Analytically Monitoring the Effect of Fracturing Activity

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Overview

Purpose: This paper presents how questions surrounding the impact of hydraulic fracturing gas extraction (fracking) can be answered using several different types of analytical instrumentation.

Methods: Inductively coupled plasma–optical emission spectroscopy (ICP-OES) and inductively coupled plasma–mass spectrometry (ICP-MS) methods have been developed according to U.S. Environmental Protection Agency (EPA) 200.7 and 200.8, respectively, and are presented here.

Results: Short synopsis of the results.

Introduction

Fracking, a process used by the petrochemical industry to increase extraction efficiency of natural gas that is trapped in bedrock, is under scrutiny due to potential hazard to the environment. The process of hydraulic fracturing uses a water/chemical/s mixture pumped at high pressure to induce fracturing of the rocks and release trapped fuel. This tactic that has been used in a large portion of wells over the last decades, but recent refinements to the process have increased its use to exploit energy resources that had previously been inaccessible. In some countries, fracking is banned and in the U.S., the State of California has recently signed new legislation, effective in 2014 that will require groundwater and air quality monitoring.

The fracking process results in the addition of chemicals to the subsurface, along with mobilization of anions, cations, metals, and radioisotopes in the shale layers that are returned to the surface as flowback waters. Analytical instrumentation is required to determine the concentrations of these analytes so that the environmental impact on groundwaters can be minimized, fracking processes can be improved, and wastewater or brines can be characterized prior to disposal.

FIGURE 1. A typical hydraulic fracturing gas extraction well head.

FIGURE 2. A groundwater well.

Methods and Results for ICP-OES

EPA Method 200.7—Determination of Metals and Trace Elements in Water and Wastes by ICP-OES

EPA Method 200.7 describes the determination of 31 elements in water samples. It suggests preferred wavelengths, calibration, and quality control (QC) procedures for determination method performance characteristics such as detection limits and linear ranges. This method is used extensively for the analysis of well water in many U.S. states and for regulatory analysis of wastewater in compliance with the permits issued within the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA, 40 CFR Part 136). These sample types are very similar to those that are associated with fracking in terms of both environmental monitoring and waste produced by the fracking procedure.

Sample Preparation

All samples, including calibration and QC standards, laboratory-fortified matrix (river and wastewater), and fracking flowback waters (10 samples collected over a 10-hour period) were prepared in nitric acid (1% Fisher Chemicals, Loughborough, UK). Calibration standards and spikes to laboratory-fortified matrix were prepared from the relevant single element stock standard (1000 mg/L Fisher Chemicals).

Instrumentation

A Thermo Scientific™ iCAP™ 7600 ICP-OES Duo was used for the analysis. The duo plasma view allows for elements expected at trace levels to be measured axially, whereas high concentrations are measured radially. The instrument is fitted with a switching valve sample introduction system which reduces uptake and wash times. Otherwise, the standard sample induction system was used (Table 1). A LabBook was created with the Thermo Scientific Qtegra™ Software to include the 31 elements required by EPA 200.7. Sulfur was included as it is often an element that is required for groundwater analysis. The LabBook contained the acquisition parameters for the analysis (Table 2), the wavelengths, and plasma views (Table 3).

TABLE 1. ICP-OES sample introduction system used.

Parameter	Value
Nebulizer	Glass Concentric
Spray Chamber	Glass Cyclonic
Sample Loop Size	4 mL
Pump Tubing i.d.	Sample 1.016 mm Waste 1.524 mm

TABLE 2. ICP-OES plasma and data acquisition parameters.

Parameter	Value
Analysis Mode	Speed
Exposure Time	10 s (Low), 10 s (High)
Number Repeats	3
Sample Flush Time	18 s
Pump Rate	50 rpm
RF Power	1150 W
Coolant Gas Flow	12 L/min
Auxiliary Gas Flow	0.5 L/min
Nebulizer Gas Flow	0.65 L/min

Results

TABLE 3. Results of the analysis of the fortified laboratory matrix and spikes with method detection limits based on 3 × SD of 10 replicate blanks.

