



QA/QC and Method Performance Considerations for Chemical Testing: Samples Impacted by HF Fluids

EPA Hydraulic Fracturing Technical Workshop
Arlington, Virginia
February 24 - 25, 2011

David Thal – Senior Technical Chemist
Environmental Standards, Inc.



Not

disabilities. If you need assistance accessing any information in this document, please contact

ORD_Webmaster@epa.gov.



Today's Discussion

- QA/QC for EPA-funded projects as a model
- Critical elements of environmental testing QA/QC
- Types of analytical methods being routinely applied
- Types of QA/QC demonstrations and QA/QC samples
- Rough Guide: What QA/QC is needed?
- Specific information on interferences encountered
- Summary



Elements of QA/QC

- **Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4**
- “The principal DQIs are precision, bias (accuracy), representativeness, completeness, comparability, and sensitivity.”
- **EPA Requirements for Quality Assurance Project Plans EPA QA/R-5**
- References “PARCC” parameters

Are the PARCC Parameters Sufficient?

Precision (Test-retest reliability)

Accuracy (Comparison of result to consensus value)

Representativeness (Does sample reflect population?)

Completeness (Data of good quality on a sufficient percentage of samples?)

Comparability (Does the data set make sense within broader data sets?)

- What about **Sensitivity**?
(EPA QA/G-4 mentions it. Among 10 states and agency guidance documents checked only Connecticut lists it – as PARCCS)
- What about **Selectivity**?
(Buried in the methods or the minds of analytical chemists.)
- SPARCCS would be a better mnemonic.

Frequently Encountered Types of Method – Related to Shale Gas

- **Classical Chemistry** - pH, TKN, Anions, Alkalinity, Hardness, HEM (oil and grease)
- **Gas Chromatography** - Methane, Ethane, Gasoline, Diesel and Oil Range Organics,
- **Metals Determinations** - Alkali Metals. Divalent and other metals including Mercury.
(ICP-AES, ICP-MS & CVAA)
- **NORM** - Gamma Spectrometry, Gross alpha, Gross beta.
- **Specialties** – Alkoxyalkylphenols, organic acids other organics.
(GC-MS, LC-MS/MS)

Types of QA/QC Samples and Demonstrations

- Initial Demonstration of Capability
- Method Detection Limit Studies
- Standard Reference Materials (Natural matrix if available!)
- Blind Performance Evaluation Samples
- Trip Blanks (VOCs)
- Equipment Blanks
- Instrument Blanks
- Laboratory Method Blanks
- Laboratory Control Samples
- Matrix Spikes
- Laboratory Duplicates or Matrix Spike Duplicates

QA/QC – Expect Good Practices

QA/QC Check	Classical Chemistry	GC-VOC (&GRO)	GC-SVOC	ICP-AES /ICP-MS	NORM	GC/LC-MS SVOC
Initial Demonstration of Capability	Yes	Yes	Yes	Yes	Some	Yes
Method Detection Limit Studies	Most	Yes	Yes	Yes	(MDA)	Yes
Standard Reference Materials	Yes	Yes	Yes	Yes	Yes*	Yes
Blind PE Samples	Yes	Yes	Yes	Yes	Some	Yes
Trip Blanks (VOCs)		Yes				
Equipment Blanks	Rare	Yes	Yes	Yes	Rare	Yes
Instrument Blanks		Yes	Yes	Yes		Yes
Method Blanks	Yes	Yes	Yes	Yes	Yes	Yes
Laboratory Control Samples	Yes	Yes	Yes	Yes	Yes	Yes
Matrix Spikes.	Some	Yes	Yes	Yes	Yes	Yes
Laboratory Dup or Matrix Spike Dups.	Yes	Yes	Yes	Yes	Yes	Yes
Dilution Check				Yes		
Post Dilution Spike				Yes		



Example Data Set

- TestAmerica Nashville provided a data set including (depending on the analysis) up to 542 samples.
- Samples were from 5 sites across the Marcellus Shale formation.
- Most frequent test was Chloride.
- Other test parameters included: Metals, GRO, DRO, ORO, 2-butoxyethanol, alkalinity, ammonia as nitrogen, arsenic, barium, bicarbonate, btu content, HEM, MBAS, Oil and Grease, Sulfate, Sulfide, TSS, TDS, TPH.
- These samples were examined for potential interferences listed in methods, and based on experience.



