

# **ANALYTICAL CHARACTERIZATION OF FLOWBACK WATERS IN THE FIELD**

Andrea Shramko  
Tor Palmgren  
Daniel Gallo  
Rahul Dixit  
M-I SWACO

## **ABSTRACT**

As the development of unconventional gas sources increases, larger amounts of fresh water are needed in fracturing operations and more flowback water is being produced. Water use in various gas shale plays is becoming an issue due to limited availability of water resources, transportation issues, contamination concerns and regulatory pressures. Operators and services companies, therefore, increasingly seek ways to reuse the flowback water generated from fracturing operations so as to minimize the environmental and economical impact. Frequently, the additives in fracturing fluids are not compatible with the flowback water thus necessitating treatment before reuse. Understanding the composition of the flowback water is key to determining the extent of required treatment.

Flowback waters are generally characterized by significant amounts of heavy metals, hardness, solids, salts, organic elements, polymers, biocides and traces of oils. Although various analytical techniques exist in the lab for their characterization, one of the greatest challenges is to analyze these waters in the field to enable rapid and reliable monitoring that allows for efficient decision making regarding required treatment or safe disposal. This paper reviews strengths and limitations of field techniques for characterization of flowback water, including colorimetric, titrimetric and absorbance methods.

## **INTRODUCTION**

Significant deposits of natural gas exist in North America and around the world in numerous shale regions such as Barnett, Marcellus, Haynesville, Fayetteville to name a few. While well known to the oil and gas industry, these shales have not received close attention from natural gas operators until relatively recently due to inherent technical challenges related to their low permeability. However, there has been a growing interest in pursuing these resources during the last fifteen years with the onset of nonconventional drilling techniques using horizontal drilling coupled with oil well stimulation methods commonly referred to as hydraulic fracturing. Fracture fluids can be oil-based or water-based. However, water-based fluids are the most common and least expensive and up to 90% or more of the fracturing fluid formulation is composed of water.

In a given well, one fracturing job can involve the injection of as much as 100,000 barrels of water and may require additional fracturing to maximize yield. In the first three weeks of the hydraulic fracturing process, approximately 20 - 30% of the water used to fracture the well comes back to the surface and is called flowback water. It is generally contaminated with spent fracturing fluid chemicals and substances present in the shale itself. Until recently, and depending on location of the fracturing job, sourcing has been from surface waters and municipal water treatment facilities and discharging of the flowback water into disposal wells. However, reconstitution and reuse of flowback water for future fracturing operations presents advantages in the form of reduced fresh water quantities for fracturing operations and for the need of disposal options, with the concomitant reduction in operational cost and issues related to environmental and regulatory concerns.

The flowback water is contaminated with suspended and dissolved solids, with the concentrations varying depending on location. Typical concentration ranges for such contaminants are captured in Table 1. Additional contaminants include traces of oil, bacteria, polymers and fracturing fluid chemicals. The goal of the flowback water treatment is to produce clear and largely desalinated water with minimum tendency to interfere with fracturing fluid components or with the shale formation. The degree of necessary desalination depends of the chemistry of the fracturing fluid and can range typically from 1,000 to 10,000 ppm total dissolved solids (TDS), although research has been cited in the literature regarding the development of fracturing fluid chemistries compatible with unaltered flowback water containing TDS levels up to 150,000 ppm.

In the field, flowback is treated in stages involving pretreatment and desalination steps. Desalination treatment approaches include membrane and thermal technologies and the necessary level of pretreatment depends on the selected desalination method. Membrane technologies require the removal of oil, hardness, bacteria, and total suspended solids (TSS) due to scaling and potential fouling of the membrane surfaces. Thermal technologies are less susceptible to some of the contaminants, yet are sensitive to hardness and TSS because of scaling issues. In addition, the concentration of divalent ions in the water such as barium, calcium and magnesium may cause scaling and plugging of the formation and therefore need to be removed from the flowback water. Understanding the composition of the flowback water is essential in determining the extent of required treatment.

While all water analyses required to characterize the flowback water before, during and after treatment can be performed at off-site laboratories, it is clear that the greatest challenge is to analyze the flowback water in the field in order to enable rapid and reliable monitoring for efficient decision making regarding required treatment, treatment performance or reuse, and safe disposal.

