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
NATIONAL EXPOSURE RESEARCH LABORATORY
ENVIRONMENTAL SCIENCES DIVISION

October 18, 2012

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NOTICE

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LIST OF ABBREVIATIONS

ADQ	Audit of Data Quality
ECB	Environmental Chemistry Branch
EPA	Environmental Protection Agency
ESD	Environmental Sciences Division
CCV	Continuing Calibration Verification
CFR	Code of Federal Regulations
CHL	Chemistry Building
DI	Deionized
DQI	Data Quality Indicator
DQO	Data Quality Objective
EI	Electron Ionization
FSP	Field Sampling Plan
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
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
LC	Liquid Chromatography
LC-MS	Liquid Chromatography - Mass Spectrometry
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
PE	Performance Evaluation

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PI	Principal Investigator
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QSA	Quality System Assessment
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
TOF	Time-Of-Flight
TDS	Total Dissolved Solids
TSA	Technical Systems Audit
TSCA CBI	Toxic Substances Control Act Confidential Business Information
USGS	United States Geological Survey

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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, Tammy Jones-Lepp, Georges-Marie Momplaisir, Lantis Osemwengie, Charlita Rosal, Wayne Sovocool, and Jade Morgan
Data storage, management, and access	Patrick DeArmond, Don Betowski, Tammy Jones-Lepp, Georges-Marie Momplaisir, Lantis Osemwengie, Charlita Rosal, Wayne Sovocool, and Jade Morgan
Ensure the quality assurance (QA) and quality control (QC) activities described in the QAPP and being implemented; Review quarterly reports; and Information management quality assurance (IM-QA), by performing Technical System Audits, Audits of Data Quality, and other audits & assessments described in the HF QMP.	George Brilis, and/or individual delegated by the QAM, TRL, and/or the PI (such as the Branch QA Representative or other project personnel).
Data QA and QC	Patrick DeArmond, Charlita Rosal, Georges-Marie Momplaisir
Periodically review notebooks, data, maintenance logbooks, and quarterly reports	Ed Heithmar

Figure 1. Organizational flowchart f
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 chemicals 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 EPA QA Category I research 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 chemicals for which methods are to be tested are listed in **Table 2.** The list of target chemicals to be tested is continually changing as the needs of the HF program change.

Questions that this project should answer include determining the chemical components, transformation products and certain physical properties of HF fluids and the analytical approaches that are needed to identify them. The main objective of this project is to develop analytical methods for selected target analytes. The primary purpose of this QAPP is to describe the type of Quality Controls intended to be used during development of analytical methods, and how Quality Assurance will be applied to ensure that the analytical methods developed during this project provide the type and quality of data needed and expected for selected target analytes. 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 source(s) of contamination. The ultimate end-product may be a Method Compendium.

Table 2. Current HF chemicals for which methods will be developed.

Chemical	Existing Methods
Acrylamide	EPA Method 8032A[2], 8316[3]
Ethoxylated linear alcohols	No EPA method
Ethoxylated alkylphenols	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
Ethylene glycol	EPA 8015C[4]
TDS	EPA 160.1[5], 160.2[6]
Gross alpha/gross beta/radionuclides	EPA Method 900.0[7], 200.7[8], 6020[9]
Nitrosamines	EPA Method 521[10]
Disinfection byproducts (haloacetic acids, trihalomethanes)	EPA Methods 552.3[11], 524.2[12], 551.1[13]
Formaldehyde/Glutaraldehyde	EPA Method 8315[14]
Metals	EPA Method 6020[9], 3015A
Glycols (di-, tri-, and tetraethylene glycol, 2-methoxyethanol and 2-butoxyethanol)	Region 3 SOP[15]

This project will be completed in two phases. Phase 1 will consist of conducting literature searches of the chemicals in **Table 2** for candidate analytical methods. Chemicals 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[16]. 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) promulgated EPA methods, 2) consensus standard methods, and 3) peer-reviewed, published methods. If methods do not exist, methods will be developed for the chemicals of interest. Methods will be implemented by screening the HF chemicals and testing the feasibility of the selected analytical methods using standards and some stable isotopic chemicals, if available, in clean deionized (DI) water. The feasibility of the method will be based on the identification of the chemicals 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 chemicals of interest using the selected methods. Methods selected from Phase 1 will first be tested using DI water fortified with analytes of interest, then in well water, and then in more complex matrices, such as flowback/produced water matrices. Methods will be further optimized, and if they provide acceptable results, they will be used to analyze flowback/produced water for HF chemicals of interest. Because this is an EPA quality system 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.

