QUALITY ASSURANCE PROJECT PLAN FOR THE CHEMICAL CHARACTERIZATION OF SELECT CONSTITUENTS RELEVANT TO HYDRAULIC FRACTURING

U. S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL SCIENCES DIVISION

August 31, 2011

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NOTICE

This document is intended for internal Agency use only. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

LIST OF ABBREVIATIONS

ECB	Environmental Chemistry Branch
EPA	Environmental Protection Agency
ESD	Environmental Sciences Division
DI	Deionized
DQO	Data quality objective
GC	Gas chromatography
GWERD	Ground Water and Ecosystem Restoration Division
HF	Hydraulic fracturing
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
IM-QA	Information management quality assurance
MDL	Method detection limit
MS	Mass spectrometry
NERL	National Exposure Research Laboratory
NRMRL	National Risk Management Research Laboratory
ORD	Office of Research and Development
PARCC	Precision, accuracy, representativeness, completeness, and comparability
PI	Principal Investigator
QA	Quality assurance
QC	Quality control
QAPP	Quality assurance project plan
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
TOF	Time-of-flight
TDS	Total dissolved solids
TSCA CBI	Toxic Substances Control Act Confidential Business Information
USGS	United States Geological Survey

SECTION A. PROJECT MANAGEMENT

A3 Distribution List

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A4 Project/Task Organization

The Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing is managed and implemented by the Environmental Sciences Division (ESD) of the EPA Office of Research and Development (ORD). Brian Schumacher is the Technical Research Lead. Ed Heithmar is the Branch Quality Assurance Representative. Analyses will be conducted by the Environmental Chemistry Branch (ECB) in Las Vegas. **Table 1** summarizes individual responsibilities for the major study activities. **Figure 1** illustrates the individual and organizational interactions of all involved parties.

Table 1. Main study activities and responsible organizations.

Study Activities	Responsible Party
Design, implementation, and management of the study	Brian Schumacher
Study coordination	Brian Schumacher
Method development and testing; data review and data analysis; report development	Patrick DeArmond, Don Betowski, Andrew Grange, Tammy Jones-Lepp, Georges-Marie Momplaisir , and Lantis Osemwengie, Wayne Sovocool
Data storage, management, and access	Patrick DeArmond, Don Betowski, Andrew Grange, Tammy Jones-Lepp, Georges-Marie Momplaisir, and Lantis Osemwengie, Wayne Sovocool, George Brilis (IM-QA)
Ensure the quality assurance (QA) and quality control (QC) activities described in the QAPP and being implemented; Review quarterly reports; Information management quality assurance (IM-QA)	George Brilis
Data QA and QC	Patrick DeArmond
Periodically review notebooks, data, maintenance logbooks, and quarterly reports	Ed Heithmar

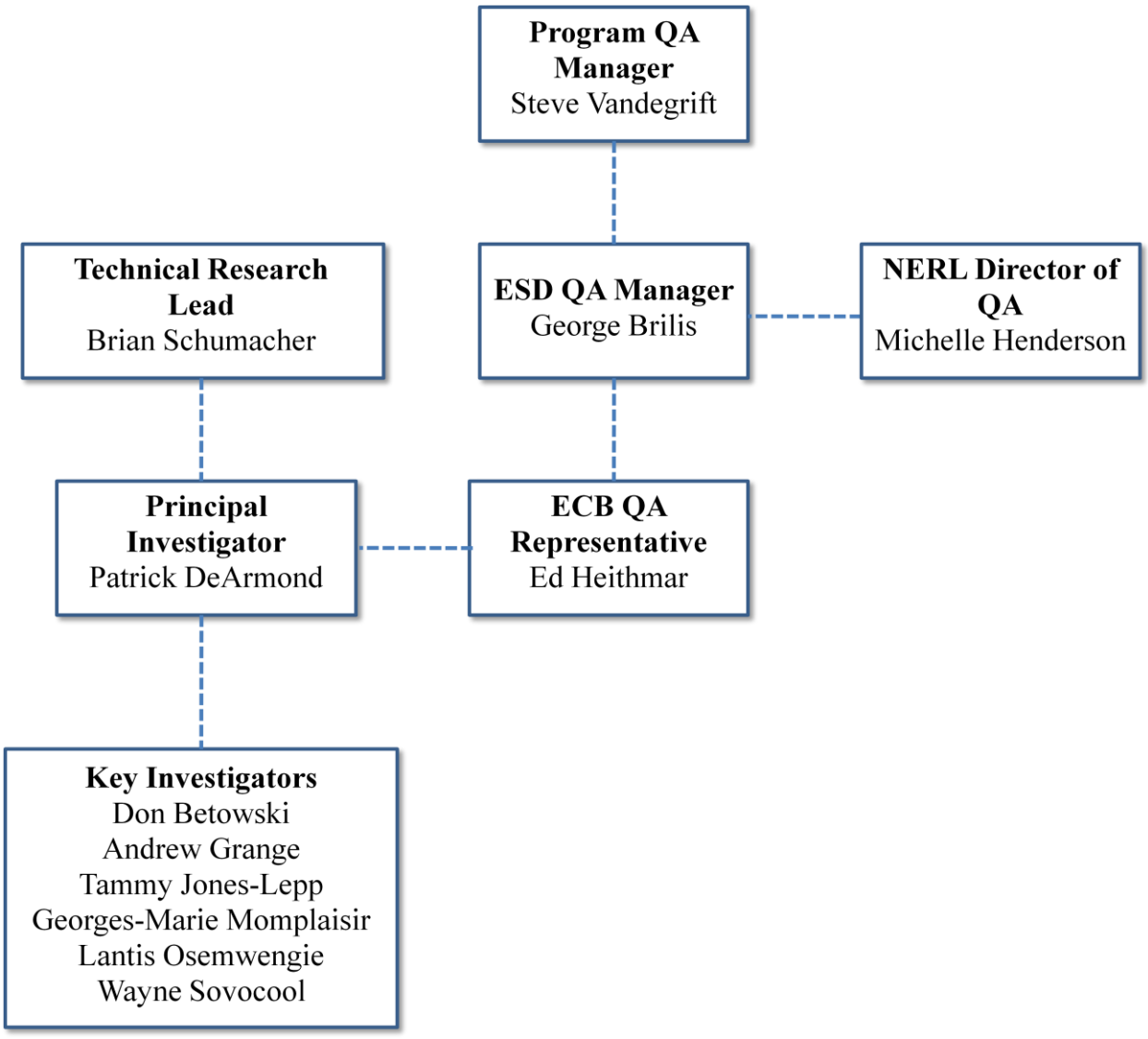

Figure 1. Organizational flowchart for The Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing.

A5 Problem Definition/Background

Hydraulic fracturing (HF) has become increasingly prevalent as a method of extracting energy resources from "unconventional" reservoirs, such as coalbeds, shales, and tight sands. HF involves the pressurized injection of a cocktail of water, chemical additives, and proppants into geological formations, thereby fracturing the formation and facilitating the recovery of natural gas. After the fracturing event, the pressure is decreased and the direction of fluid flow is reversed, allowing fracturing fluid and naturally occurring substances to flow out of the wellbore to the surface; this mixture of fluids is called "flowback." The initial flow rate at which the flowback exits the well can be relatively high (e.g., > 100,000 gallons per day) for the first few days. However, this flow diminishes rapidly with time, ultimately dropping to the rate of "produced water" flow from a natural gas well (e.g., 50 gallons per day).[1]

Produced water is generally considered to be the fluid that exits the well during oil or gas production. However, there is no clear transition between flowback and produced water. Like flowback, produced water also contains fracturing fluid and naturally occurring materials, including oil and/or gas. Produced water, however, is generated throughout the well's lifetime. Concerns about HF center on potential risks to drinking water resources, notably the contamination of these resources from HF fluids, either from the compromised integrity of the well itself or from leaks during storage in tanks and waste impoundment pits.[1]

Much of the existing data on the composition of flowback and produced water focuses on the detection of major ions in addition to pH and TDS measurements. For example, data provided by the USGS produced water database indicates that the distributions of major ions, pH, and TDS levels are not only variable on a national scale (e.g., between geologic basins), but also on the local scale (e.g., within one basin). However, less is known about the composition and variability of flowback and produced water with respect to the chemical additives or radioactive materials found in hydraulic fracturing fluids. In 2010, the EPA compiled a list of chemicals that were publicly known to be used in hydraulic fracturing. An inventory of these compounds associated with HF activities is provided in **Appendix A**. Analytical methods will be identified, tested, and modified or developed to detect potential chemicals of concern and their transformation products, including fracturing fluid additives, metals, and radionuclides, in HF wastewaters.

A6 Project/Task Description

The primary objective of this exploratory project will be to test analytical methods for certain HF chemicals and transformation products in environmental matrices, including flowback and produced waters, based on a prioritization strategy informed by risk, case studies, and experimental and modeling investigations. Initial compounds for which methods are to be tested are listed in **Table 2.** At the time of writing this QAPP (August 2011), the target compounds have not yet been identified. Consequently, this research will focus on HF-relevant classes of compounds, including some stable isotopes, that may later be used for quantitation. As research progresses, and when target analytes are identified, this QAPP may be revised.