Laboratory methods for analysis of flowback water range from titration to spectroscopic determinations such as atomic absorption (AA) and inductively coupled plasma (ICP), X-Ray Fluorescence (XRF); in some cases, these methods are cited as standard ASTM methods or practices. However, field operations for flowback water treatment frequently require evaluation techniques that are less delicate and easier to mobilize and use, yet are adequately accurate and reliable to permit operators and service providers to monitor key operational variables for timely process adjustment to ensure that target objectives are achieved. Available field methods, the subject of this paper, are typically based on colorimetric, conductometric and titration techniques.

**Table 1.** Approximate Flowback Water Contaminant Ranges

Contaminants	Concentration Range (ppm)	Contaminants	Concentration Range (ppm)
Alkalinity	100 - 600	Iron	50 – 300
Calcium	500 – 12,000	Silica	50 - 300
Magnesium	50 – 2,000	Sulfate	10 – 400
Barium	50 – 9,000	Chloride	5,000 – 80,000
Strontium	50 – 6,000	TDS	1,000 – 150,000
Sodium	4,000 – 40,000	TSS	1,000 – 7,000

## EXPERIMENTAL METHODS AND MATERIALS

### Sample Collection

Flowback water samples were collected in clean polypropylene containers from different shale locations in North America and shipped to the laboratory where both field techniques and analytical methods were used in their characterization. For preservation purposes, prior to shipment the samples were spiked with nitric acid and kept at 43°F (6°C) in accordance with EPA Guidelines Establishing Test Procedure for the Analysis of Pollutants under the Clean Water Act (CFR 40, Part 122, 136, et al.) as briefly summarized in Table 2. Samples were held at room temperature (68°F/20°C) before the analysis.

**Table 2.** Summary of Collection and Preservation Methods  
in Accordance with EPA Test Procedure Guidelines  
(40 CFR, Part 122, 136, et al.)

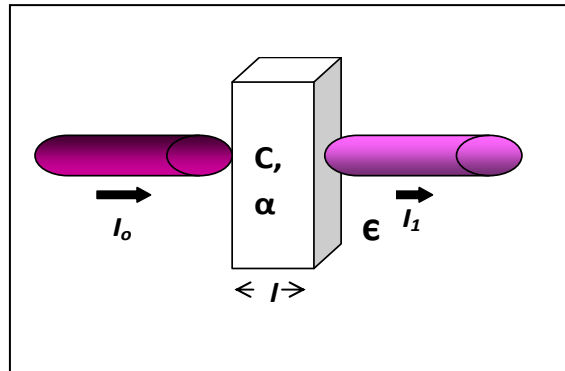
Analyte	Acid Preservation/ Temperature	Storage Time
Alkalinity	6°C*	14 days
Hardness and Metals	Preservation pH ≤2 Nitric Acid (1.5 ml/L)/NA	Up to 6 months
Chloride	NA	Up to 28 days
Silica	NA/6°C	Up to 28 days
Sulfate	NA/6°C	Up to 28 days
* No acid preservative needed.		

### Testing Methods

Field analytical methods and laboratory analysis were employed in this study. The analytical determinations were done for benchmarking purposes. For the laboratory characterization AA and in some instances ICP was used for aluminum, barium, calcium, magnesium, manganese and silica, whereas ion chromatography (IC) was used for determining anionic species such as sulfate and chloride. Additionally, the laboratory

used titration for chloride and alkalinity, and gravimetric methods for TSS and TDS. For the field analysis, colorimetric methods were used for the analysis of aluminum, barium, calcium, chloride, iron, magnesium, manganese, sulfate and silica. Titration methods were used for alkalinity, chloride, calcium and magnesium. Conductivity was used to evaluate TDS. Turbidity measurements were used in lieu of TSS measurement for the field due to the lack of a suitable field TSS method.

The principle of colorimetric analysis involves the introduction of a reagent that produces a color when reacting with the element to be analyzed. The intensity of the color is proportional to the amount of that element in the specimen. The concentration of the element can be quantified in accordance with the Lambert-Beer Law by passing a light beam through the specimen as depicted in Figure 1.



