APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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The Analysis of Fracking Fluids with the Optima 8300 ICP-OES

Introduction

As oil prices climbed sharply during the early part of the 2000s, previously non-economically viable methods for extracting oil from the earth were implemented. Among the more popular techniques which saw a rapid growth was hydraulic fracturing, better known as fracking. In this process, a well is drilled vertically into the earth to a certain depth, followed by horizontal drilling. Small explosions are then actuated in the hole to crack the rock to create pathways for the oil to escape. To extract the oil, complex, proprietary fluids are pumped into the hole and then collected along with the oil. These fluids are known as fracking fluids.

The composition of fracking fluids varies widely, depending primarily on the geology of the area being fracked. However, these fluids generally consist of a variety of chemicals and high levels of dissolved solids. The solutions are "clean" prior to introduction into the drill holes, but the post-use solutions contain many more components, including high levels of dissolved organics. As a result, analysis is challenging.

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Because of their complexity, it is important to determine the metal content of fracking fluids, both pre- and post-use; examples of fracking solutions are shown in Figure 1. These analyses are used to evaluate how often the fluids can be reused and the measures that must be taken for safe disposal.

This work focuses on the analysis of commercial fracking fluids with the PerkinElmer Optima® 8300 inductively coupled plasma optical emission spectrometer (ICP-OES). Through the use of proper instrumentation and analytical conditions, these difficult matrices can be successfully analyzed.

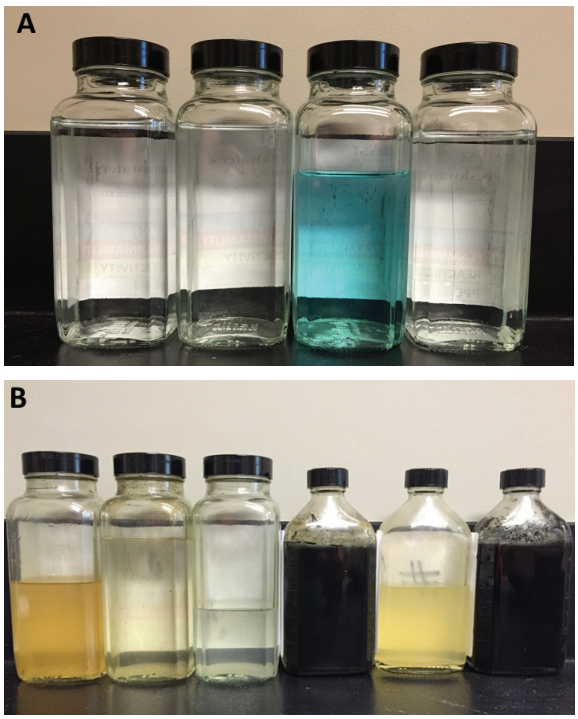

Figure 1. Fracking solutions, pre-use (A) and post-use (B).

Experimental

Samples consisted of fracking fluids acquired from multiple well sites, both from pre- and post-use. Aliquots of the samples were taken beneath the organic layer residing on their surfaces and then diluted 10x with 2% HNO_3 (v/v) and 1% HCl (v/v). The samples were analyzed for the 18 elements shown in Table 1, along with their analytical wavelengths. Yttrium was added to all standards and samples as an internal standard.

All analyses were performed with an Optima 8300 ICP-OES using the conditions in Table 2. The combination of the PFA-ST nebulizer and C2 dual cyclonic spray chamber introduced a fine aerosol which the plasma was able to easily handle. Due to the high salt content of the samples, an argon humidifier was used to prevent salt buildup on the nebulizer and injector tips. Flat Plate™ plasma technology, which comes standard on the Optima 8300, allowed for the use of low-argon plasma flows. Additionally, the HybridXLT™ quartz/ceramic torch (PerkinElmer Part Number N0780128) is more robust than conventional quartz torches, resulting in significantly longer lifetimes when analyzing highly complex samples.

Table 1. Elements and Analytical Wavelengths.