Questions that this project should answer include determining the chemical components and physical properties of HF fluids (and transformation products) and the analytical approaches that are needed to identify the reactions, fate, and transport of injected and mobilized constituents. Data collected from this project may be used to ascertain if there is a threat to public health or the environment and to locate and identify potential sources of contamination. The ultimate end-product will be a Hydraulic Fracturing

Methods Selection Document.

Table 2. Initial HF compounds for which methods will be developed.

Compound	Existing Methods
Acrylamide	EPA 8032A, 8316
Ethoxylated linear alcohols	No EPA method
Diethanolamine (2,2-iminodiethanol)	No EPA method
Sugars and borated sugars	No EPA method
Alkylphenols	No EPA method, ASTM D 7485-09

This project will be completed in two phases. Phase 1 will consist of conducting literature searches of the compounds in **Table 2** for candidate analytical methods. Compounds may be added to **Table 2** over time. The general approach to the selection of appropriate candidate methods for sample preparation and analysis is based on a critical review of the techniques employed. **Figure 2** illustrates the general, organized approach used for literature reviews for methods development projects.[2] Often, the results of a literature search will yield a peer-reviewed method. In these cases, the method found may be evaluated or further developed for EPA purposes. Method preference would be given to 1) EPA methods, 2) consensus standard methods, and 3) peer-reviewed, published methods. If methods do not exist, methods will be developed for the compounds of interest. Methods will be implemented by screening the HF compounds and testing the feasibility of the selected analytical methods using standards and some stable isotopic compounds, if available, in clean DI water. The feasibility of the method will be based on the identification of the compounds of interest and the quality of the quantitation. Simple system parameters can then be adjusted and assessed for whether the adjustments significantly improve the method. If the method is improved, then Phase 2 will be implemented.

Phase 2 will provide definitive measurements, including PARCC parameters (precision, accuracy, representativeness, completeness, and comparability), of the compounds of interest using the selected methods. Methods will first be tested using DI water fortified with analytes of interest, and then in flowback/produced water matrices. Methods from Phase 1 will be implemented, beginning with outcomes from Phase 1 method development. Methods will be further optimized, and if they provide acceptable results, they will be used to analyze flowback/produced water for HF compounds of interest. Because this is an EPA quality program Category I project, rigorous QA/QC will be implemented and assessed to meet data quality objectives (see Section A7, Table 3). Extraction efficiency, reproducibility, and PARCC parameters will be evaluated.

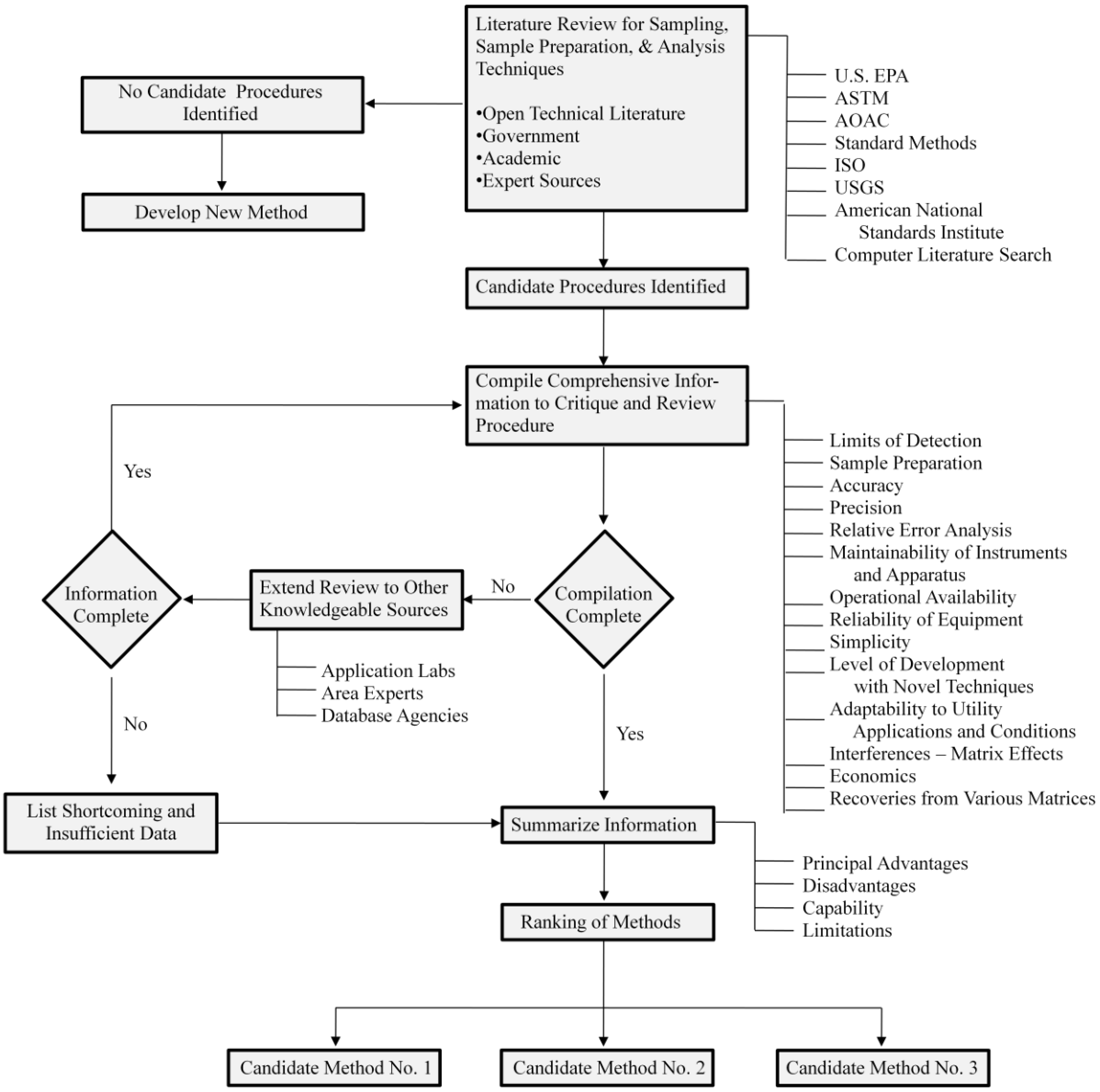

Figure 2. Literature review flow chart for methods development.

A7 Quality Objectives and Criteria for Measurement Data

After performing a search of the literature, the objective of this project will be to conduct methods testing, modification, and development to determine appropriate methods for specific, selected compounds present in HF flowback/produced water. Data quality objectives (DQOs) are typically assessed by evaluating the PARCC parameters of all aspects of the data collection.

Precision is defined as the degree of mutual agreement among individual measurements and provides an estimate of random error. Precision for determination of response factors and of target analytes in spiked samples and duplicate un-spiked samples will be expressed as relative standard deviation (RSD) for replicates of three or more or as relative percent difference (RPD) for duplicates.

Accuracy refers to correctness of the data and is the difference between the population mean of the determination and the true value or assumed true value. Bias is the systematic error inherent in the method or caused by an artifact in the measurement process. Standard reference materials (SRMs) will be used if available to check for accuracy and bias.

Representativeness will refer to the degree with which a small number of samples are representatives of the total possible data sets from which they are drawn.

Completeness may be defined as the amount of data collected during the measurement process that is valid relative to the total amount of collected data. A relatively high ratio of at least 0.9 is expected.

Comparability is the relative confidence that one data set can be compared to another. In this study, a variety of cleanup/extraction and detection techniques will be utilized.

The data quality indicators (DQIs) for precision, accuracy, and completeness for each major measurement parameter are summarized in **Table 3**.

Table 3. Data Quality Indicators for Measurement Data.

QC Check	Frequency	Completeness	Precision	Accuracy	Corrective Action
5-point calibration	Prior to sample analysis	100%	<30%	$R^2 > 0.99$	No samples will be run until calibration passes criteria.
Laboratory blank	One per batch of samples[a]	100%	<50%	< PQL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Instrument blank	In between samples	100%	<50%	< PQL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory control sample	One per batch of samples[a]	100%	<30%	>70%	Check the system and reanalyze the standard. Re-prepare the standard if necessary. Recalibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory fortified matrix	One per batch of samples[a]	100%	<30%	>70% recovery	Review data to determine whether matrix interference is present. If so, narrate interference and flag recovery. If no interference is evident, verify the instrument is functioning properly by running a lab blank. Reanalyze recollected sample to verify recovery. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory replicates	One per batch of samples[a]	100%	<30%	>70% recovery	Inspect the system, narrate discrepancy. Samples must be bracketed by acceptable QC or they will be invalidated.
Continuing calibration verification	One at beginning of each 8-hr analytical day, one at beginning of each batch of samples[a], and one at end of analytical day	100%	<30%	>70% recovery	Inspect system and perform maintenance as needed. If system still fails CCV, perform a new 5-point calibration curve. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory fortified blank	One per batch of samples[a]	100%	<30%	>70% recovery	Inspect the system and reanalyze the standard. Re-prepare the standard if necessary. Re-calibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be invalidated.
Minimum detection limit	Each chemical	100%	TBD for each HF chemical	TBD for each HF chemical	TBD for each HF chemical

[a]Batch of samples not to exceed 20

[b]PQL=practical quantitation limit, 5 times the MDL

A8 Special Training/Certification

Special Training

To achieve the stated quality objectives, only analysts trained and experienced in the use of the various instrumentation (e.g., extraction, chromatography, mass spectrometry) will carry out measurements. Scientists involved in this in-house exploratory project have demonstrated competency on various instruments through performing research activities and subsequently publishing peer-reviewed journal articles. To earn his Ph.D. in Analytical Chemistry, the Principal Investigator (PI) demonstrated competency in applying computer-controlled gas chromatography, high performance liquid chromatography (HPLC), as well as time-of-flight (TOF) and quadrupole mass spectrometers to conduct research.