**Figure 1.** Schematic of the Lambert-Beer Law

The concentration is automatically computed by the colorimetric spectrometer using the Lambert-Beer equation shown below:

$$A = -\log\left(\frac{I_1}{I_0}\right) = \epsilon c l$$

where:

A: Absorbance

$I_0$ : Initial intensity

$I_1$ : Transmitted intensity

C: Extinction coefficient

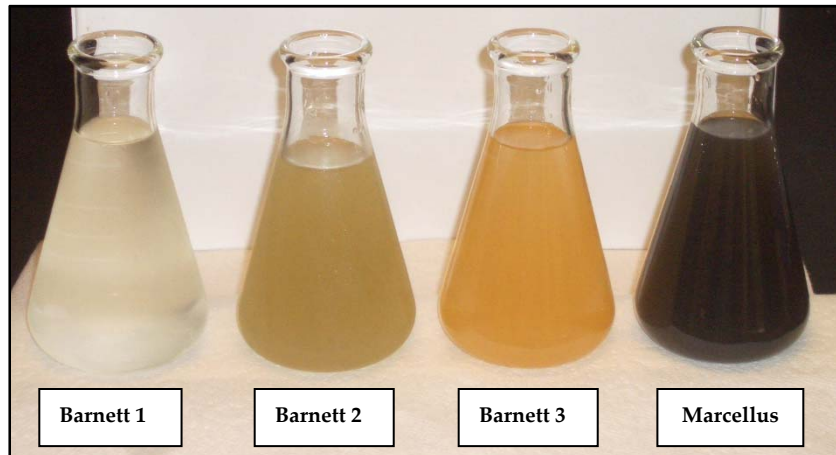
Any preexisting color in the sample to be analyzed would interfere and will adversely affect the result of the colorimetric test. Flowback water is not always colorless and also typically turbid, which can cause interferences when using colorimetric techniques. Samples collected during the course of our analysis are depicted in Figure 2. In order to eliminate interference due to the color or turbidity of the analyzed samples, dilution techniques and filtration using a 0.45  $\mu\text{m}$  filter were implemented. In addition to optical interferences, chemical interferences can also occur due to the presence of one or more elements that can react with the reagent added to produce the color or with the target analyte obscuring the true intensity of the color attributed to the concentration of

the analyte of interest. Chemical interferences associated with the analytes investigated in this study are summarized in Table 3.

The principle of turbidimetric analysis involves the introduction of a reagent that produces a precipitate when reacted with the element to be analyzed, such as for the determination of barium and sulfate. The turbidity relies on detecting the transmittance of the light through the suspension and any inherent precipitate in the sample. Interferences are similar to those observed in the colorimetric methods. Chemical interferences associated with the analytes investigated in this study are summarized in Table 3.

Conductivity methods measure the overall conduction associate with ions present in the water. The output of conductivity measurement, if given in units of microsiemens per centimeter ( $\mu\text{s}/\text{cm}$ ), can be used to calculate concentration of TDS in the water in accordance with the following formula:

$$\text{TSD (ppm)} = \text{Conductivity } (\mu\text{s}/\text{cm}) \times 0.67$$



**Figure 2.** Flowback Water Samples from Different Shales and Locations

**Table 3.** Chemical Interferences Factors for Colorimetric Analysis of Flowback Waters

Analyte	Interferences
Aluminum	alkalinity
Barium	calcium, magnesium, silica, sodium chloride and strontium.
Chloride	pH below 3 or above 10.
Iron	calcium, chloride, magnesium, pH below 3 or above 10.
Magnesium	chromium, copper, iron, manganese and zinc.
Manganese	calcium, chloride, magnesium, iron, and pH below 3 or above 10.
Silica	phosphate and sulfide
Sulfate	calcium, magnesium, chloride and silica.

Titration methods are used in this study for quantification of alkalinity and as an alternative method for quantification of chloride, calcium and magnesium. Interferences for this method are similar to those in the aforementioned section.

Differences in temperature and time of conducting the analysis are sources of error for colorimetric and turbidimetric methods. Measures to control these parameters should be taken in the field for the analysis. Recommended temperatures are 68 – 77°F (20 – 25°C). These conditions were controlled in our study. Reaction times were monitored for each chemical added in the colorimetric and turbidimetric methods.