Element	Λ nm	Plasma View	MDL (µg/L)	Spiked (mg/L)	River Water Found (mg/L)	River Water Spiked (mg/L)	River Water Recovery (%)	Wastewater Found (mg/L)	Wastewater Spiked (mg/L)	Wastewater Recovery (%)
Ag	328.608	Axial	0.56	0.25	<MDL	0.252	101.1	0.001	0.261	104
Al	308.215	Radial	25	1	0.108	1.159	105.2	0.191	1.233	104.2
As	193.759	Axial	4.4	0.25	0.003	0.23	91	0.022	0.289	107.1
B	249.678	Axial	2.1	1	0.048	0.963	91.5	0.136	1.151	101.5
Ba	455.403	Axial	0.06	0.25	0.047	0.282	93.9	0.108	0.372	105.6
Be	234.861	Axial	0.1	0.25	<MDL	0.255	102.1	0.018	0.286	107
Ca	315.887	Radial	11	2.5	162.1	164.5	95.9	144.5	146.8	91.8
Cd	226.502	Axial	0.19	0.25	<MDL	0.246	98.2	0.018	0.286	107.2
Co	228.616	Axial	0.32	0.25	<MDL	0.241	96.5	0.019	0.261	97.1
Cr	284.325	Axial	1.4	0.25	0.002	0.257	101.9	0.024	0.293	107.7
Cu	224.7	Axial	0.99	1	<MDL	1.031	102.4	0.15	1.2	105
Fe	259.94	Radial	3.1	1	0.097	1.128	103.1	0.252	1.308	105.6
Hg	194.227	Axial	1.3	0.25	<MDL	0.252	101.2	<MDL	0.255	101.4
K	766.49	Axial	28	2.5	5.33	7.9	102.8	6.58	9.29	108.4
Li	670.784	Axial	0.05	0.25	0.019	0.272	101.1	0.04	0.272	92.8
Mg	279.079	Radial	26	2.5	6.26	8.88	104.5	5.49	7.95	98.2
Mn	257.61	Axial	0.28	1	0.011	0.969	95.7	0.082	1.089	100.7
Mo	203.844	Axial	1.2	0.25	<MDL	0.227	91.1	0.018	0.281	105.3
Na	589.592	Radial	8	2.5	53.7	56.1	96.9	42.5	44.9	98.1
Ni	231.604	Axial	1.1	1	0.002	1.07	106.8	0.071	1.06	98.9
P	177.495	Axial	4.9	2.5	0.48	2.97	99.5	2.84	5.43	103.3
Pb	220.353	Axial	3.2	0.25	0.004	0.249	98.2	0.023	0.257	93.9
SO4	182.034	Axial	19	7.5	82.9	90.3	98.5	64.1	71.5	98.3
Sb	206.833	Axial	4.2	0.25	<MDL	0.237	95	0.019	0.278	103.6
Se	196.09	Axial	7.3	0..25	<MDL	0.231	93.9	0.022	0.287	105.8
SiO2	251.611	Radial	17	5.36	13.6	18.8	97.1	15.9	21.4	102.7
Sn	189.989	Axial	1.7	0.25	<MDL	0.262	105.5	0.057	0.308	100.3
Sr	421.552	Axial	0.07	0.25	0.99	1.248	103.2	0.811	1.081	108.1
Tl	334.941	Axial	0.24	0.25	0.007	0.276	107.4	0.034	0.272	95.1
Ti	190.856	Axial	1.9	0.25	<MDL	0.249	99.7	0.021	0.254	93.3
V	292.402	Axial	0.52	0.25	0.001	0.242	96.7	0.019	0.284	105.9
Zn	213.856	Axial	0.2	1	0.008	1.025	101.7	0.104	1.115	101.1
Zr	343.823	Axial	0.29	0.25	<MDL	0.253	101.3	0.002	0.263	104.3

FIGURE 3. Flowback element reduction.

Flowback elemental reduction over time

Al 167.079 {502} (Axial)
Cr 284.325 {119} (Axial)
P 177.495 {490} (Axial)
S 182.034 {485} (Axial)
Si 251.611 {134} (Axial)
V 311.071 {108} (Axial)
Zn 213.856 {458} (Axial)
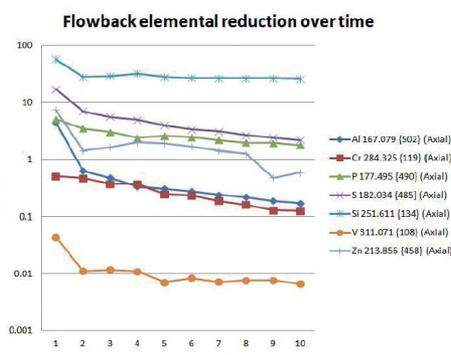
FIGURE 4. Flowback element increase.