After target analytes are selected for a class of chemicals, and a method developed and tested, then an analytical equipment-specific SOP will be written. Each resultant SOP will be added to the compendium of methods.

The ESD follows the NERL mandate to review and/or update this QAPP on an annual basis. In addition,

as research progresses knowledge i
annual revisions are distinguished
revisions are written and distingu
Secondary revisions may results f
foreseen. These factors may includ

- Knowledge gained from res
- Changes in the overarching
- Changes in overarching EP.
- Changes in personnel and/o

Figure 2. Liter

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 chemicals present in HF 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. See Section D3.2 of this document for the calculation of precision measurements.

Accuracy refers to the 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. Certified standards will be used as calibration standards and internal standards, if available, to check for accuracy and bias, and standard reference materials (SRMs) will be used, if available, to ensure accurate measurements. The criteria and how standards will be used are dependent on the compounds, or class of compounds being researched. Specific use of standards and SRMs will be described in resultant research products, such as SOPs. As research progresses and target analytes are established for each class of chemicals, SRMs shall be procured if available and within budget constraints.

Representativeness has two different aspects. Since sampling is not part of this program, if samples are received for analysis, it will be assumed that they are representative and that their representativeness has been addressed in the relevant QAPP or Field Sampling Plan (FSP). However, for this research effort, representativeness of these samples will be ensured by the proper handling, homogenizing, compositing, and storage of samples and analysis within the specified holding times so that the material analyzed reflects the material collected as accurately as possible. For samples collected for testing and verification purposes, representativeness will be addressed by obtaining samples from known locations and known geological formations, maintaining their locational information. These samples will be tested and analyzed prior to spiking and after spiking to determine if any matrix effects occur and to determine the efficacy of the method for determining the chemical of concern.

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 completeness of 100% is expected.

Comparability is the relative confidence that one data set can be compared to another. Comparability can be measured using split samples or comparing data to historical data. When additional research is performed on existing cleanup/extraction and detection techniques, then the selected and/or modified techniques shall be cited in the resultant SOP.

Method detection limits (MDLs) will be determined specifically for each chemical.

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

> CALIBRATION CURVE: Prepared from calibration standards (and internal standards, if applicable) at a minimum of 5 concentrations, used to calibrate the instrument response with respect to analyte concentration.

CALIBRATION STANDARD: A solution of the target analytes prepared from the primary dilution standard solution(s) or stock standard solution(s) and internal standards.

CONTINUING CALIBRATION VERIFICATION: A calibration standard containing the method analytes and internal standards that is analyzed periodically to verify the accuracy of the existing calibration.

INSTRUMENT BLANK: A blank matrix that is identical to the matrix the analytes are analyzed in, and is analyzed periodically to determine if the method analytes have contaminated the instrument used for analysis.

LABORATORY BLANK: An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all storage containers, buffers, preservatives, and internal standards. The laboratory blank is used to determine if the method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

LABORATORY REPLICATE: A minimum of two sample aliquots taken in the laboratory from a single sample bottle and analyzed separately with identical procedures. Analyses of replicates indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation, and storage procedures.

LABORATORY FORTIFIED BLANK: An aliquot of reagent water or other blank matrix to which a known quantity of the method analytes is added. The laboratory fortified blank is analyzed exactly like a sample, including any applicable preservation procedures. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements.

LABORATORY FORTIFIED MATRIX: An aliquot of a sample to which a known quantity of the method analytes is added. The laboratory fortified matrix is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analytes in the sample matrix must be determined in a separate aliquot, and the measured value in the laboratory fortified matrix corrected for background concentrations.