The concentration ranges for the field test methods vary widely by analyte and are summarized in Table 4. Therefore, it is frequently necessary to dilute the samples 100- or 1,000-fold depending on the concentration of the analyte in the sample and the chemical interferences. Some trial and error experiments are usually required to hone into the proper dilution level. For this study, dilutions as high as 1:10,000 were used for ions such as calcium, magnesium and chlorides due to their high concentration in the flowback waters.

**Table 4.** Field Analysis Concentration Ranges

Analyte	Range (mg/L)
Alkalinity	10 to 4,000
Iron	0.02 to 3.00
Aluminum	0.008 to 0.8
Calcium	0.05 to 1
Magnesium	0.05 to 0.25
Total Hardness (Titration for Ca and Mg)	10 to 4,000
Barium	2 to 100
Chloride (colorimetric)	0.1 to 25
Chloride (titration)	10 to 10,000
Manganese	0.1 to 20
Silica	1 to 100
Sulfate	2 to 70

## Sample Preparation

The samples were equilibrated to room temperature prior to analysis and subsequently filtered through a 13-mm diameter, 45- $\mu$ m PVDF syringe filter to remove suspended solids to reduced interference with the analyses. The filtration was done for two reasons: first to duplicate the procedure used by the analytical lab, and secondly to remove TSS and all coarse contaminants that are usually removed during prefiltering stages prior to the actual flowback water treatment. Also, the samples were diluted to eliminate chemical and any other sources of interference and to be within the range specified by a given method.

## Equipment and Materials

The experiments were conducted using a standard water quality field test kit. The equipment included in the test kit and used for this study included a combined pH/conductivity probe, turbidimeter, spectrometer, volumetric flasks (10, 50 and 100 mL), a micropipette adjustable 0.1 to 1 mL, 10-mL pipette and 1-in/10-mL square glass

sample cells. Chemical reagents in sealed aluminum packets were provided in the test kit. An instruction manual with a detailed test protocol was provided and validated during the experiments. The water quality field test kit was selected due to its portability, compactness and ability to provide methods for a wide range of analytes present in flowback water.

## RESULTS

For the first round of experiments flowback water from Barnett Shale (Barnett 2) was tested using the field test kit, one day after sample collection including transportation and storage. The same sample was tested the following day by the analytical laboratory. At collection and for subsequent storage the sample was preserved in ice and brought to room temperature prior to analysis.

After detecting discrepancies between the two data sets, it was decided that the field testing instrument needed to be tested for accuracy. Instrument accuracy was verified after running standard solutions of the ions of concern. For barium, an additional experiment was conducted to understand the interference with strontium for the method. Results for the barium method indicated that strontium would interfere strongly at concentrations higher than 100 ppm, subsequently increasing exponentially as the strontium concentration increases. After the potential instrument issues, the same sample was reanalyzed 26 days after collection by both the analytical lab and using the field test kit. Also, during the evaluation, it was noted that more accurate results were achieved by using volumetric flasks rather than graduated cylinder during the sample preparation. This was attributed to the precise calibration of the volumetric flask. Results for the first and second round of experiments are depicted in Table 5. Results for the field test kit using standards are shown in Table 6.

**Table 5.** Comparison of Analytical Laboratory and Field Test Kit Results

Analyte	First Run (1 and 2 days after collection)		Second Run (26 days after collection)	
	Field (mg/L)	Analytical (mg/L)	Field (mg/L)	Analytical (mg/L)
Alkalinity	640	510	NA	NA
Iron	21.9	12	10	7.8
Aluminum	0.098	<0.1	0.021	<0.05
Calcium	450	1,260	1,157	1,450
Magnesium	1,320	171	181	172
Barium	47	12	25	10
Strontium	-	275	-	-
Chloride (colorimetric)	16,200	16,800	16,300	16,700
Chloride (titration)	18,650		NA	
Manganese	2.0	0.27	40	1.9
Potassium	0.0	90	105	91
Silica	159	20	58.8	33
Sulfate	500	169	180	174