Certification

The laboratory has demonstrated competency through routine internal and external assessments, including, but not limited to:

- A Laboratory Competency Audit (LCA) was performed by NERL/ESD on June 3 and 4, 2009, and the findings were stated in an LCA Report dated July 13, 2009. The plans to address LCA findings that are within the control of the ESD were provided by the ESD Acting Division Director to the NERL Director of Quality on August 27, 2009.
- An onsite Quality System Assessment (QSA), performed by members of the EPA Quality Staff, from September to December 2009, and reported in April 2010, noted "No Findings" for the NERL/ESD.
- The ESD QA Manager performs scheduled Internal Technical Systems Audits (TSAs) of the Environmental Chemistry Branch (ECB).

All internal and external quality-related audits and assessments are available in the Organizational Assessment (OA) Module of the NERL QA Tracking System.

NOTE 1: Since the LCA of 2009 and the QSA of 2009, the ORD Policies and Procedure Manuals, Chapter 13, have been under revision.

NOTE 2: Annual calibration and certification of various equipment, including, but not limited to, gravimetric and volumetric measurement devices, is routinely performed by a certified technician during September of each year.

A9 Documents and Records

Laboratory activities must be documented according to both the NERL Information Integrated Information and Quality Management Plan (IIQMP) Appendix 6 "NERL Scientific Record Keeping Policy"[3] and the ORD SOP on paper laboratory records.[4] These policies require the use of laboratory notebooks and the management of lab records, both paper and electronic, such that the data acquisition may continue even if a researcher or an analyst participating in the project leaves the project staff. The Technical Research Lead will have ultimate responsibility for any and all changes to records and documents.

Electronic copies of QA documents, such as this QAPP, SOPs, and audit reports, will be kept in the NERL QATS database.

The QA Representative shall retain all updated versions of the QAPP. The Technical Research Lead will be responsible for distribution of the current version of the QAPP and will retain copies of all management reports, memoranda, and correspondence between project personnel identified in A4.

A *document* provides guidance and/or direction for performing work, making decisions, or rendering judgments which affect the quality of the products or services that customers receive.

A *record* on the other hand proves that some type of required quality system action took place.
Typically a form gets filled in and becomes a record. The form is a document and after it is filled-in, it becomes a record.

Hardcopy Records - Hardcopy records will be maintained in accordance with ORD PPM 13.2.[4] These records include, but are not limited to, recorded information such as the standard and sample preparation, blanks, calibration standards, and QCs will be retained in a laboratory notebook that is kept by the researchers. The laboratory notebook will contain a record of all sample analysis preparation activities and any other data that may be used to interpret results. All samples will be recorded in the laboratory notebook by a unique sample ID. The date of analysis, amount of internal standard/extraction solution made on each day of analysis will be recorded in a laboratory notebook. The location of electronic data generated from analysis of samples will also be recorded in the laboratory notebook, similar to an index, but expressed as a data management path. For example: EPA Computer Number; Hard Drive / Folder Name (Program name) / Subfolder Name (Project name) / Item Folder Name / File name with extension.

Electronic Records created or converted from hardcopies and/or generated by electronic devices, shall be maintained in a manner that maximizes the confidentiality, accessibility, and integrity of the data. All electronic data and notes shall be indexed and cross-referenced in a hardcopy notebook to record data and notation location and facilitate retrieval. The use of Project Titles shall be used to maintain an index of electronic of data and those who contribute shall be "Data Stewards." Data may be transferred to electronic spreadsheets for analysis and presentation.

Research Record Retention: The laboratory notebook and records will be retained in the laboratory (or office area) where these operations are performed until the conclusion of the study. At the end of the research study, the research records shall be archived in a manner consistent with the appropriate EPA National Records Management Records Disposition Schedule.

Records and documents that will be produced in conjunction with this project include:

- Raw Data
- Laboratory notebooks
- Progress reports
- Documentation of audits
- Project interim report
- Project final report
- Standard operating procedures
- E-mails

Disposition

Record-keeping will be permanent according to EPA Records Schedule 501:

Nonelectronic project files

- Includes documentation related to the formulation and approval of the research plan, the selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, or other data collection media, copies of interim reports showing data tabulation results and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.
    - **Permanent**
    - Close inactive records upon completion of project.
    - Transfer to the National Archives 20 years after file closure.

Electronic project files

- Includes documentation related to the formulation and approval of the research plan, the selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, or other data collection media, copies of interim reports showing data tabulation results and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.
    - **Permanent**
    - Close inactive records upon completion of project.
    - Transfer to the National Archives 5 years after file closure.

Project workpapers and administrative correspondence

- Includes completed questionnaires or other documents used for data collection, drafts or copies of interim progress reports, and other workpapers created in the course of the study
    - **Disposable**
    - Close inactive records upon completion of the project.
    - Destroy 3 years after file closure.

Maintenance and calibration and inspection of equipment

- **Disposable**
- Close inactive records upon completion of the project.
- Destroy 5 years after file closure.

SECTION B. MEASUREMENT/DATA ACQUISITION

B1 Sampling Process Design

The sampling process design is not applicable to this project because HF flowback and produced water samples will be collected from other case studies and sent to ECB for analysis when available. However, laboratory-generated, matrix-free samples spiked with standard compounds, which may include stable isotopic compounds, will be analyzed prior to the analysis of flowback and produced water samples to establish optimized method and instrument conditions for the target compounds. Analyses of class compounds, such as acrylamide, ethoxylated alcohols, and alkylphenols, will be performed prior to the identification of target compounds to establish instrument conditions and create mass spectral libraries. Extraction efficiencies of the class compounds from the aqueous matrix will be determined. Research may also include performing analyses of standards in representative matrixes prior to the analysis of flowback and produced water samples.

B2 Sampling Methods

Quality assurance in sampling is critical to the production of useful data because it must be assumed that the acquired sample is representative of the processes under investigation. Sampling must provide sufficient material for analysis, be representative of the sample source, and must not compromise sample integrity. To accomplish these ends, a series of good sampling practices must be combined with a quality control program, and these in turn must be monitored for effectiveness through the quality assurance program.[2]

HF samples will be collected in clean, capped glass containers, or trace-cleaned polyethylene bottles for metals analysis, and labeled with the source and date of sampling. DI water is generated on site using a Barnstead NANOpure system, and the cartridges are changed when the resistivity is ≤ 14.0 MΩ·cm.

Sample documentation sheets should be provided for each sample acquired. These sheets will be maintained by the ECB sample control person, Nellie Dujua. The sheets should include the following items:

- Sample identification code number – ECB Las Vegas will add its own sample identification to each sample received. (LVYYXXXZZZ, where LV stands for Las Vegas; YY is the year, e.g., 11 for 2011; XXX are 3 letters designating the project, e.g., HYF for hydraulic fracturing; and ZZZ are 3 numbers designating the specific sample number, i.e., 001, 002, etc.)
- Sample location (longitude, latitude, altitude [where applicable])
- Brief description of sample source
- Date and time of acquisition
- Volume or weight of sample (approximations acceptable)
- Comments describing any unusual aspects of the sample or its acquisition

B3 Sample Handling and Custody

If real-world samples will be used to develop and/or test analytical methods, the following procedures will be invoked:

Custody records – The chain-of-custody documentation describing when samples were received and eventually disposed of or shipped off-site should include:

(1) The project name
(2) Signatures of samplers
(3) The sample number, date and time of collection, and grab or composite designation
(4) Signatures of individuals involved in sample transfer
(5) If applicable, the air bill or other shipping number

Proper documentation will be maintained, security of samples ensured, and analyst procedures documented. Samples will be properly labeled and stored in either the walk-in refrigerator located in the CHL building, which is locked at all times, or the freezer located in CHL 26. The sample storage units (refrigerators and freezers) are monitored with temperatures recorded in a log book. Analyte hold time studies will be performed when the target analytes are identified.

EPA National Geospatial Data Policy (NGDP) and Procedures (NGDPP)
Whenever applicable and to the extent practical for the purposes of this research, this research shall adhere to the *EPA National Geospatial Data Policy* (NGDP)[5] and the *EPA National Geospatial Data Policy Procedure for Geospatial Metadata Management.*[6] These policies and procedures establish principles, responsibilities, and requirements for collecting and managing geospatial data used by Federal environmental programs and projects within the jurisdiction of the U.S. Environmental Protection Agency (EPA). This Policy also establishes the requirement of collecting and managing geospatial metadata describing the Agency's geospatial assets to underscore EPA's commitment to data sharing, promoting secondary data use, and supporting the National Spatial Data Infrastructure (NSDI). The intended geospatial accuracy for this project is Tier 9, [>5000 meters] as described in the NGDP, Appendix A.