METHOD DETECTION LIMIT: The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination (Section B5.3 and D3.4), and accurate quantitation is not expected at this level.

Data Quality Indicators from existing EPA Methods for certain analytes (e.g., nitrosamines and haloacetic acids) will be followed according to those specified methods.

Table 3. Data Quality Indicators of Measurement Data.

QC Check	Frequency	Completeness	Precision	Accuracy	Corrective Action
Initial 5-point calibration	Prior to sample analysis	100%	RSD≤20%	$R^2 > 0.99$, calculated values of cal. stds must be within ± 30% of known value	No samples will be run until calibration passes criteria.
Laboratory	One per batch of	100%	N/A	< PQL[b]	Inspect the system and reanalyze

blank	samples[a]				the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Instrument blank	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%	N/A	< PQL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory fortified matrix	One per batch of samples[a]	100%	RPD≤30%[c]	>60% 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%	RPD≤30%[c]	>60% recovery	Inspect the system, narrate discrepancy. Samples must be bracketed by acceptable QC or they will be invalidated.
Continuing calibration verification (CCV)	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%	RSD≤30%[c]	± 30% of known value	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%	RPD≤30%[c]	>60% 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.

[a]Batch of samples not to exceed 20
[b]PQL=practical quantitation limit, 5 times the MDL
[c]Precision among replicates if more that 1 batch of samples are analyzed. RSD may be applicable if more than 2 replicates are analyzed.

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. Charlita Rosal and Georges-Marie Momplaisir have been working in the field of trace metals analysis for more than 15 years.

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 and unscheduled 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 performed by a certified technician.

NOTE 3: Evidentiary copies of documentation for training and certifications, such as college degrees are maintained by the EPA Office of Personnel Management, and/or a copy maintained by line management as required by the NERL QMP [2012], Revision 4, Sections 3.0, and 3.1.3.

A9 Documents and Records

Laboratory activities, results, and conclusions must be documented to the extent that requirements or guidance is provided in the HF Quality Management Plan.[17] Where the overarching HF QMP is not applicable, documentation must be kept according to both the NERL Quality Management Plan (QMP) Appendix 6 "NERL Scientific Record Keeping Policy"[18] and the ORD policy on paper laboratory records.[19] 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. These policies also describe the requirements for limited access. The Technical Research Lead will have ultimate responsibility for any and all changes to records and documents. These documents and records also include analytical chemistry metadata. The metadata includes, but is not limited to:

- Instrument type, make, model number;
- Chromatography column, make model, length, temperature conditions, and solvent gradient ramps if used;
- Standards materials source and certifications;
- Certification of Compliance for bottles.

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.[19] These records, which 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.

Once an analytical method is developed and applied, a "Deliverables Package" shall be created and submitted for review by interested parties. The package shall have a structure similar to that of an organic analysis in the Superfund Contract Laboratory Program (CLP). That is, it shall contain, but not be limited to:

- A copy of the Chain-of-Custody;
- Calibration curve data and information;
- Chromatograms and spectra of chemicals of interest;
- Continuing Calibration Curve analysis;
- Data and analysis of chemicals of interest;
- Quality Control data and information, such as blanks, duplicates, and spikes;
- Standard operating procedures (SOPs) for the determinations of chemicals of interest.

The contents and/or structure of the "Deliverables Package" may change as the EPA HF Study progresses.

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 water samples will be collected from other case studies and sent to ECB for analysis when necessary. However, laboratory-generated, matrix-free samples or clean groundwater samples spiked with standard chemicals, which may include stable isotopic chemicals, will be analyzed prior to the analysis of water samples to establish optimized method and instrument conditions for the target chemicals. Analyses of class chemicals, such as acrylamide, ethoxylated alcohols, and alkylphenols, will be performed prior to the identification of target chemicals to establish instrument conditions and create mass spectral libraries. Extraction efficiencies of the class chemicals from the aqueous matrix will be determined. Research may also include performing analyses of standards in representative matrixes prior to the analysis of HF water samples. The final analytical method is verified after the method can reproducibly meet the DQIs described in Table 3.

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.