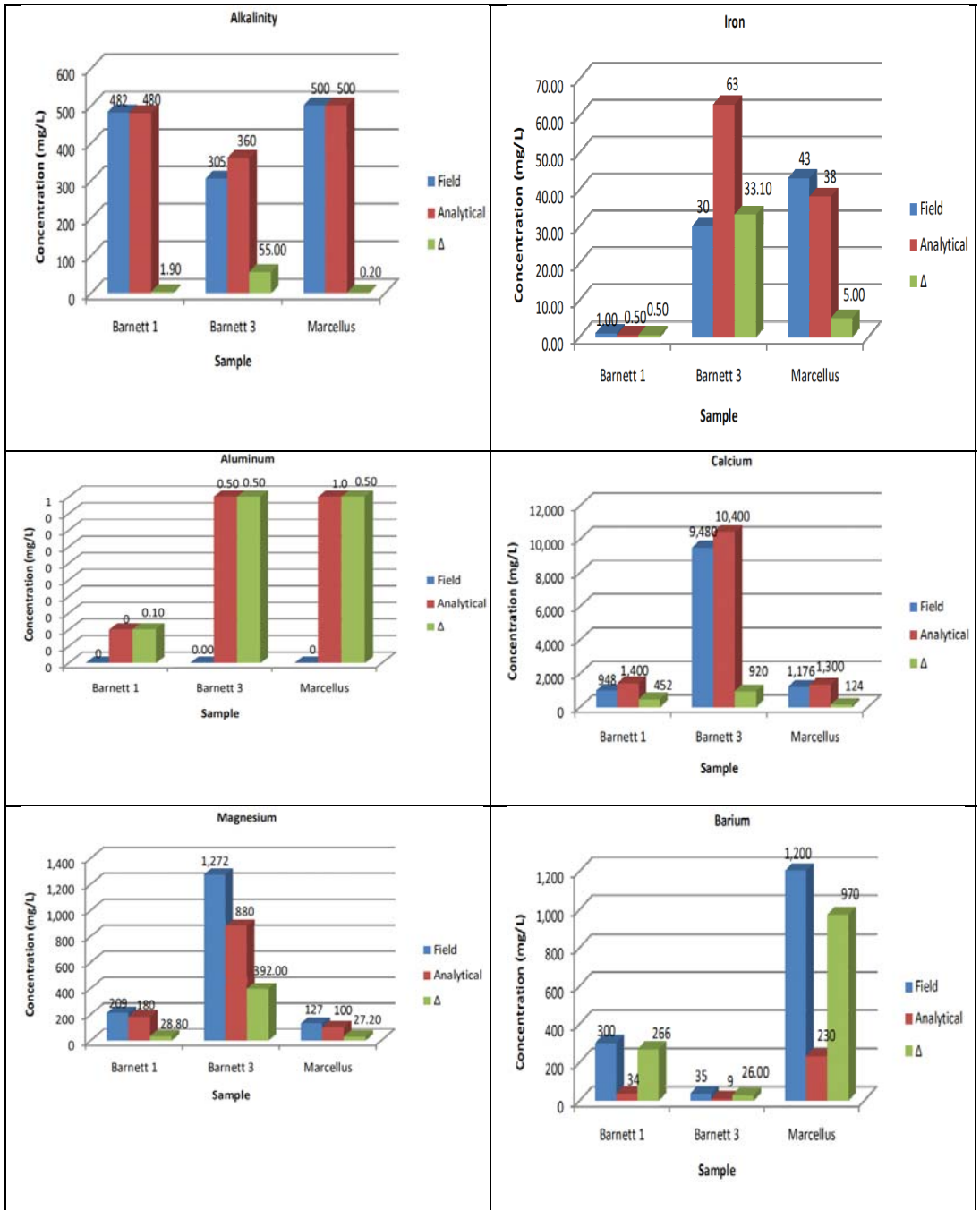
**Table 6.** Standard Analysis for Verification of Field Test Kit

Analyte	Concentration (mg/L)	Standard Concentration (mg/L)
Barium	10	13
Strontium	100	1
	150	2
	200	44
Calcium <sup>1</sup>	1,000	1,240
Calcium <sup>2</sup>		1035
Magnesium <sup>1</sup>	100	70
Magnesium <sup>2</sup>		97
Manganese	2.0	2.6
Silica <sup>2</sup>	1,000	1,050
Sulfate	100	94
Notes:		
1. Results using graduated cylinder for dilution		
2. Results using volumetric flasks for dilution		