B4 Analytical Methods

The goal of the project is to develop accurate measurement tools for the determination of HF compounds that represent compounds for which definitive analysis is required. Preliminary screening (Phase 1) and quantitation (Phase 2) of HF compounds will be based on various analytical methods, including chromatographic, mass spectrometric, and spectroscopic techniques. If a method already exists for a compound of interest, then that method's standard operating procedure and QA/QC will be used. The method will be optimized by modifying the extraction, cleanup, instrument settings, etc., if necessary. If no method currently exists, an analytical method will be developed according to the best information available.

Aqueous samples will typically require concentration using liquid-liquid extraction or solid phase extraction (SPE), followed by evaporation using an automated evaporator. Cleanup methods may be appropriate to eliminate sample interferences. These methods will be developed for standards added to flowback water and then applied to real world samples. At least three replicate analyses should be performed.

Volatile, semi-volatile, and non-volatile organic compounds will be identified from GC-MS or LC-MS spectra and retention times. Volatile and non-polar, semi-volatile compounds will generally be identified by comparison of electron ionization (EI) mass spectra obtained using GC-MS with those in the large NIST and Wiley mass spectral libraries. Polar, semi-volatile and non-volatile compounds will be analyzed by LC-MS employing electrospray ionization (ESI). In the positive ionization mode an adduct

ion of the molecule (M) is usually observed. The $[M+H]^+$ and $[M+Na]^+$ adducts are most common. By applying a collision induced dissociation (CID) voltage, the adduct ions can usually be fragmented to produce product ions characteristic of the compound. ESI mass spectral libraries, less extensive than those for EI, can be used to match the fragmentation pattern observed and provide tentative identification of the compound. Where no library matches are plausible, the exact masses of the ions in the spectrum and the relative isotopic abundance distribution for the precursor or a prominent product ion can be obtained using a time-of-flight mass spectrometer. This information provides the elemental composition of the ions and that of the molecule. The elemental composition would be entered into the ChemSpider or CAS data bases to obtain a list of known isomers and the number of references discussing each isomer. When available, standards of the isomers with the most citations would be purchased so that their mass spectra and retention times could be compared to those of the compound found in the flowback water to identify the compound.

For inorganic compounds, analyses will be performed using appropriate techniques, such as those specified in SW-846 Chapter 3 (i.e., ICP-MS, EPA Method 6020A; isotope dilution mass spectrometry, EPA method 6800; etc.).[7]

For radionuclides, gamma-ray and alpha-particle spectroscopy will be used to identify and quantify components following proper cleanup.

Shown in **Figure 3** is a decision tree for the determination of appropriate methods.

An estimation of the method detection limit (MDL) and linear dynamic range for individual analytes identified from the HF constituents will be made according to procedures as outlined by McDougall et al.[8] In brief, a series of five standards of HF constituents, ranging in concentrations from low to high, will be analyzed by the instrumentation. Masses, retention times, and area counts will be determined, and linear regression will be performed on the data sets, as outlined by McDougall et al. Concentration detection limits will vary by compound.

Calibration procedures will be followed as listed in Section B7. For HPLC and GC separations, particular emphasis will be placed on the instrument manufacturer's recommendations and manuals, in addition to the current scientific literature.

Where possible, data will be compared to published results.

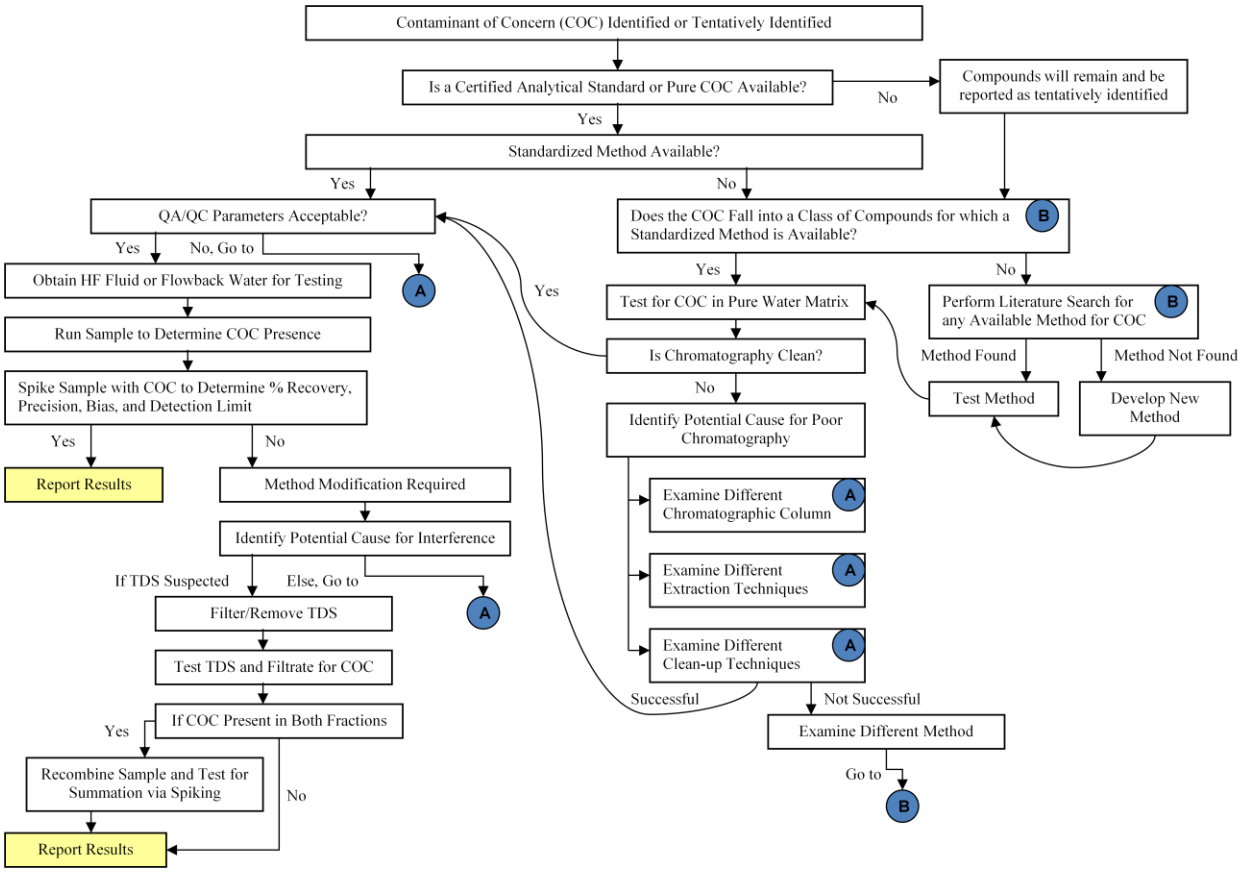

Figure 3. Decision Tree for Methods Development

B5 Quality Control

Experiments to evaluate replicate analysis, fortified matrix analysis, split samples, blanks, internal standards, surrogate samples, calibration standards, etc. are to be performed as part of on-going QA. Instrument performance must be assessed daily.

Single-laboratory testing at ECB is designed to evaluate the quality of measurement data that can be obtained in a single laboratory using the written method protocol. The results of single-laboratory testing will be used to identify and quantify (1) the sources of significant variability in method performance, (2) probable systematic error, or method bias, (3) the usable dynamic range and limits of detection for method measurements, (4) method sensitivity, the ability of the method to respond to small changes in analyte concentration, and (5) method ruggedness, the relative stability of method performance for small variations in critical method parameter values.

Single-laboratory testing will typically be conducted in five stages as follows:

(1) Preliminary method evaluation
(2) Ruggedness testing
(3) Method range and detection limits

(4) Referee validation
(5) Matrix validation

Each of these stages is discussed briefly in the following subsections.

B2.1 Preliminary method evaluation

Preliminary method evaluation tests a candidate method for its general performance characteristics, the presence of major technical difficulties, and the potential for successful optimization and application. Properly conducted, the familiarization and optimization tests involved with the preparation of a written protocol and the development of validation criteria constitute an appropriate and complete preliminary method evaluation. As a result of this evaluation, unsuitable methods, whose performance characteristics fail to meet minimum validation criteria, may be screened out, thereby reducing the cost and time involved in overall methods development.

B2.2 Ruggedness testing

Ruggedness testing is conducted on suitable candidate methods by systematically varying the identified critical method parameters and observing the performance sensitivity of the method to the variations introduced. ECB employs appropriate standard ruggedness test protocols, such as those described by: Youden and Steiner,[9] Williams,[10] and Cole et al.[11] to conduct all ruggedness tests for method development projects. The results of ruggedness tests are used to specify appropriate performance limits for critical method parameters, within which no statistically significant adverse effects on method performance are expected.

The quality control procedures will be intensified during the ruggedness testing stage of method development. Multiple laboratory control spikes prepared in a minimum of three concentration levels are routinely employed to probe the effects of critical parameter variation. Evaluations of the variations of critical parameters on method response will be conducted using statistical procedures called out in the particular ruggedness test procedure and include tests for outliers and the calculation of means, standard deviations, and *t*-tests of significance. Ruggedness tests also typically require statistical evaluations of results for a minimum of two ranges of variation for the critical method parameters, to provide estimates of the degree of method performance sensitivity to variations in each parameter, and to define the limits of acceptable performance for each parameter.