In general, the proper collection of field samples will be performed under relevant QAPPs or FSPs and is not the responsibility of researchers in this program. 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 a Water PS Station, Labconco Model 900601 system, and the cartridges are changed when the resistivity is ≤ 18.0 MΩ cm.

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) The location of where the sample was obtained
(5) Signatures of individuals involved in sample transfer
(6) 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 Chemistry building (CHL), which is locked at all times, or the freezer located in CHL 25. The sample

storage units (refrigerators and freezers) are monitored with temperatures recorded in a log book. The monitoring frequency for refrigerators and freezers can be found in SOP ECB-008.1 "Cold Storage Unit Inspection".[20] Analyte hold time studies will be performed when the target analytes are identified, if necessary.

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

- Sample identification code number - ECB Las Vegas will add its own sample identification to each sample received. (e.g., 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., WAT for water samples; and ZZZ are 3 numbers designating the specific sample number, i.e., 001, 002, etc.)
- Sample location (longitude, latitude, altitude [where available])
- 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

Samples that are generated in-house do not require sample documentation sheets. However appropriate sample labeling should include the preparer's initials, the date of preparation, and the identity of the sample. Sample handling for in-house samples is identical to that of real-world samples.

B4 Analytical Methods

The goal of the project is to develop accurate and precise measurement tools for the determination of HF chemicals. Preliminary screening (Phase 1) and quantitation (Phase 2) of HF chemicals will be based on various analytical methods, including chromatographic, mass spectrometric, and spectroscopic techniques. If a method already exists for a chemical 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, and modified methods will be documented in modified SOPs. 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.

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, using methods 8260B and 8270D. These compounds will generally be introduced into the GC-MS using vacuum distillation according to EPA SW-846 Methods 5032 and 8261A, direct aqueous injection via method 8260C, purge-and-trap as described in 5030C and 5035A, or via headspace analyzers following method 5021A.[21]

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 $[M+H]^+$, $[M+Na]^+$, and $[M+NH_4]^+$ 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 chemicals, 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.).[21]

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.

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.

B4.1 Exploratory Research

For new chemicals that do not have standard methods presently developed for their analytical determination, exploratory research/method feasibility studies will initially be conducted to determine the best approach for the analytical determination of the chemical of interest. Initially, various analytical techniques will be assessed to determine whether the analyte of interest provides a measureable analytical signal and which technique provides the best sensitivity. These will often involve various forms of mass spectrometry (e.g., LC-MS, GC-MS, ICP-MS) and various sample introduction techniques (e.g., vacuum distillation, direct aqueous injection). The chosen approaches for analytes of interest will be investigated for improvement of the methods to increase sensitivity and overall performance. The criteria for evaluating preliminary methods are described in Section B5.1.

Figure 3. Decision Tree for the D

B5 Quality Control

Experiments to evaluate replicate
standards, surrogate samples, calib
Instrument performance must be ass

Single-laboratory testing at ECB i
obtained in a single laboratory usin
will be used to identify and quantif
probable systematic error or method
measurements, (4) method sensitivi
concentration, and (5) method ru
variations in critical method parame

Single-laboratory testing will typica

(1) Preliminary method evalu
(2) Ruggedness testing
(3) Method range and detecti
(4) Method verification
(5) Matrix validation

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

B5.1 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.

B5.2 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,[22] Williams,[23] and Cole et al.[24] 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.

B5.3 Method range and detection limits

During this stage of method verification, 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. See Glaser et al.[25] and 40 CFR 136 Appendix B in the Code of Federal Regulations for how to determine MDLs.

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 B5.2 for ruggedness testing.

B5.4 Method verification

In method verification, 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. These 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. Method verification tests the reproducibility of the method and the clarity and correctness of the written protocol.

Quality assurance for method verification 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.

B5.5 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 B5.3 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.

All instruments are maintained as per manufacturers' maintenance manuals. Maintenance manuals are kept for all instruments as per the NERL Scientific Record Keeping Policy.[18] Balances and pipettes are calibrated annually by an outside vendor. Sample storage units (refrigerators and freezers) are monitored with temperatures recorded in a log book.