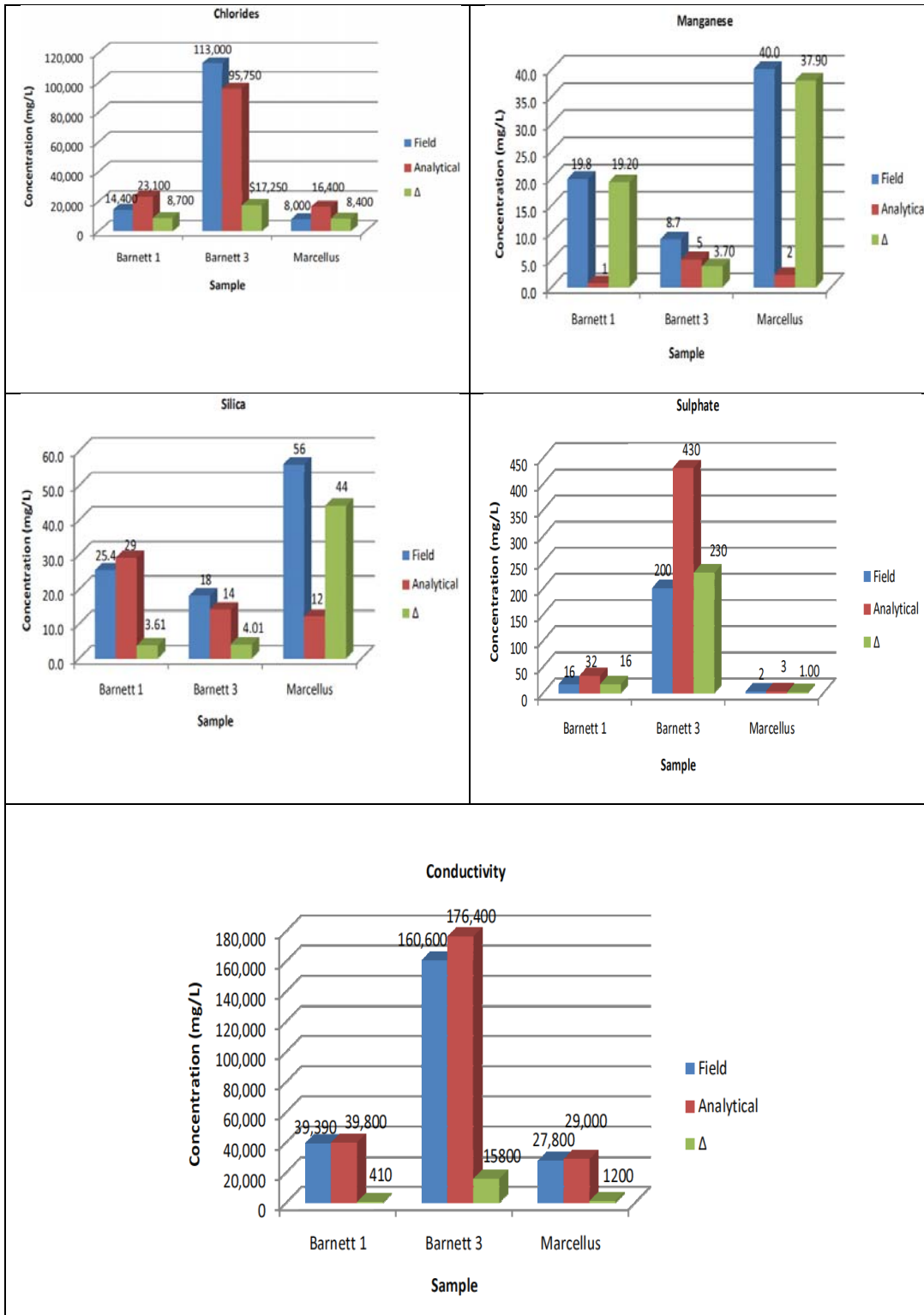
After verification of proper operation of the instrument, various flowback water samples were analyzed both by the laboratory and using the test field kit. The results are summarized in Table 7 and Figures 3a and 3b.