B2.3 Method range and detection limits

During this stage of method validation, the concentration range over which the method is sufficiently reliable, precise, and accurate is determined for each method analyte. The method detection limit (MDL) will also be determined for each analyte at a 99 percent level of confidence that the concentration of the analyte is greater than zero.

The level of quality control for range and MDL determinations is similar to that for ruggedness testing. Multiple laboratory control spikes prepared at a minimum of five concentration levels are analyzed in random order by the candidate method. The resulting data are tested for outliers and statistically evaluated according to the specifications of the test procedure, which includes the calculation of means, standard deviations, and levels of confidence, and which stipulates appropriate means for the generation and use of evaluation criteria for the results.

Data from this stage of method development will be used to determine the limits of method precision and recovery for each method analyte. The equations for these determinations are given in Section D3 of this document.

Quality assurance for method range, detection limits, precision, and recovery follows that described in Section B2.2 for ruggedness testing.

B2.4 Referee validation

In referee validation, an experienced analyst not otherwise involved in the method development effort performs the entire method protocol on a set of replicate laboratory control, matrix spikes using equipment not otherwise employed in the method development project. Referee data are evaluated for method precision and accuracy, and the results are compared with similar data obtained by the method development team and with the method performance requirements. Referee validation tests the repeatability of the method and the clarity and correctness of the written protocol.

Quality assurance for referee validation involves the critical review of all laboratory procedures, notebooks, logs, and all data reports to ensure that correct procedures have been closely followed and that all measurement data and calculated results are properly documented.

B2.5 Matrix validation

This final stage of single-laboratory testing involves the acquisition and demonstrative analysis of a minimum of two relevant environmental samples spiked with known quantities of method analytes at a minimum of two concentrations spanning the method range. The results of matrix validation are used to evaluate method precision, accuracy, and range for the representative environmental matrices.

Quality control and quality assurance measures for matrix validation are the same as those specified in Section B2.3 for method range and MDL.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

Preventative maintenance will be scheduled as needed and may be triggered by criteria in Table 3 (section A7). An instrument maintenance log book is maintained in the laboratory with each instrument.

Daily monitoring of instrument performance may include source cleaning, chromatography troubleshooting, detector troubleshooting, or electronic troubleshooting. Daily monitoring of chromatographic and mass spectral peak shapes and resolution are required, as well as all critical instrumental parameters.

B7 Instrument Calibration and Frequency

Various mass spectrometers will be used for obtaining mass spectra of the HF samples. All of the mass spectrometers have distinctly different analyzers and operating conditions. Initial conditions will be

based on instrument installation specifications and modifications made to these during the installation process. These offer the optimum starting points for subsequent experiments during the course of the study.

Mass calibration of the mass spectrometers will be conducted using a prepared mixture containing a wide mass range of analytes (manufacturer specified) injected through their interfaces (e.g., LC or GC). The instrument manufacturer provides software for this calibration. The calibration will be conducted as often as required because of instrument instabilities. The mass calibration will be checked at least annually and after source cleaning.

Retention times of individual components will be monitored with standards, if commercially available. The response of standards will be monitored daily. Changes in response of standards will indicate a need for recalibration. The calibration should be checked daily and redone periodically.

All instruments are maintained as per manufacturers' maintenance manuals. Maintenance manuals are kept for all instruments as per the NERL Scientific Record Keeping Policy.[3] Balances and pipettors are calibrated annually by an outside vendor. Sample storage units (refrigerators and freezers) are monitored with temperatures recorded in a log book.

Calibration response factors (CFs) based on each individual standard will be determined by triplicate injections of the same concentration each 8-hr analytical day. One CCV standard will be analyzed at the beginning of each 8-hr analytical day, at the beginning of each batch of samples (not to exceed 20) and one at the end of each sample analytical day. A constant CF of less than ±30% RSD will be sought. Daily checks of CF will be carried out. The CF is defined as:

$$\mathrm{CF} = \frac{A_x}{(C_x \times v_{inj})}$$

Where:
A_x = area of the ion chromatographic peak(s) of the substance being measured
v_{inj} = volume of standard injection (µL)
C_x = concentration of the compound being measured (ng/µL)

B8 Inspection/Acceptance of Supplies and Consumables

Reagents are purchased of the highest purity required to fulfill laboratory requirements. Standard preparations, reagent and chemical lot numbers, as well as lot numbers for critical supplies, such as SPE cartridges or disks, are recorded on sample and standard preparation log books or in laboratory notebooks. Supplies, equipment, and consumables may include, but are not limited to, the following.

B8.1 Supplies

- Variable volume standard pipettors (0.5 -10 µL, 20-200 µL, 100-1000 µL)
- Pipet tips
- Glass beakers, volumetric flasks
- Lab tape
- Permanent markers
- Nitrile gloves

- Disposable borosilicate Pasteur pipets
- Ultra-high purity grade compressed nitrogen
- Ultra-high purity grade compressed helium
- Breathable grade compressed air
- 1-mL autosampler vials with PTFE/silicone septa (amber and clear)

B8.2 Laboratory Equipment

- Fume hood
- Solvent cabinet
- Mettler UM3 microgram balance
- Sartorius 200 g balance
- Caliper Sciences Auto Trace SPE Workstation
- ASE 200 Automated Solvent Extractor
- TurboVap II Concentration Evaporator Workstation
- Refrigerator
- -20°C freezer
- Barnstead Nanopure water purification system
- Liquid chromatograph/mass spectrometer
- Gas chromatograph/mass spectrometer
- Inductively coupled plasma mass spectrometer
- MARS 5 microwave digestion system

B8.3 Chemicals and Reagents

- Acetonitrile, water, and methanol (HPLC grade)
- Formic acid
- Trace-pure nitric acid

B9 Non-Direct Measurements

At times, this project may rely upon secondary data provided by HF service companies. Access to proprietary information from HF companies will require TSCA CBI certification.

B10 Data Management

Data will be managed according to NERL IIQMP (2005), Section 8 and Appendix 6.[3] A daily laboratory notebook will be maintained to document all experiments carried out, principle results, data examples, sample identification, masses, standards concentrations, spikes, sample calculations, and volumes. Estimates of uncertainty should also be included. Because data is acquired under computer control, a hard copy and a disk copy will be maintained separate from the notebook due to the volume of data generated. Electronic data and information will be cross-indexed in the hardcopy notebook(s).

An instrument maintenance log book will be kept in the same room with the instrument. Significant maintenance activities and problems will be documented. Instrument manuals will also be readily accessible and are used in lieu of a standard operating procedure for instrument procedures.

SECTION C. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

This project will have a Technical Systems Audit (TSA) and Performance Evaluation (PE) performed at each stage of method testing and development for each analyte. The findings of the PE analyses will be reported to the Program QA Manager.

After the critical target analytes have been selected, a representative sample of data for critical target analytes (those that are necessary to support the primary objectives of the project) will undergo an Audit of Data Quality (ADQ). NRMRL has an SOP for this activity that will be used by the ESD QA Manager and/or ECB QA Representative.

Additionally, Data Quality Assessments (DQAs) are required, which will be performed quarterly by the Branch QA representative to evaluate the data.

A schedule of the applicable audits is listed in **Table 4**.

If corrective actions are identified in any of these audits, the Program QA Manager must be informed by the ESD QA Manager and/or ECB QA Representative.

Table 4. Schedule of Audits

Type of Audit	Frequency	Details
TSA	Conducted at each stage of method testing and development (e.g., during optimization of instrumental parameters, during optimization of method parameters such as extraction efficiency, etc.)	Performed by ESD QAM
PE	Conducted at each stage of method testing and development (e.g., during optimization of instrumental parameters, during optimization of method parameters such as extraction efficiency, etc.)	Project personnel will be given PE samples generated by the PI to analyze. During instrumental optimization, PE samples will simply consist of standards of the analytes of interest.
Surveillance audit	Conducted during PEs	Performed by ESD QAM and/or delegate.
ADQ	Conducted after each stage of method testing and development once data has been collected and verified by project personnel.	Performed by ESD QAM and/or the ECB QA representative.
DQA	Conducted quarterly	Performed by Branch QA representative

C2 Reports to Management

Audit reports and quarterly status reports of corrective actions will be provided to the Program QA Manager.

SECTION D. DATA VALIDATION AND USABILITY

D1 Data Review, Verification, and Validation

This QAPP shall govern the operation of the project at all times. Each responsible party listed in Section A4 shall adhere to the procedural requirements of the QAPP and ensure that subordinate personnel do likewise.

This QAPP shall be reviewed at least annually to ensure that the project will achieve all intended purposes. All the responsible persons listed in Section A4 shall participate in the review of the QAPP. The Technical Research Lead and the Quality Assurance Representative are responsible for determining that data are of adequate quality to support this project. The project will be modified as directed by the Technical Research Lead. The Technical Research Lead shall be responsible for the implementation of changes to the project and shall document the effective date of all changes made.