Interferences

- **Dissolved Solids** - Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate.
- Total residue should be limited to about 200 mg. (On a 100 mL sample this would be 2000 mg/L, 3.4% of the anecdotal samples.
- **Alkalinity** - (Titrimetric Method 310.1) and pH. Oil and grease may coat the electrode causing sluggish response.
- For samples having high concentrations of mineral acids, method modifications are needed (titrate to an electrometric endpoint of pH 3.9, using ASTM Standard, D- 067, Method D or superseding methods.
- **Anions (Chloride, Fluoride, Bromide, Nitrite, Nitrate, Phosphate, Sulfate)** - Any species with a retention time similar to that of the desired anion will interfere. Example, high levels of organic acids that may interfere with inorganic anion analysis may be present. Several organic acid homopolymers, polymers and telomers are used in fracturing fluids.

Interferences (Cont.)

- **Total Kjeldahl Nitrogen** (Automated Colorimetry 351.2) - High nitrate concentrations (10X or more than the TKN level) result in low TKN values. Ion Selective Electrode 351.4): The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.
- **Barium** (ICP-AES or MS, e.g. 200.7, 6010, 6020) - The total recoverable sample digestion procedure will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate.
- **Metals by ICP-AES** (e.g., 200.7, 6010) - High viscosity and low surface tension can impair sample nebulization and transport processes, causing significant inaccuracies esp. in samples w/ high dissolved solids or high acid concentrations.
- **Barium** can be an interference above the SIC level for ICP-AES. Barium can cause interferences both in the metals analysis and the NORM analyses. (Co-precipitation.)



Interferences (Cont.)

ICP-MS Interference Check Standard (concentration in check std):
Ca (300 mg/L); Fe (250 mg/L); Mg (100.0 mg/L); Na (250 mg/L)
250.0; K (100 mg/L); Cl (2000 mg/L).

- 3.0% of 439 samples exceeded the Ca check standard level. Higher literature values exceed the check standard concentration 100-fold.
- One of 74 samples exceeded the Fe check standard level.
- 1.3% of 381 samples exceeded the Mg check standard level. Higher values reported in the literature exceed 25 times the interference check standard level.
- 10% of the samples exceeded the Na check standard level.
- 4% exceeded the K check standard level.
- 1.8% of the 542 samples exceeded the Cl check standard level.

Summary – and some thoughts to spur discussion

- Many standard analytical methods apply; however, they will perform poorly in some cases involving high levels of interferents. The interferences are well characterized, but a careful evaluation of the entire data set is needed to understand the potential biases.
- For Metals, ICP-MS alone is not a good fit.
 - ICP-Atomic Emission Spectrometry is needed to overcome many interferences.
- Total Dissolved Solids data should be scrutinized.
 - Use field duplicates and evaluate carefully.
- If anion data set does not make sense, consider method of standard additions.
- Watch barium levels.
 - If they are not consistent, or high engage a senior analytical chemist to evaluate.
- Watch sulfate levels.
 - They can cause a low bias in barium.
- Watch nitrate levels.
 - They can cause low bias in TKN.

Questions?



Environmental Standards, Inc.

“Setting the Standards for Innovative Environmental Solutions”

Headquarters

1140 Valley Forge Road
P.O. Box 810
Valley Forge, PA 19482
Tel: 610.935.5577
solutions@envstd.com

Virginia

1208 East Market Street
Charlottesville, VA 22902
Tel: 434.293.4039
solutions-virginia@envstd.com

Tennessee

1013 Brentwood Way
Kingston, TN 37763
Tel: 865.376.7590
solutions-tn@envstd.com

Web: www.envstd.com

Quality Assurance, Quality Control and Method Performance Considerations for Chemical Testing of Environmental Samples Impacted by Hydraulic Fracturing Fluids

David Thal
Environmental Standards Inc.