Element	Wavelength (nm)
Aluminum (Al)	396.153
Boron (B)	249.677
Barium (Ba)	413.065
Calcium (Ca)	315.887
Chromium (Cr)	267.716
Copper (Cu)	327.393
Iron (Fe)	238.204
Lead (Pb)	220.353
Magnesium (Mg)	285.213
Manganese (Mn)	257.610
Molybdenum (Mo)	202.031
Nickel (Ni)	231.604
Phosphorus (P)	213.617
Potassium (K)	766.490
Silicon (Si)	251.611
Sodium (Na)	330.237
Strontium (Sr)	460.733
Zinc (Zn)	206.200

Table 2. Instrumental Parameters.

Parameter	Value
Nebulizer	PFA-ST
Spray Chamber	C2 Dual Cyclonic
Sample Uptake Rate	0.5 mL/min
Peristaltic Pump Tubing	Tygon, black/black
Injector	1.6 mm sapphire
Torch	HybridXLT quartz/ceramic
Plasma Flow	10 L/min
Aux Flow	0.2 L/min
Nebulizer Flow	0.7 L/min
RF Power	1500W
Viewing Distance	15 mm
View	Radial

Measurements were made against external calibration curves with standards prepared in the diluent. It was found most effective to prepare the calibration standards in two groups from single element standards at the levels specified in Table 3. All calibrations curves resulted in $R^2 > 0.999$.

Table 3. Calibration Standards (all units in mg/L).

Group	Element	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
1	Al	0.25	1.00	5.00	12.5	50.0	—
	Ba	5.00	20.0	100	250	1000	—
	Cr	0.25	1.00	5.00	12.5	50.0	—
	Cu	0.25	1.00	5.00	12.5	50.0	—
	Mn	0.25	1.00	5.00	12.5	50.0	—
	Mo	0.25	1.00	5.00	12.5	50.0	—
	Na	25.0	100	500	1250	5000	10000
	Ni	0.25	1.00	5.00	12.5	50.0	—
	P	0.25	1.00	5.00	12.5	50.0	—
	Pb	0.25	1.00	5.00	12.5	50.0	—
	Sr	5.00	20.0	100	250	1000	—
	Zn	0.25	1.00	5.00	12.5	50.0	—
2	B	0.50	2.00	10.0	25.0	100	—
	Ca	25.0	100	500	1250	5000	—
	Fe	0.50	2.00	10.0	25.0	100	—
	K	5.00	20.0	100	250	1000	—
	Mg	5.00	20.0	100	250	1000	—
	Si	0.50	2.00	10.0	25.0	100	—

Results and Discussion

To establish the lower limits of each element which can be measured, method detection limits (MDLs) were first determined. For MDL analysis, one of the samples was diluted 10x, spiked with low levels of the elements, and run with ten replicates. The resulting standard deviation was then multiplied by 3.169 (student's t-test), followed by another multiplication by ten to account for the dilution factor. The resulting MDLs, along with the spike levels for each element, are shown in Table 4. For most elements, the MDLs are less than 1 mg/L.

With the MDLs established, the samples were then analyzed, with the analytical results shown in Table 5. A broad range of elemental concentrations were observed, from some elements not being detected in most samples (such as Cr, Cu, and Ni), to other elements being present at high concentrations (such as Mg, Na, and K, indicative of brines). The robustness of the plasma is indicated with the internal standard recoveries (i.e. Y) being greater than 80% for all samples.

Since fracking fluids vary greatly, there are no certified reference materials available. Therefore, the accuracy of the method was assessed by spiking the samples and measuring the recoveries, with the results being displayed in Table 6. The accuracy of the method is demonstrated by all recoveries being within +/- 15%, with the majority being within 5% of the spiked value.

Table 4. Method Detection Limits.

Element	Spike (mg/L)	MDL (mg/L)
Al	0.25	0.57
B	0.5	0.35
Ba	5	1.92
Ca	25	27.2
Cr	0.25	0.18
Cu	0.25	0.17
Fe	0.5	0.44
K	5	2.96
Mg	5	2.45
Mn	0.25	0.14
Mo	0.25	0.30
Na	25	25
Ni	0.25	0.31
P	0.25	1.11
Pb	0.25	0.89
Si	0.5	0.40
Sr	5	2.86
Zn	0.25	0.21

Table 5. Results of Fracking Fluid Analysis (all units in mg/L).