It is expected that from time to time ongoing and perhaps unexpected changes will need to be made to the project. The Technical Research Lead shall authorize all changes or deviations in the operation of the project. Deviations should be documented using the Deviation Report found in Appendix B, and these will be disseminated to those on the distribution list by the principal investigator. Deviation reports should not be written each time QC is not attained, but instead should be written when the same QC is missed multiple times and an overall change in the process is warranted. All verification and validation methods will be noted in the analysis provided in the final project report.

D2 Verification and Validation Methods

Generated data will be reviewed by the PI to verify how they were recorded, transformed, analyzed, and qualified. The data will be validated by a senior analyst who is external to the data generator but is fully knowledgeable about the analysis to determine whether the quality of the specific data set is relevant to the end use and to confirm that it was generated in accord with this QAPP.

The data are deemed acceptable and useable if no issues are identified that compromise the anticipated use of the data and if DQOs are met.

D3 Reconciliation with User Requirements

The calculation of data quality indicators will be based on the following equations:

D3.1 Accuracy

Accuracy will be assessed through the analysis of quality control samples. The analytical accuracy will be expressed as the percent recovery (%R) of an analyte that has been added to the environmental sample at a known concentration before analysis and is calculated according to the following equation:

$$\%\mathrm{R} = 100\% \times \frac{(S-U)}{C_{sa}}$$

Where:
%R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

The following formula should be used to for measurements where a standard reference material is used:

$$\%\mathrm{R} = 100\% \times \frac{C_m}{C_{srm}}$$

Where:
%R = percent recovery
C_m= measured concentration of standard reference material
C_{srm} = actual concentration of standard reference material

D3.2 Precision

Precision will be determined through the use of field duplicates, matrix spike/matrix spike duplicates and duplicate quality control samples. The Relative Percent Difference (RPD) between the two results will be calculated and used as an indication of the precision of the analyses performed.
The following formula should be used to calculate precision:

$$\mathrm{RPD} = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

Where:
RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values

If calculated from three or more replicates, use %RSD rather than RPD:

$$\%\mathrm{RSD} = (s/\bar{y}) \times 100\%$$

Where:
%RSD = relative standard deviation
s = standard deviation
$\bar{y}$ = mean of replicate analyses

D3.3 Completeness

Completeness is defined as the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Data completeness will be expressed as the percentage of valid data obtained from the measurement system. For data to be considered valid, it must meet all the acceptable criteria, including accuracy and precision, as well as any other criteria required by the prescribed analytical method. The following formula should be used to calculate completeness:

$$\%\mathrm{C} = 100\% \times \frac{V}{n}$$

Where:
%C = percent completeness
V = number of measurements judged valid
n = total number of measurements necessary to achieve a specified statistical level of confidence in decision making.

D3.4 Method Detection Limit
Defined as follows for all measurements:

$$\text{MDL} = t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)} \times S$$

Where:
MDL = method detection limit
$t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)}$ = Student's *t*-value approximate to a 99 percent confidence level and a standard deviation estimate with (n – 1) degrees of freedom
S = standard deviation of the replicate analyses

APPENDICES

and

REFERENCES

APPENDIX A: Chemicals Identified in Hydraulic Fracturing Fluid and Flowback/Produced Water

Information in Appendix A taken from EPA/600/D-11/001/February 2011, *Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*.[1]

Table A1. Chemicals found in hydraulic fracturing fluids.

Chemical	Use	Ref.
[[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis phosphonic acid ammonium salt		12
1-(phenylmethyl) quinolinium chloride		12
1-(phenylmethyl)-ethyl pyridinium, methyl derivatives	acid corrosion inhibitor	13,14
1,2,4-trimethylbenzene/1,3,5-trimethylbenzene	non-ionic surfactant	15,16
1,2-diethoxyethane	foaming agent	13
1,2-dimethoxyethane	foaming agent	13
1,4-dioxane		12
1,2-benzisothiazolin-2-one		12
1-eicosene		12
1-hexadecene		12
1-methylnaphthalene		13
1-octadecene		12
1-tetradecene		12
1-undecanol	surfactant	
1,6 hexanediamine	clay control, fracturing	
2-(2-butoxyethoxy)ethanol	foaming agent	13
2-(2-ethoxyethoxy)ethanol	foaming agent	13
2-(2-methoxyethoxy)ethanol	foaming agent	13
2,2'-azobis-{2-(imidazlin-2-yl)propane dihydrochloride		12
2,2-dibromo-3-nitrilopropionamide	biocide	12,13,14, 16
2,2-dibromomalonamide		12
2,2',2''-nitriloethanol		15
2-acrylamido-2-methylpropansulphonic acid sodium salt		12
2-acrylethyl(benzyl)dimethylammonium chloride		12
2-bromo-2-nitro-1,3-propandiol	microbiocide	14,15
2-bromo-2-nitro-3-propanol	microbiocide	13
2-bromo-3-nitrilopropionamide	biocide	13,14
2-butoxyethanol	foaming agent	13,14,17
2-ethoxyethanol	foaming agent	13,14
2-ethoxyethyl acetate	foaming agent	13
2-ethoxynaphthalene		12
2-ethyl hexanol		15,17
2-methoxyethanol	foaming agent	13
2-methoxyethyl acetate	foaming agent	13
2-methylnaphthalene		13
2-methyl-quinoline hydrochloride		12
2-monobromo-3-nitrilopropionamide	biocide	16
2-propen-1-aminium,N,N-dimethyl-N-2-propenyl-chloride, homopolymer		12
2-propenoic acid, homopolymer, ammonium salt		12
2-propenoic acid, polymer with sodium phosphinate		12
2-propenoic acid, telomer with sodium hydrogen sulfite		12

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Chemical	Use	Ref.
2-propoxyethanol	foaming agent	13
2-(thiocyanomethylthio) benzothiazole	biocide	
2-ethyl-3-propylacrolein	defoamer	
3,5,7-triaza-1-azoniatricyclo(3.3.1.13,7)decane, 1-(3-propenyl)-chloride		12
3-methyl-1-butyn-3-ol		12
4-(1,1-dimethylethyl)phenol, methyloxirane formaldehyde polymer		12
4-nonylphenol polyethylene glycol ether		12
5-chloro-2-methyl-4-isothiazolin-3-one	biocide	
acetic acid	acid treatment, buffer	14,15,16
acetic anhydride		15
acetone	corrosion inhibitor	14,15
acrolein	biocide	
acrylamide		12
acrylamide-sodium acrylate copolymer		12
acrylamide-sodium-2-acrylamido-2-methylpropane sulfonate copolymer	gelling agent	12
adipic acid	linear gel polymer	14
aldehyde	corrosion inhibitor	16
aliphatic acids		12
aliphatic alcohol polyglycol ether		12
aliphatic hydrocarbon (naphthalenesulfonic acid, sodium salt, isopropylated)	surfactant	
alkenes		12
alkyl (C14-C16) olefin sulfonate, sodium salt		12
alkyl amines	foaming agent	15
alkyl aryl polyethoxy ethanol		12
alkylamine salts	foaming agent	14,15
alkylaryl sulfonate		12
alkylphenol ethoxylate surfactants		12
aluminum	crosslinker	14
aluminum chloride		12
aluminum oxide	proppant	
aluminum silicate	proppant	
amine treated hectorite	viscosifier	
ammonia		12
ammonium acetate	buffer	15,16
ammonium alcohol ether sulfate		12
ammonium bifluoride		
ammonium bisulfite	oxygen scavenger	18
ammonium chloride	crosslinker	13,14,16
ammonium citrate		12
ammonium cumene sulfonate		12
ammonium hydrogen difluoride		12
ammonium nitrate		12
ammonium persulfate	breaker fluid	13,14
ammonium sulfate	breaker fluid	14,15
ammonium thiocyanate		12
anionic polyacrylamide copolymer	friction reducer	14,15
anionic surfactants	friction reducer	14,15
aromatic hydrocarbons		

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Chemical	Use	Ref.
aromatic naphtha	surfactant	
aromatic solvent		15
aromatics		13
asphalite	viscosifier	
attapulgite	gelling agent	
barium sulfate		15
bauxite	proppant	
bentonite	fluid additive	14,15
benzene	gelling agent	13
benzyl chloride-quaternized tar bases, quinoline derivatives		12
bis(1-methylethyl) naphthalene		12
bis(2-methoxyethyl)ether	foaming agent	13
bis(chloroethyl) ether dimethylcocoamine, diquaternary ammonium salt		12
blast furnace slag	viscosifier	
borate salts	crosslinker	18
boric acid	crosslinker	13,14
boric oxide		12
butan-1-ol		12
butane		15
C12-C14-tert-alkyl ethoxylated amines		12
calcium carbonate	pH control	
calcium chloride		12
calcium hydroxide	pH control	
calcium magnesium phosphate		12
calcium oxide	proppant	
carbohydrates		15
carbon black	resin	
carbon dioxide	foaming agent	14,15
carboxymethyl guar	linear gel polymer	14
carboxymethylhydroxypropyl guar	linear gel polymer	14
cationic polymer	friction reducer	14,15
cellulose		12
chlorine	lubricant	
chlorine dioxide		12
chloromethylnaphthalene quinoline quaternary amine	corrosion inhibitor	16
chromium	crosslinker	14
chrome acetate		
citric acid	iron control	17,18
citrus terpenes		12
cocamidopropyl betaine		12
cocamidopropylamine oxide		12
coco-betaine		12
copper compounds	breaker fluid	13,14
copper iodide	breaker fluid	14,15
copper(II) sulfate		12
cottonseed flour		
crissanol A-55		12
crystalline silica	proppant	14,15
cupric chloride dihydrate		12