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

A discussion of the traditional quality assurance and quality control (QA/QC) as practiced in environmental studies directed by the USEPA is presented, focused on the most common analyses provided for samples of hydraulic fracturing (HF) fluids, flowback waters and related samples. The types of analyses being applied most commonly are presented, based on interviews and correspondence with five commercial laboratory companies. The specific types of QA/QC studies and samples applied in a robust quality assurance program are presented for each type of analysis. A survey of interferences is presented, based on hundreds of samples of HF fluids and flowback waters, along with a cautionary summary, alerting the data user to the need for review of HF data by senior analytical chemists.

The USEPA requires that a systematic planning process be used to plan for data quality in environmental data operations that receive funding from the agency. To support this requirement, EPA developed a process called the Data Quality Objectives (DQO) Process. The DQO Process is a reasonable starting point to build a model for data quality planning in general. It identifies the data quality indicators (DQIs) that need to be measured to help assure that data of known quality will be obtained. The DQO process and DQIs are described in the publication *Guidance for the Data Quality Objectives Process (QA/G-4)*.¹ Other agencies have also developed and have collaborated on guidance that define essential data quality parameters for Department of Defense and Federal Facilities in general.^{2,3} A review of these documents reveals very close agreement between them on the list of DQI's.

The USEPA also provides instructions and specific requirements for the information needed in a QA Project Plan (QAPP) for environmental data operations funded by EPA. This document is titled *EPA Requirements for Quality Assurance Project Plans (QA/R-5)*.⁴ Conducting the DQO Process and developing a QAPP that covers all the requirements in the R-5 document is a very good foundation for quality planning. However, experience has shown that the traditional approaches can fall short in providing data for difficult matrices and cases in which the need for high confidence at low detection limits affects decision making. It is important to understand how the properties and composition of hydraulic fracturing fluids and flowback waters can impact data quality.

The G-4 lists principal DQIs as precision, bias, representativeness, completeness, comparability, and sensitivity. (PARCCS). In many derivative publications, and guidance documents these are referred to as the “PARCC” parameters, leaving sensitivity out of the mnemonic, and unfortunately, out of the data quality planning process. Additionally, the sensitivity of a method as practiced in laboratories is usually demonstrated on a reference matrix, with no chemical interferences present. In reality, interferences often result in dilutions, or reduced sample volumes being analyzed in the laboratory. In many (but by no means all) cases, the EPA methods themselves direct the use of dilutions and reduced sample volumes to overcome the impacts of matrix-borne interferences. Here again, and understanding of the types of interferences likely to be encountered.

A survey of commercial laboratories (5 companies) was conducted to determine the commonly applied testing technologies for samples impacted by or suspected of containing hydraulic fracturing fluids or flow back waters. The following types of testing method were common to almost all responses. The testing technologies applied were:

Classical Chemistry, often referred to as wet chemistry. This general category of testing usually involves wet chemical techniques and physical characterization, and may rely on more than one type of determinative technique (e.g., titrimetry, spectrometry, gravimetry, ion selective electrodes, ion chromatography, voltatmetry). Examples typical of classical chemistry techniques used fracturing fluid and flow back water studies include: Alkalinity, Ammonia, BTU Content, Carbonate, Chloride, Methylene Blue Active Substances, Oil and Grease, Potassium, Sodium, Specific Conductance, Sulfate, Sulfide, Total Dissolved Solids, Total Suspended Solids. Most interferences on anionic evaluations come from competing anions.

Gas Chromatography of Volatile Organic Compounds and Gasoline Range Organics, (GC-VOC &GRO). This type of testing involves the collection of samples which will be purged with nitrogen in the laboratory to bring volatile components into a gas chromatograph (GC). The GC which separates the components by physicochemical properties (polarity, molecular weight, electrostatic interactions), and ports them into a detector such as a flame ionization detector or mass spectrometer. Examples of HF analytes measured by this type of test include: 2-butoxyethanol, gasoline range organics, methane, ethane. Most interferences are from non target volatile organic compounds. Cross contamination can be a significant issue due the mobility of the analytes.

