10) were collected from successively later times during the fracking process.

Samples were diluted 5 times with 2% concentrated nitric acid in deionized water. A 10 mg·L<sup>-1</sup> yttrium internal standard was introduced online, which creates a further dilution of 12% (i.e. the final concentration of the sample is 0.88 times the initial concentration), the wavelengths used are shown in Table 3.

**Table 3. Yttrium internal standard wavelengths used.**

Wavelength (nm)	Wavelength range	Plasma view
377.433	Visible (Vis)	Axial
377.433	Visible (Vis)	Radial
224.306	Ultra Violet (UV)	Axial

Sample spikes, equivalent to 0.5 mg·L<sup>-1</sup>, were performed on 3 samples from the beginning, middle and end of flowback. The results for these samples, spikes and recoveries can be seen in Table 4.

## Results and discussion

The nature of fracking flowback samples is that there is an initial recapture of the fracking material, and a long term leaching of the native rock into the water. Therefore we see two main fingerprints of flowback water over time. Certain elements present in the fracking process will be at initially high concentrations, with lowering concentrations over time (Figure 1). Minerals leaching from the native rock will be low initially, and increase over time (Figure 2).

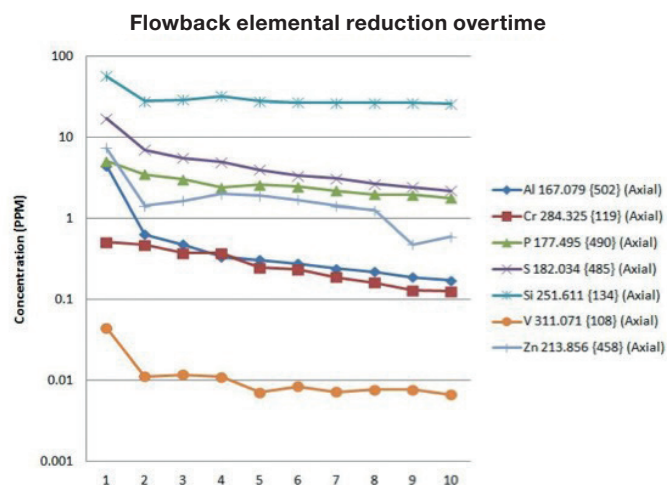


Figure 1. Flowback water reduction of elemental components over time.

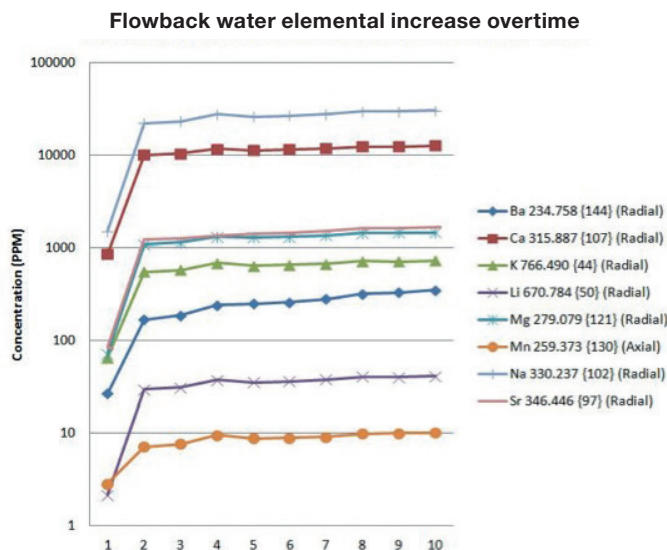


Figure 2. Flowback water increase of elemental components over time.

The data displayed in Table 4 shows the spike recovery values obtained for the fracking flowback samples analyzed. All recoveries are within  $\pm 15\%$ , with the majority within  $\pm 10\%$ , demonstrating that the analytical method used is capable of performing the required analysis at all stages of the fracking flowback procedure.

Table 4. Spikes and recoveries for flowback water samples. N2 (beginning), N5 (middle), N10 (end).

Element	N2 (mg·L <sup>-1</sup> )	N2 spike (mg·L <sup>-1</sup> )	Recovery (%)	N5 (mg·L <sup>-1</sup> )	N5 spike (mg·L <sup>-1</sup> )	Recovery (%)	N10 (mg·L <sup>-1</sup> )	N10 spike (mg·L <sup>-1</sup> )	Recovery (%)
Al	0.1269	0.6241	99.4	0.0614	0.5219	92.1	0.0342	0.4985	92.9
As	<MDL	0.5191	103.8	<MDL	0.5163	103.3	<MDL	0.5247	104.9
Be	<MDL	0.5320	106.4	<MDL	0.5340	106.8	<MDL	0.5270	105.4
Cd	0.0011	0.5292	105.6	0.0011	0.5302	105.8	0.0012	0.5361	107
Co	<MDL	0.4359	87.2	0.0006	0.4397	87.8	0.0014	0.4417	88.1
Cr	0.0970	0.5524	91.1	0.0528	0.5231	94.1	0.0302	0.5038	94.7
Cu	0.0359	0.5232	97.5	<MDL	0.5210	104.2	<MDL	0.5282	105.6
Mn	1.4247	1.9547	106	1.7555	2.1957	88	2.0322	2.5326	100.1
Mo	0.0090	0.4667	91.5	0.0057	0.4702	92.9	0.0047	0.4671	92.5
Ni	0.0055	0.4328	85.5	0.0025	0.4375	87	0.0019	0.4362	86.9
Pb	0.0113	0.4368	85.1	0.0111	0.4421	86.2	0.0120	0.4413	85.9
Sb	0.1529	0.6623	101.9	0.1495	0.6536	100.8	0.1503	0.6557	101.1
Se	<MDL	0.5094	101.9	<MDL	0.5123	102.5	<MDL	0.5089	101.8
Ti	0.0042	0.4861	96.4	0.0017	0.4837	96.4	0.0014	0.4871	97.2
Tl	0.0045	0.4716	93.4	0.0048	0.4758	94.2	0.0074	0.4750	93.5
V	0.0023	0.4793	95.4	0.0014	0.4777	95.3	0.0013	0.4801	95.8
Zn	0.2437	0.7508	101.4	0.3203	0.7465	85.2	0.0987	0.5345	87.2

\* <MDL: measured concentration below the method detection limit.

## Conclusion

Knowing the consequences of fracking on ground water is important. It will be imperative to know how much of the initial fracking solutions are initially recovered, where any excess may be going or how long a complete recovery will take. This can be determined by monitoring the elements fingerprinted in Figure 1. Likewise, ground waters are being affected by the native rock over time, and it will be important to know which elements are being leached, and at what rate. The US EPA has put forth a maximum contaminant level (MCL) for some elements in drinking waters. Of these, arsenic and selenium were initially higher than the MCL in the first sample only (assumed from the fracking solution). Barium, lead, mercury, and thallium were above the MCL throughout the 10 barrels tested, indicating a long washout of fracking solution, or presence in the bedrock at high concentrations. Further studies will need to be done to determine the impact of local wells, and the length of time for flowback waters to return to a stable level, or remediation will have to occur.

## References

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