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Al	0.68	0.89	—	—	—	—	—	—	—	—
B	17.0	20.5	39.6	61.0	—	—	—	38.5	38.7	34.2
Ba	—	—	12.9	7.65	—	—	—	—	—	—
Ca	8540	9680	30800	656	53.2	346	45.3	1180	1260	1150
Cr	—	—	—	—	—	—	—	—	—	—
Cu	—	—	—	—	—	—	—	—	—	—
Fe	0.50	1.32	0.82	—	—	—	—	12.5	13.1	15.9
K	912	910	1350	188	4.16	15.0	3.21	279	267	224
Mg	1660	1600	4440	—	11.3	151	9.64	164	175	146
Mo	—	—	—	—	—	—	—	—	—	—
Mn	0.26	0.28	10.0	0.05	—	—	—	0.87	1.10	0.59
Na	70100	55700	67300	14700	42.5	598	55.7	22600	22200	19540
Ni	—	—	—	—	—	—	—	—	—	—
P	—	—	—	—	—	—	—	—	—	—
Pb	1.84	—	0.68	—	—	—	—	—	—	—
Si	10.0	9.49	3.15	26.3	17.7	21.8	16.8	21.5	25.7	26.6
Sr	193	229	1570	185	—	7.21	—	110	124	124
Zn	—	—	—	—	—	0.41	—	1.52	—	0.21
Y (IS)	87%	86%	82%	91%	95%	96%	95%	88%	85%	84%

— = < MDL

Table 6. Spike Recoveries in Fracking Fluids.

Element	Spike (mg/L)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Al	5	105%	106%	107%	103%	103%	104%	106%	105%	106%	108%
B	10	88%	91%	89%	95%	94%	95%	96%	95%	95%	98%
Ba	10	95%	99%	97%	100%	99%	100%	102%	101%	101%	101%
Ca	2000	102%	98%	103%	102%	97%	104%	104%	104%	102%	102%
Cr	5	100%	101%	95%	103%	102%	103%	105%	102%	102%	106%
Cu	5	102%	104%	103%	101%	99%	101%	101%	102%	96%	105%
Fe	10	103%	105%	98%	106%	105%	106%	107%	105%	107%	109%
K	100	105%	108%	113%	101%	95%	96%	98%	103%	104%	105%
Mg	10	106%	108%	108%	111%	109%	111%	113%	113%	111%	113%
Mn	5	101%	103%	98%	103%	103%	104%	105%	103%	104%	105%
Mo	5	101%	103%	99%	104%	102%	102%	105%	102%	104%	104%
Na	5000	98%	101%	92%	100%	98%	99%	98%	103%	99%	100%
Ni	5	101%	103%	98%	106%	105%	105%	108%	104%	105%	106%
P	5	100%	106%	111%	109%	104%	104%	110%	107%	105%	108%
Pb	5	92%	104%	94%	101%	101%	99%	102%	101%	98%	103%
Si	10	107%	109%	108%	106%	105%	106%	107%	107%	107%	110%
Sr	150	108%	110%	97%	104%	99%	101%	102%	106%	106%	107%
Zn	5	97%	98%	89%	101%	100%	100%	102%	100%	101%	103%

The robustness of the methodology was evaluated by analyzing all samples repeatedly over nine hours. Figure 2 shows the stability plot of one of the post-fracking samples, which was analyzed every 30 minutes throughout the run. In this plot, each analysis is normalized to the first measurement. The results indicate exceptional stability, with results within 10% of the original measurement. It was noted that Ba started falling out of solution after five hours, verified by using two different wavelengths and observing the same results for each.