Flowback water elemental increase over time

Ba 234.758 {144} (Radial)
Ca 315.887 {107} (Radial)
K 766.490 {44} (Radial)
Li 670.784 {50} (Radial)
Mg 279.079 {121} (Radial)
Mn 259.373 {130} (Axial)
Na 330.237 {102} (Radial)
Sr 346.446 {97} (Radial)
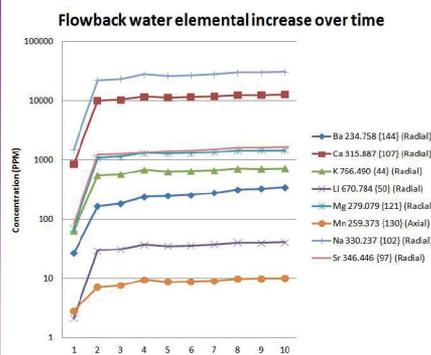
The ICP-OES analysis of the fortified samples using EPA Method 200.7 (Table 3) shows that all spike recoveries are within acceptable limits of +/- 10% of the target values. The method detection limits obtained for all elements are below 10 µg/L with the exception of potassium and magnesium, both of which were found at significantly higher concentrations in the samples. The analysis of the flowback waters show that elements fall into two groups: those that decrease over time (Figure 3) and those that increase over time (Figure 4). It is likely that the elements that decrease over time are being absorbed by the shale substrates, whereas the elements increasing are being leached, which could cause a possible issue when disposing the flowback waters.

FIGURE 5. The Thermo Scientific iCAP Qc ICP-MS and iCAP 7000 ICP-OES.

Methods and Results for ICP-MS

EPA Method 200.8: Determination of Metals and Trace Elements in Water and Wastes by ICP-MS

The U.S. EPA first developed and published Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in 1994, and updated it with Version 5.5 in 1999. This method is now widely used for the determination of 22 dissolved elements in aqueous matrices (ground, surface and drinking waters) in the U.S. and elsewhere. Samples from fracking activities generally fall within the scope of EPA 200.8 due to the similarity in matrix and requirements for elemental determination. Although ICP-MS measurements using collision and reaction cell technology interference removal is the most accurate approach for multi-elemental analysis, the U.S. Federal Register currently mandates that 200.8 measurements must rely solely on mathematical corrections for interference removal.

Sample Preparation

A predefined Productivity Package for Method 200.8 with all appropriate standards and quality control solutions (QCSs) was employed. All solutions were prepared with 1% Nitric Acid (Fisher Chemicals, Loughborough, UK) according to the instructions in the Productivity Package.

Instrumentation

A Thermo Scientific iCAP Qa ICP-MS was used for all measurements. This method, originally developed for drinking water, was based on analysis without the use of collision cell technology (CCT), although CCT use is not excluded when performing analysis of samples. The iCAP Qa was configured with the standard sample introduction system (Table 4) and a SC-4Q autosampler with FAST valve (ESI, Omaha, NE, USA). The developed method had a complete measurement time of 60 s for uptake, data acquisition, and washout for the 22 elements required by EPA 200.8.

TABLE 4. ICP-MS sample introduction system used.

Parameter	Value
Nebulizer	Glass Concentric
Spray Chamber	Glass Cyclonic
Sample Loop Size	1 mL
Pump Tubing i.d.	Sample 0.38 mm Internal Std 0.38 mm

TABLE 5. ICP-MS plasma and data acquisition parameters.

Parameter	Value
Analysis Mode	Standard
Signal Stabilization Time	15 s
Pump Rate	30 rpm
RF Power	1550 W
Coolant Gas Flow	14 L/min
Auxiliary Gas Flow	0.8 L/min
Nebulizer Gas Flow	0.98 L/min

TABLE 6. ICP-MS QCS and SLRS laboratory control standard (LCS) recovery.