Gas Chromatography of Semivolatile Organic Compounds, Diesel and Oil Range Organics,GC-SVOC, DRO, ORO). This type of testing involves the collection of samples which will be extracted with solvents in the laboratory to bring semivolatile components into a gas chromatograph (GC). The GC which separates the components by physicochemical properties (polarity, molecular weight, electrostatic interactions), and ports them into a detector such as a flame ionization detector or mass spectrometer. Examples of HF analytes measured by this type of test include: Diesel Range Organics, Oil Range Organics, Ethylene Glycol, Formaldehyde and many other analytes. Most interferences are from non-target organic compounds including fats, oils, organic acids and sulfur in the extracts.

Inductively Coupled Plasma – Atomic Emission Spectrometry. (ICP-AES) The sample is typically digested with acids under heated conditions and the liquid digestate is aspirated into an inductively coupled plasma. Light focused on the excited metals further excites the electron states, and they emit spectral light that is passed through a gradient filter and detected by wavelength and intensity. Examples of analytes that are detected by this technique include Calcium, Barium, Iron, Potassium and Sodium and many others.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) The sample is typically digested with acids under heated conditions and the liquid digestate is aspirated into an inductively coupled plasma. The analytes are then passed into a quadrupole mass analyzer, where they are separated by their mass-to-charge ratio. Some instruments pass the analytes through a collision cell prior to the quadrupole to reduce polyatomic interferences. The analytes then strike an electron multiplier and are detected by the current generated. Examples of analytes of interest in HF studies that are detected by this technique include: aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium selenium, silver, sodium, zinc.

Naturally Occurring Radioactive Materials. (NORM). Several radiochemical methods can be applied to this general field of testing. In each case the fundamental analytical technique involves carefully arranging the sample into a reproducible geometry and measuring the radioactive emissions using gross alpha, gross beta or gamma spectrometry when information on specific radionuclides is needed. Examples of nuclides of interest would include radium 226, radium 228.

Specialized Gas Chromatography or Liquid Chromatography – Mass Spectrometry. (GC/LC-MS SVOC). Liquid chromatography is well suited to highly polar, or ionic compounds, such as some phenols, glycols and organic acids. Specialized GC-MS can be used for alkylphenols, and some glycols and alcohols. For analytes that are easily fragmented, or in need of highly specific analyses, specialized mass spectrometry, such as m_s/m_s , m_s^n , negative ion chemical ionization and high resolution mass spectrometry may be of use. The suite of QA/QC measures for these tests should be the same as those indicated for routine GC/MS, as long as the methods of sample preparation are analogous.

The commonly practiced types of QA Study or QC sample are defined and briefly described below.

Initial demonstration of proficiency or capability. (IDOC) This QA measure is typically comprised of a series of tests on positive controls (spiked reference samples) analyzed as a part of staff training or method capability testing. Precision and percent recovery are evaluated. This may be set up as four consecutive, or four simultaneously prepared samples.

Laboratory control sample (LCS). The LCS is a sample comprised of a reference matrix spiked with analytes of concern and taken through all steps of preparation and analysis within the

laboratory. Recovery is compared to control limits established in the method, QAPP, or laboratory (based on historical data). It is prepared and analyzed with each batch of (20 or fewer) samples, and may be prepared in duplicate (LCSD) if insufficient sample material is available to perform the matrix spike/matrix spike duplicate or sample duplicate.

Matrix Spike (MS). An aliquot of the field sample is analyzed as received, and another aliquot is analyzed with a known quantity of analyte added prior to sample preparation and analysis. This measures recovery in the presence of matrix interferences.

Matrix Spike Duplicate (MSD). A separate aliquot of the field sample used for the MS is spiked and prepared in the same manner as the MS. The results are compared and are measures of both precision and recovery in the presence of the sample matrix. For metals analyses, if the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike.

Post digestion spike. For metals analyses, this step involves adding the metals directly to the prepared sample to determine whether the recovery problem is related to the original matrix, or the analytical technique.

Unspiked Duplicate, also termed Laboratory Duplicate. This is useful when the parameter being studied is always present, or when the parameter is difficult to add. It is simply a separate aliquot of sample analyzed alongside the original, and compared to the original sample as a measure of precision.