**Table 7.** Analytical and Field Test Kit Results for Various Flowback Waters

Analyte	Barnett 1		Barnett 3		Marcellus	
	Field (mg/L)	Analytical (mg/L)	Field (mg/L)	Analytical (mg/L)	Field (mg/L)	Analytical (mg/L)
Alkalinity	482	480	305	360	500	500
Iron	1.00	0.50	30	63	43	38
Aluminum	<0.008	<0.1	0.00	0.50	<0.008	1
Calcium	948	1,400	9,480	10,400	1,176	1,300
Magnesium	209	180	1,272	880	127	100
Chloride	14,400	23,100	113,000	95,750	8,000	16,400
Manganese	19.8	1	8.7	5	40.0	2
Silica	25.4	29	18.0	14	56.0	12
Sulfate	16	32	200	430	<2	3
Conductivity/ TDS	39,390	39,800	160,600	176,400	27,800	29,000
Turbidity (NTU)	11	-	264	-	319	-
pH	7	-	6	-	7	-
Temperature (°C)	20	-	20	-	19	-



**Figure 3a.** Analytical and Field Test Kit Results for Various Flowback Waters



**Figure 3b.** Analytical and Field Test Kit Results for Various Flowback Waters

The results indicated relatively minor discrepancies between the two methods for alkalinity, calcium and TDS as measured by conductivity. Rather significant differences were observed for the remaining analytes. In the case of iron, the Barnett 1 and Marcellus

samples showed similar results between the two methods whereas some deviation was seen for the Barnett 3 sample. The Barnett 3 sample presented a reddish color indicating iron precipitation, which could account for the lower reading using the field method requiring a 3-minute waiting period for chemical reaction with the colorimetric reagent whereas the atomic absorption techniques used in the analytical lab atomizes the sample avoiding the issue of precipitation. For aluminum, the discrepancy may be exaggerated due to the fact that the concentrations appear to be below the detection limits for both methods used. For magnesium, Barnett 1 and Marcellus samples results were relatively consistent between the two methods, whereas a greater discrepancy was observed for the Barnett 3 sample. A possible reason is the concentration of the sample was higher than 0.25 mg/L, which is the maximum concentration allowed for the method to obtain accurate results. Further dilution would have been required for the sample.

Regarding barium, the field method is not feasible due to unavoidable interference from the presence of strontium in the samples. For chloride, results obtained for all samples are inconsistent requiring further investigation. With respect to manganese, there were difficulties in making an accurate assessment of the violet color to be developed in the presence of manganese. Therefore, there could be issues with manganese regarding the use of colorimetric techniques. Further studies are needed. In the case of silica, the Barnett 1 and Barnett 3 samples appeared to exhibit similar results for both methods, whereas significant deviation was seen for the Marcellus sample, which may be attributable to the presence of sulfide in the sample. Although an analysis for sulfides was not performed on the Marcellus sample, it exhibited an unpleasant sulfur odor. Furthermore, the sulfate content in the Marcellus was not detectable, indicating the speciation of sulfur was towards sulfides. For sulfate analysis, discrepancies were observed between the methods and additional investigation is required to elucidate the causes.

## **CONCLUSIONS AND RECOMMENDATIONS**

Four flowback water samples were evaluated for a string of analytes both by analytical laboratory techniques and by a field test kit. The purpose was to assess the feasibility of using the field test kit during flowback water treatment operations in the field. Comparison of the results indicates that additional work is needed to assess the implementation of the field instrument for analysis of chloride, iron, magnesium, silica, sulfate and manganese. The field method for barium is not appropriate for the analysis of barium due to interferences with strontium that is generally present in flowback waters. Research should be undertaken to develop a suitable field method to analyze barium and strontium, another common constituent in flowback waters. Current methods for these two analytes involve coprecipitation by sulfate thus masking the quantification of either one. For alkalinity, calcium and TDS the field test methods appear to be reliable to guide in assessing progress and performance and in decision making during treatment processes.

It is recommended that a more in-depth study involving statistical analysis to determine repeatability of the field methods be pursued.

## REFERENCES

Bergman, Elaine. *Techniques for Water Analysis*. The Royal Australian Chemical Institute, August 2009.

Laidler, Kith. *The World of Physical Chemistry*. Oxford University Press. 1993.

American Water Works Association. *Standard Methods for the Examination of Water and Wastewater*. Fifth Edition. 2005