Isotope	Quality Control Solutions			Laboratory Control Standards		
	Spike	Found	Recovery	Certified	Found	Recovery
	(μg/L)	(μg/L)	(%)	(μg/kg)[†]	(μg/L)	(%)
^{9}Be	50	50.3	101.7	0.005*	0.005	100.0
^{27}Al	50	52.8	106.2	49.5	51.6	104.2
^{51}V	50	52.3	106.0	0.317	0.333	104.9
^{52}Cr	50	51.8	104.6	0.208	0.222	106.7
^{55}Mn	50	52.0	104.6	4.33	4.45	102.8
^{56}Fe	500	508.3	102.8	91.2	88.1	96.6
^{59}Co	50	51.8	104.2	0.05*	0.048	96.0
^{60}Ni	50	51.7	104.2	0.476	0.462	97.1
^{63}Cu	500	510.5	102.7	17.4	18.4	105.5
^{66}Zn	500	518.7	104.4	0.845	0.925	109.5
^{75}As	50	50.2	101.3	0.413	0.420	101.8
^{82}Se	50	51.9	104.7	na	0.060	na
^{95}Mo	50	50.1	99.9	0.27	0.23	83.7
^{107}Ag	50	44.9	90.3	na	0.079	na
^{111}Cd	50	49.1	98.9	0.006	0.006	104.3
^{123}Sb	50	49.4	99.5	0.3*	0.315	105.0
^{135}Ba	500	503.7	101.1	14	14.4	103.0
^{201}Hg	5	5.1	101.8	na	0.012	na
^{205}Tl	50	49.8	100.2	na	0.004	na
^{208}Pb	50	50.6	101.8	0.081	0.081	100.0
^{232}Th	50	49.1	98.7	na	0.024	na
^{238}U	50	49.3	99.7	0.093	0.092	98.9
Isotope	**(mg/L)**	**(mg/L)**	**(%)**	**(μg/g)**	**(mg/L)**	**(%)**
^{23}Na	25	25.4	101.9	5.38	5.58	103.7
^{25}Mg	2.5	2.5	101.3	2.54	2.65	107.5
^{39}K	2.5	2.6	105.4	0.839	0.892	106.3
^{43}Ca	25	26.0	104.7	10.5	10.1	96.2

† The LCS-certified values are expressed in w/w and have not been converted into w/v: the density of SLRS-5 is 1.0007 g/mL

* Information values only

An integral part of EPA Method 200 is regular QC checks. The QCS is a second source standard that is used to check the accuracy of the calibration, and must return values to within 10% of the known concentration for each element. During the analysis run, the QCS was analyzed every 10 samples as the Continuing Calibration Verification (CCV) to assess the accuracy of the calibration. All elements measured were found to be accurate to within ± 10% of the known concentration. The certified reference material, SLRS-5, was repeatedly measured as a LCS QC throughout the analytical run. All concentration data for the reference material (apart from molybdenum) fell within the required +/- 10% concentration window over a wide range of concentrations (Table 7).

Driven by Qtegra ISDS

Single Software Platform for ICP-OES and ICP-MS

In analytical service laboratories where the highest flexibility is required, the use of a single software package on multiple instruments (Qtegra supports the iCAP 6000 and 7000 series ICP-OES as well as the iCAP Q) allows operators to easily move between hardware platforms, eliminating the learning curve.

Qtegra offers powerful quality control and data review features that simplify protracted Methods such as 200.7 and 200.8. Figure 6 shows the signal response for the seven internal standards during a 14-hour analytical run of (>900) natural water samples against EPA Method 200.8 without recalibration, as displayed in the Qtegra software. The internal standard recoveries are well within the 60–125% range defined in Method 200.8.

FIGURE 6. Internal standard recovery (%) over 14 hours of Method 200.8 on an iCAP Q ICP-MS.
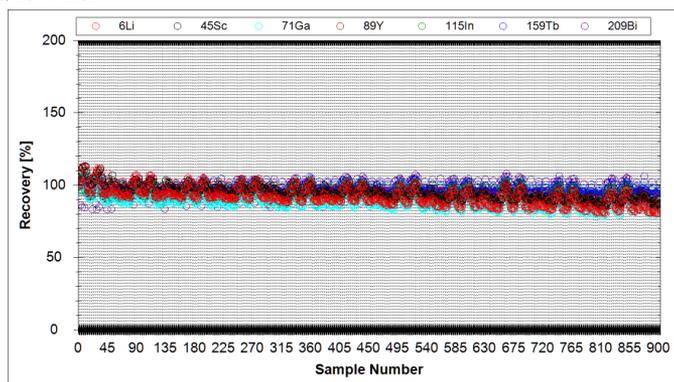
Conclusion

- The iCAP 7000 ICP-OES and the iCAP Q ICP-MS have demonstrated compliance for EPA Methods 200.7 and 200.8, respectively.

- The iCAP 7000 ICP-OES provides robust, accurate, low-cost multielemental analysis in a range of aqueous samples.

- The iCAP Qa ICP-MS offers high productivity, stability, and a high-sensitivity approach for determination of lower analyte concentrations in 60 samples/hr.

- Qtegra ISDS is a common platform for the iCAP 7000 ICP-OES and iCAP Q ICP-MS, offering automated features, predefined method templates, and integrated QC that drive productivity and simplicity in analysis for regulated environments.

Acknowledgements

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