Dilution test. For metals analyses. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within $\pm 10\%$ of the original determination. If not, then a chemical or physical interference effect should be suspected.

Method Blank (Sample Preparation Blank). A reference matrix is taken through all the steps of sample preparation and analysis, alongside the field samples, to determine whether contamination may be present in the laboratory environment or materials. This is a measure that helps evaluate the accuracy of the data, particularly at low levels.

Instrument Blank. A pure aliquot of the sample carrier (e.g., gas, aqueous acid, solvents depending on the type of method) is introduced to the instrument in the same manner as a sample. This checks for sample-to-sample carryover potential in the analysis.

Trip Blank (Volatile Organic Compounds). A sample of analyte-free water is placed in a sample shipment cooler and travels with the sampling materials to the sampling location, and then travels with the samples back to the laboratory. This sample is analyzed to identify the potential for contamination of samples or sample bottles in the field or under shipping conditions.

The types of QA/QC that may reasonably be expected and required in a robust QA/QC program are presented in Table 7.

Table 7. Types of QC Samples Expected in Mature QA Programs

Quality Check	Classical Chemistry	GC-VOC (&GRO) & GC/MS-VOC	GC-SVOC	ICP-AES /ICP-MS	NORM	GC/LC-MS SVOC
Initial Demonstration of Capability	Yes	Yes	Yes	Yes	Yes	Yes
Method Detection Limit Studies	Most methods	Yes	Yes	Yes	Note 1	Yes
Standard Reference Materials (NIST traceable if available.)	Yes	Yes	Yes	Yes	Yes	Yes
Blind PE Samples	Yes	Yes	Yes	Yes		Yes
Trip Blanks (VOCs)		Yes				
Equipment Blanks	Rare	Yes	Yes	Yes	Yes	Yes
Instrument Blanks	Some	Yes	Yes	Yes	Yes	Yes
Field Duplicates	Yes	Yes	Yes	Yes	Rare	Yes
Method Blanks	Yes	Yes	Yes	Yes	Yes	Yes
Laboratory Control Samples	Yes	Yes	Yes	Yes	Yes	Yes
Matrix Spikes/ Matrix Spike Duplicates	Some	Yes	Yes	Yes	Yes	Yes
Laboratory Duplicates	Yes	Yes	Yes	Yes	Yes	Yes
Dilution Check				Yes		
Post Dilution Spike				Yes		

Notes

1. For NORM Minimum detectable activities are calculated using instrument backgrounds and sample characteristics.

Matrix Interferences Typical of HF Fluids, Flowback Waters and Related Samples

A series of chemical testing results from hydraulic fracturing fluid and flowback waters (within the first 5 days post-fracturing) from various Marcellus sites was examined for potential matrix-borne interferences. The results were provided by a commercial laboratory providing analytical services to many sites across the Marcellus formation. (TestAmerica Nashville). Ranges of observed levels of interferences were also taken from literature sources.^{5,6} Known interferences for the test methods are described below, along with an evaluation of the potential impact from matrix-borne interferences in this data set. Many of the known interferences are described *verbatim* as they appear in the USEPA Methods being applied.

Total Dissolved Solids (Gravimetric Method 160.1). Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing. Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate. Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg. (On a 100 mL sample this would be 2000 mg/L, 3.4% of the sample)

Alkalinity (Titrimetric Method 310.1): Oil and grease may coat the electrode causing sluggish response for both alkalinity and pH. Salts of weak organic and inorganic acids may cause interference in the electrometric pH measurements. For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, method modifications are needed (i.e., the laboratory is to titrate to an electrometric endpoint of pH 3.9, using ASTM Standard, D- 067, Method D or superseding methods).

Anions (Chloride, Fluoride, Bromide, Nitrite, Nitrate, Phosphate, Sulfate): Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present. Two common species, formate and acetate, elute between fluoride and chloride. (Several organic acid homopolymers, polymers and telomers are used in fracturing fluids.