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Chemical	Use	Ref.
dazomet	biocide	
decyldimethyl amine		12
diammonium peroxidisulfate	breaker fluid	13,14
diammonium phosphate	corrosion inhibitor	
diatomaceous earth	proppant	
dibromoacetonitrile		12
didecyl dimethyl ammonium chloride	biocide	
diesel	linear gel delivery	13,14
diethanolamine	foaming agent	13,14
diethylbenzene		12
diethylene glycol		15,17
diethylenetriamine	activator	16
diethylenetriamine penta (methylenephonic acid) sodium salt		12
diisopropyl naphthalenesulfonic acid		12
dimethyl formamide		15
dimethyldiallylammonium chloride		12
dipotassium phosphate		15
dipropylene glycol		12
disodium EDTA		12
ditallow alkyl ethoxylated amines		12
D-limonene		12,15
dodecylbenzene		12
dodecylbenzene sulfonic acid		12
dodecylbenzenesulfonate isopropanolamine		12
D-sorbitol		12
EDTA copper chelate	breaker fluid, activator	14,15,16
eo-C7-C9-iso-,C10rich-alcohols		17
eo-C9-11-iso, C10-rich alcohols		17
erucic amidopropyl dimethyl detaine		12
erythorbic acid, anhydrous		12
ester salt	foaming agent	13
ethane		15
ethanol	foaming agent, non-ionic surfactant	13,14,16
ethoxylated 4-tert-octylphenol		12
ethoxylated alcohols		15,17
ethoxylated alcohols, C6-C10		15
ethoxylated castor oil		12
ethoxylated hexanol		12
ethoxylated 4-nonylphenol	acid inhibitor	
ethoxylated octylphenol		12
ethoxylated sorbitan trioleate		12
ethoxylated, propoxylated trimethylolpropane		12
ethyl lactate		12
ethyl octynol	acid inhibitor	15
ethylbenzene	gelling agent	13
ethylcellulose	fluid additive	
ethylene glycol	crosslinker/breaker fluid/ scale inhibitor	13,14,17

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Chemical	Use	Ref.
ethylene glycol monobutyl ether		15
ethylene oxide		12
ethyloctynol		12
exxal 13		12
fatty acids		12
fatty alcohol polyglycol ether surfactant		12
ferric chloride		12
ferrous sulfate, heptahydrate		12
fluorene		13
formaldehyde		12
formamide		12
formic acid	acid treatment	13,14
fuller's earth	gelling agent	
fumaric acid	water gelling agent	13,14
galactomannan	gelling agent	
glutaraldehyde	biocide	17,18
glycerine	crosslinker	12,16
glycol ether	foaming agent, breaker fluid	13,14
graphite	fluid additive	
guar gum	linear gel delivery, water gelling agent	13,14,16
gypsum	gellant	
heavy aromatic petroleum naphtha	non-ionic surfactant	15,16
hemicellulase enzyme		15
heptane		15
hydrochloric acid	acid treatment, solvent	13,14,16, 17
hydrodesulfurized kerosene		12
hydrofluoric acid	acid treatment	
hydrogen peroxide		12
hydrotreated heavy naphthalene		15
hydrotreated light petroleum	friction reducer	15,16,17
hydrotreated naphtha		12
hydroxy acetic acid		12
hydroxy acetic acid ammonium salt		12
hydroxycellulose	linear gel polymer	14
hydroxyethyl cellulose	gel	18
hydroxylamine hydrochloride		12
hydroxypropyl guar	linear gel polymer	14
iron	emulsifier/surfactant	
iron oxide	proppant	
isobutyl alcohol	fracturing fluid	
isomeric aromatic ammonium salt		12
isooctanol		15
isoparaffinic petroleum hydrocarbons		12
isopropanol	foaming agent/surfactant	13,14,17
isopropylbenzene		12
kerosene		12

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Chemical	Use	Ref.
kyanite	proppant	
lactose		12
light aromatic solvent naphtha		12
light paraffin oil		12
lignite	fluid additive	
lime		15
magnesium aluminum silicate	gellant	
magnesium chloride	biocide	
magnesium nitrate	biocide	
mercaptoacetic acid	iron control	
metallic copper		15
methane		15
methanol	acid corrosion inhibitor	13,14,16, 17
methyl isobutyl ketone		15
methyl tert-butyl ether	gelling agent	13
methyl-4-isothiazolin	biocide	
methylene bis(thiocyanate)	biocide	
methylene phosphonic acid	scale inhibiter	
mica	fluid additive	14,15
mineral oil	friction reducer	18
mineral spirits		12
monoethanolamine	crosslinker	13,14
mullite	proppant	
muriatic acid	acid treatment	18
N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-ethanaminium chloride homopolymer		12
N,N-dimethylformamide	breaker	18
N,N-dimethyl-methanamine-n-oxide		12
N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-benzenemethanaminium chloride		12
naphthalene	gelling agent, non-ionic surfactant	13,16,17
N-benzyl-alkyl-pyridinium chloride		12
N-cocamidopropyl-N,N-dimethyl-N-2-hydrooxypropylsulfobetaine		12
n-hexane		15
nickel sulfate	corrosion inhibitor	
nitrogen	foaming agent	14,15
nitrilotriacetamide	scale inhibiter	
nonylphenol polyethoxylate		12
organophilic clays		12
oxyalkylated alkylphenol		12
oxylated alcohol		15
polyaromatic hydrocarbons	gelling agent/bactericide	13,14
pentane		15
petroleum distillates		15
petroleum grease mix		15
petroleum naphtha		12
phenolic resin	proppant	

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Chemical	Use	Ref.
phenanthrene	biocide	13,14
pine oil		12
poly anionic cellulose		15
poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy	acid corrosion inhibitor, non-ionic surfactant	13,14,16
polyacrylamide	friction reducer	14,18
polycyclic organic matter	gelling agent/bactericide	13,14
polyethene glycol oleate ester		12
polyethoxylated alkanol		12
polyethylene glycol		15,17
polyglycol ether	foaming agent	13,14
polyhexamethylene adipamide	resin	
polyoxyethylene sorbitan monooleate		12
polyoxylated fatty amine salt		12
polypropylene glycol	lubricant	
polysaccharide		
polyvinyl alcohol	fluid additive	
potassium acetate		12
potassium aluminum silicate		15
potassium borate		12
potassium carbonate	pH control	16,18
potassium chloride	brine carrier fluid	13,14
potassium formate		12
potassium hydroxide	crosslinker	13,14
potassium metaborate		15
potassium persulfate	fluid additive	
potassium sorbate		12
propan-2-ol	acid corrosion inhibitor	13,14,16
propane		15
propanol	crosslinker	16
propargyl alcohol	acid corrosion inhibitor	13,14,17
propylene		
propylene glycol monomethyl ether		12
pyridinium,1-(phenylmethyl)-, Et Me derivs., chlorides	corrosion inhibitor	
quartz sand	proppant	18
quaternary ammonium compounds	corrosion inhibitor	12
raffinates (petroleum)		15
salts of alkyl amines	foaming agent	13,14
silica	proppant	18
sodium 1-octanesulfonate		12
sodium acetate		12
sodium acid polyphosphate		15
sodium aluminum phosphate	fluid additive	
sodium benzoate		12
sodium bicarbonate		15
sodium bisulfate		12
sodium bromate	breaker	
sodium bromide		12
sodium carbonate	pH control	18

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Chemical	Use	Ref.
sodium carboxymethylcellulose	fluid additive	
sodium chloride	brine carrier fluid, breaker	15,16
sodium chlorite	breaker	12,16
sodium chloroacetate		12
sodium citrate		12
sodium dichloro-s-triazinetrione	biocide	
sodium erythorbate		12
sodium glycolate		12
sodium hydroxide	gelling agent	13
sodium hypochlorite		12
sodium ligninsulfonate	surfactant	
sodium mercaptobenzothiazole	corrosion inhibitor	
sodium nitrate	fluid additive	
sodium nitrite	corrosion inhibitor	
sodium metaborate octahydrate		12
sodium perborate tetrahydrate	concentrate	12,16
sodium persulfate		15
sodium polyacrylate		12
sodium sulfate		12
sodium tetraborate decahydrate	crosslinker	13,14
sodium thiosulfate		12
sodium α-olefin sulfonate		12
sorbitan monooleate		12
starch blends	fluid additive	14
styrene	proppant	
sucrose		12
sulfamic acid		12
sulfomethylated tannin		15
talc	fluid additive	14,15
tallow fatty acids sodium salt		12
terpene and terpenoids		12
terpene hydrocarbons		12
tetrachloroethylene		12
tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione		12
tetrakis(hydroxymethyl)phosphonium sulfate		12
tetramethyl ammonium chloride		12
tetrasodium EDTA		12
thioglycolic acid		12
thiourea	acid corrosion inhibitor	13,14
titanium	crosslinker	14
titanium dioxide	proppant	
toluene	gelling agent	13
tributyl phosphate	defoamer	
tributyl tetradecyl phosphonium chloride		12
triethanolamine hydroxyacetate		12
triethanolamine zirconate	crosslinker	16
triethylene glycol		15
trimethylbenzene	fracturing fluid	
trimethyl polyepichlorohydrin		15