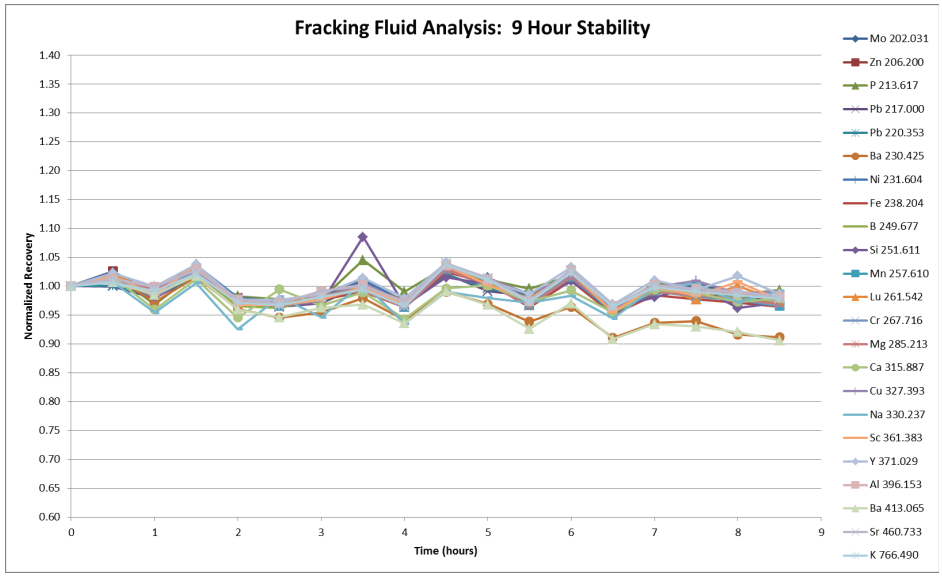

Figure 2. 8.5-hour stability plot of a post-fracking sample during a 9-hour run of all the fracking fluid samples. Results are normalized to the first reading.

Conclusions

This work has demonstrated the ability of the Optima 8300 ICP-OES to accurately measure samples with both high salt and organic content, in the form of fracking fluids. The robustness of the method is demonstrated through long-term stability with minimal drift and minimal suppression of the internal standard. The decision to use the HybridXLT quartz/ceramic torch significantly extends the torch lifetime when analyzing high-matrix samples, resulting in more time spent performing analyses and less downtime with instrument maintenance.

Consumables Used

Component	Part Number
Black/Black Tygon Pump Tubing	09908587
Gray/Gray Pharmed Pump Tubing	N0777444
PFA-ST Nebulizer	N0777049
C2 Dual Cyclonic Spray Chamber	N0782012 (quartz) N0782011 (glass)
1.5 mm Sapphire Injector	N0782004
HybridXLT Quartz/Ceramic Torch	N0780128
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Aluminum Pure-Grade Standard, 1000 mg/L	N9300184 (125 mL) N9300100 (500 mL)
Barium Pure-Grade Standard, 1000 mg/L	N9300181 (125 mL) N9300103 (500 mL)
Calcium Pure-Grade Standard, 1000 mg/L	N9303763 (125 mL) N9300108 (500 mL)
Chromium Pure-Grade Standard, 1000 mg/L	N9300173 (125 mL) N9300112 (500 mL)
Copper Pure-Grade Standard, 1000 mg/L	N9300183 (125 mL) N9300114 (500 mL)
Iron Pure-Grade Standard, 1000 mg/L	N9303771 (125 mL) N9300126 (500 mL)

Component	Part Number
Lead Pure-Grade Standard, 1000 mg/L	N9300175 (125 mL) N9300128 (500 mL)
Magnesium Pure-Grade Standard, 1000 mg/L	N9300179 (125 mL) N9300131 (500 mL)
Manganese Pure-Grade Standard, 1000 mg/L	N9303783 (125 mL) N9300132 (500 mL)
Molybdenum Pure-Grade Standard, 1000 mg/L	N9303784 (125 mL) N9300134 (500 mL)
Nickel Pure-Grade Standard, 1000 mg/L	N9300177 (125 mL) N9300136 (500 mL)
Phosphorus Pure-Grade Standard, 1000 mg/L	N9303788 (125 mL) N9300139 (500 mL)
Potassium Pure-Grade Standard, 1000 mg/L	N9303779 (125 mL) N9300141 (500 mL)
Silicon Pure-Grade Standard, 1000 mg/L	N9303799 (125 mL) N9300150 (500 mL)
Sodium Pure-Grade Standard, 1000 mg/L	N9303785 (125 mL) N9300152 (500 mL)
Strontium Pure-Grade Standard, 1000 mg/L	N9303802 (125 mL) N9300153 (500 mL)
Zinc Pure-Grade Standard, 1000 mg/L	N9300178 (125 mL) N9300168 (500 mL)

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