Total Kjeldahl Nitrogen (Methods 350.1,2,3,4 -Automated Colorimetry, Titrimetry, Potentiometry, Ion Selective Electrode): High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

Barium (ICP-AED or MS, e.g. 200.7, 6010, 6020): The total recoverable sample digestion procedure will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown

concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

Metals by ICP-AED (e.g., 200.7, 6010): Flow variation due to physical interferences with the sample nebulization and transport processes can result from changes in viscosity and surface tension. This in turn can result in significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. The use of a high-solids nebulizer or sample dilution is often necessary. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. Here again, use of a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample may help alleviate the difficulty. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. The QA/QC program should provide for matrix matching, and standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element. The Spectral Interference Check addresses most interferences at 50 mg/L. (300 mg/L Fe; 200 mg/L Al; 50 mg/L Ba; 50 mg/L Be; 50 mg/L Cd; 50 mg/L Ce; 50 mg/L Co; 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO₂; 50 mg/L Ti; 50 mg/L Tl and 50 mg/L

Of all these limits, barium was exceeded for one sample.

For ICP-MS (6020A)

The interference check standards for this method check for interferences at the following levels: Ca (300 mg/L); Fe (250 mg/L); Mg (100.0 mg/L); Na (250 mg/L) 250.0; K (100 mg/L); Cl (2000 mg/L).

- Of these, 10 percent of the samples exceeded the Na check standard level.
- Four percent (4%) exceeded the K check standard level.
- One percent (1.3%) of the 381 samples exceeded the Mg check standard level. Higher values reported in the literature exceed 25 times the interference check standard level.
- One of 74 samples exceeded the Fe check standard level.
- Two percent (1.8%) of the 542 samples exceeded the Cl check standard level.
- Three percent (3.0%) of the 439 samples exceeded the Ca check standard level. Higher literature values exceed the check standard concentration 100-fold.

Both metals methods note that dissolved solids should not exceed 0.2 % (True for 4% of 462 samples.) Literature values range up to 2.5%.

Finally, memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber.

Summary

Many standard analytical methods apply to the analysis of HF fluids and flowback water samples. However, they will perform poorly in some cases involving high levels of interferents. The interferences are well characterized, but a careful evaluation of the entire data set is needed to understand the potential biases.

For Metals, ICP-MS method alone is not a good fit for this matrix. ICP-Atomic Emission Spectrometry is needed to help overcome the many interferences well above the interference check standard.

Total Dissolved Solids data should be scrutinized for potential impacts on the metals data, and classical chemistry parameters.

Field duplicates should be used and evaluated carefully. If the anion data set does not make sense, consider using the method of standard additions.

Watch barium levels closely. If they are not consistent, or if they are high, engage a senior analytical chemist to help evaluate the data set.
It is important to evaluate the sulfate levels.

References

- USEPA. Guidance on Systematic Planning Using the Data Quality Objectives Process. EPA QA/G-4. EPA/240/B-06/001. Office of Environmental Information Washington, DC. February, 2006.
- Intergovernmental Data Quality Task Force Uniform Federal Policy for Quality Assurance Project Plans, Evaluating, Assessing, and Documenting Environmental Data Collection and Use Programs Part 1: UFP-QAPP Manual
<http://www.epa.gov/fedfac/documents/qualityassurance.htm>.
- DoD Quality Systems Manual for Environmental Laboratories Version 4.2. Based on NELAC Voted Revision 5 June 2003. Issued 10/25/2010. <http://www.navylabs.navy.mil/>
- USEPA. EPA Requirements for Quality Assurance Project Plans. EPA QA/R-5. EPA/240/B-01/003. Office of Environmental Information Washington, DC, March 2001.
- Kirby, Carl S., Pritz, Molly E., Lunde, A. Scott, and Tate, Garyn P., Inorganic Geochemistry of Marcellus Shale Natural Gas Hydrofracturing Waters. University, Department of Geology, Bucknell University, Lewisburg PA.
- Blausch, M.E., Meyers, R.R., Moore, T.R., Lipinski, B.A., Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From? Proceedings of the Society of Petroleum Engineers Eastern Regional Meeting, Sept 2009.