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Chemical	**Use**	**Ref.**
tripropylene glycol methyl ether	viscosifier	
trimethylamine hydrochloride		15
trimethylamine quaternized polyepichlorohydrin		12
trisodium nitrilotriacetate		12
trisodium ortho phosphate		12
urea		12
vermiculite	lubricant	
vinylidene chloride		12
water	water gelling agent/ foaming agent	13
xanthum gum	corrosion inhibitor	
xylenes	gelling agent	13
zinc	lubricant	
zinc carbonate	corrosion inhibitor	
zirconium complex	crosslinker	15,16
zirconium nitrate	crosslinker	13,14
zirconium oxychloride	crosslinker	
zirconium sulfate	crosslinker	13,14
zirconium,tetrakis[2-[bis(2-hydroxyethyl)amino-kN]ethanolato-kO]-	crosslinker	
α-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-poly(oxy-1,2-ethandiyl)		12

Table A2. Chemicals identified in flowback/produced water

Chemical	Ref.
1,1,1-trifluorotoluene	12
1,4-dichlorobutane	12
2,4,6-tribromophenol	12
2,4-dimethylphenol	19
2,5-dibromotoluene	12
2-butanone	19
2-fluorobiphenyl	12
2-fluorophenol	12
4-nitroquinoline-1-oxide	12
4-terphenyl-d14	12
aluminum	19
anthracene	19
antimony	12
arsenic	19
barium	19
benzene	19
benzo(a)pyrene	19
bicarbonate	12
bis(2-ethylhexyl)phthalate	12
biochemical oxygen demand	12
boron	12,19
bromide	12
bromoform	12
cadmium	19
calcium	19
carbonate alkalinity	12
alkalinity	
chloride	19
chlorobenzene	19
chlorodibromomethane	12
cobalt	12
chemical oxygen demand	12
copper	19
cyanide	12
dichlorobromomethane	12
di-n-butylphthalate	19
ethylbenzene	19
fluoride	12
iron	19
lead	19
lithium	8
magnesium	19
manganese	19
methyl bromide	12
methyl chloride	12
molybdenum	12
n-alkanes, C10-C110	19
n-alkanes, C18-C70	19
n-alkanes, C1-C2	19
n-alkanes, C2-C3	19
n-alkanes, C3-C4	19
n-alkanes, C4-C5	19
n-alkanes, C5-C10	19
naphthalene	19
nickel	19
nitrobenzene-d5	12
oil and grease	19
o-terphenyl	12
p-chloro-m-cresol	19
petroleum hydrocarbons	12
phenol	19
phosphorus	12
potassium	12
radium (226)	19
radium (228)	19
selenium	12
silver	12
sodium	19
steranes	19
strontium	12
strontium (89&90)	
sulfate	12,19
sulfide	12
sulfite	12
TDS	12,19
thallium	12
titanium	19
total organic carbon	12
toluene	19
triterpanes	19
xylene (total)	19
zinc	19
zirconium	12
1,2-bromo-2-nitropropane-1,3-diol (2-bromo-2-nitro-1,3-propanediol or bronopol)	20
1,6-hexanediamine	20
1-3-dimethyladamantane	20
1-methoxy-2-propanol	20
2-(2-methoxyethoxy)ethanol	20
2-(thiocyanomethylthio) benzothiazole	20
2,2,2-nitrilotriethanol	20

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Chemical	Ref.
2,2-dibromo-3-nitrilopropionamide	20
2,2-dibromoacetonitrile	20
2,2-dibromopropanediamide	20
2-butoxyacetic acid	20
2-butoxyethanol	20
2-butoxyethanol phosphate	20
2-ethyl-3-propylacrolein	20
2-ethylhexanol	20
3,5-dimethyl-1,3,5-thiadiazinane-2-thione	20
5-chloro-2-methyl-4-isothiazolin-3-one	20
6-methylquinoline	20
acetic acid	20
acetic anhydride	20
acrolein	20
acrylamide (2-propenamide)	20
adamantane	20
adipic acid	20
ammonia	21
ammonium nitrate	20
ammonium persulfate	20
atrazine	20
bentazon	20
benzyl-dimethyl-(2-prop-2-enoyloxyethyl)ammonium chloride	20
benzylsuccinic acid	20
beryllium	21
bis(2-ethylhexyl)phthalate	21
bisphenol a	20
boric acid	20
boric oxide	20
butanol	20
cellulose	20
chloromethane	21
chrome acetate	20
chromium	21
chromium hexavalent	
citric acid	20
cyanide	21
decyldimethyl amine	20
decyldimethyl amine oxide	20
diammonium phosphate	20
didecyl dimethyl ammonium chloride	20
diethylene glycol	20
diethylene glycol monobutyl ether	20
dimethyl formamide	20
dimethyldiallylammonium chloride	20
dipropylene glycol monomethyl ether	20
diethylene glycol monobutyl ether	20
dimethyl formamide	20
dimethyldiallylammonium chloride	20
dipropylene glycol monomethyl ether	20
dodecylbenzene sulfonic acid	20
eo-C7-9-iso-,C10rich-alcohols	20
eo-C9-11-iso, C10-rich alcohols	20
ethoxylated 4-nonylphenol	20
ethoxylated nonylphenol	20
ethoxylated nonylphenol (branched)	20
ethoxylated octylphenol	20
ethyl octynol	20
ethylbenzene	20
ethylcellulose	20
ethylene glycol	20
ethylene glycol monobutyl ether	20
ethylene oxide	20
ferrous sulfate heptahydrate	20
formamide	20
formic acid	20
fumaric acid	20
glutaraldehyde	20
glycerol	20
hydroxyethylcellulose	20
hydroxypropylcellulose	20
isobutyl alcohol (2-methyl-1-propanol)	20
isopropanol (propan-2-ol)	20
limonene	20
mercaptoacidic acid	20
mercury	21
methanamine,N,N-dimethyl-,N-oxide	20
methanol	20
methyl-4-isothiazolin	20
methylene bis(thiocyanate)	20
methylene phosphonic acid (diethylenetriaminepenta[methylenephosphonic] acid)	20
modified polysaccharide or pregelatinized cornstarch or starch	20
monoethanolamine	20
monopentaerythritol	20
nitrazepam	20

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Chemical	**Ref.**
muconic acid	20
N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy ethanaminium chloride	20
nitrobenzene	20
n-methyldiethanolamine	20
oxiranemethanaminium, N,N,N-trimethyl-, chloride, homopolymer	20
phosphonium, tetrakis(hydroxymethly)-sulfate	20
polyacrylamide	20
polyacrylate	20
polyethylene glycol	20
polyhexamethylene adipamide	20
polypropylene glycol	20
polyvinyl alcohol [alcotex 17f-h]	20
propane-1,2-diol	20
propargyl alcohol	20
pryidinium, 1-(phenylmethyl)-, ethyl methyl derivatives, chlorides	20
quaternary amine	20
quaternary ammonium compound	20
quaternary ammonium salts	20
sodium carboxymethylcellulose	20
sodium dichloro-s-triazinetrione	20
sodium mercaptobenzothiazole	20
squalene	20
sucrose	20
tebuthiuron	20
p-terphenyl	20
m-terphenyl	20
o-terphenyl	20
terpineol	20
tetrachloroethene	21
tetramethyl ammonium chloride	20
tetrasodium ethylenediaminetetraacetate	20
thiourea	20
tributyl phosphate	20
trichloroisocyanuric acid	20
trimethylbenzene	20
tripropylene glycol methyl ether	20
trisodium nitrilotriacetate	20
urea	20

Table A3. Naturally occurring substances mobilized by fracturing activities

Chemical	Common Valence States	Ref.
aluminum	III	13
antimony	V,III,-III	13
arsenic	V, III, 0, -III	13
barium	II	13
beryllium	II	13
boron	III	13
cadmium	II	13
calcium	II	13
chromium	VI, III	13
cobalt	III, II	13
copper	II, I	13
hydrogen sulfide	N/A	22
iron	III, II	13
lead	IV, II	13
magnesium	II	13
molybdenum	VI, III	13
nickel	II	13
radium (226)	II	22
radium (228)	II	22
selenium	VI, IV, II, 0, -II	13
silver	I	13
sodium	I	13
thallium	III, I	13
thorium	IV	22
tin	IV, II, -IV	13
titanium	IV	13
uranium	VI, IV	22
vanadium	V	13
yttrium	III	13
zinc	II	13

APPENDIX B: Quality Assurance Project Plan Deviation Report

QAPP TITLE AND DATE: Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing, 8/25/11

DEVIATION NUMBER:

DATE OF DEVIATION:

DESCRIPTION OF DEVIATION:

CAUSE OF DEVIATION:

IMPACT OF DEVIATION ON THE PROJECT:

CORRECTIVE ACTION:

ORIGINATED BY:

_____ _____
Date

ACKNOWLEDGED BY:

_____ _____
Brian Schumacher, Branch Chief, Line Manager, Technical Research Lead Date

_____ _____
Ed Heithmar, ECB QA Representative Date

Required Distribution: All individuals listed in Table 1 of Section A4.

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