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, and will be performed according to each instrument's user instructions.

Retention times of individual components will be monitored with standards, if commercially available. The responses 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.

Calibration curves based on the responses (i.e., integrated area under extracted chromatogram) of the chemicals of interest will be performed to determine dynamic ranges of measurements for each chemical on the specific instrument used for measurement. A minimum of 5 different concentrations must be used to determine the calibration curve, with appropriate spacing between calibration standards (i.e., ranging from 1-3 orders of magnitude from low to high calibration standard). Either linear or quadratic equations may be used to fit the calibration curve data, as well as appropriate weighting of the data points, per the results from the calibration standards. See Table 3 for the criteria in accepting calibration curves.

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 pipettes (0.5 -10 µL, 20-200 µL, 100-1000 µL) (calibrated annually)
- Pipette tips
- Glass beakers
- Lab tape
- Permanent markers
- Nitrile gloves
- Disposable borosilicate Pasteur pipettes
- Ultra-high purity grade compressed nitrogen
- Ultra-high purity grade compressed helium
- Ultra-high purity liquid argon
- Breathable grade compressed air
- 1-mL autosampler vials with PTFE/silicone septa (amber and clear)
- Class A volumetric glassware
- Trace-cleaned polyethylene bottles and centrifuge tubes
- Trace-cleaned Teflon bottles

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
- Water pro PS station Labconco, Model 900601 water purification system (used for trace metals work)
- 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 concentrated nitric acid
- High-purity hydrochloric acid
- Available standards, including those for ethoxylated alcohols and alkylphenols, alkylphenols, acrylamide, ethylene glycol
- Isotopically labeled standards when available
- Inorganic metal standards

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

Prior to the HF QMP,[17] data management was performed by following the NERL QMP Appendix 6 "NERL Scientific Record Keeping Policy"[18] and the ORD policy on paper laboratory records.[19]

After Revision 0.0 of this QAPP, the overarching Quality Management Plan "Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources" (HF QMP), Revision 0.0 was finalized in December 2011. The HF QMP Revision 0.0 was revised and then released as Revision 1.0 January 2012.[17] The HF QMP provides guidance regarding Documents and Records in Section 5 of the QMP. Where the HF QMP is not applicable, documentation must be kept according to both the NERL Quality Management Plan (QMP) Appendix 6 "NERL Scientific Record Keeping Policy"[18] and the ORD policy on paper laboratory records.[19] Regardless of existing and/or forthcoming policies, procedures, and guidances, all electronic data are backed-up using the LabLAN which has been put in place for the CHL and POS buildings.

EPA Scientific Data Management Policies and Procedures are currently under review and revision. As the

EPA, ORD, NERL, and/or the HF QMP are revised, the ESD will make every attempt to implement any new policy, procedure, or guidance regarding data management when and where applicable. The ability of ESD to implement new or revised data management procedures may be affected by time and/or resource constraints (e.g., funding and/or personnel).

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). When data is transcribed, a second person will verify the accuracy of the data transcription. Most major instruments, such as an HPLC/MS, are connected to a LabLan. A LabLan is an instrument-Intranet and is designed to enable:

- Back-up of electronic data at a source other than the instrument;
- Examination of data and/or information at a station other than the instrument that is integrated with a computer.

The retrieval of back-up data and/or information on a LabLan is accessible only by a few IT personnel.

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

The types of assessments that will be conducted under the HF Research Program are described in the Quality Management Plan for the "Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources". [17]

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, approximately 50% of the 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), as per guidelines for an EPA QA Category 1 project found at http://www.epa.gov/nrmrl/qalchapter2.html. NRMRL has an SOP for this activity that will be used by the ESD QA Manager and/or ECB QA Representative. NRMRL's SOP, *Performing Audits of Data Quality (ADQs)*, is located at the following URL: http://intranet.epa.gov/nrmintra/lsas/eqmp/pdf/SOPL SASQA020.pdf.

Data Usability Assessments are required, which will be performed by the PI or Technical Research Lead on each data set associated with a project to use the information collected during data verification and ADQs to assess whether the data can be used for the intended purposes.

Data verification, as described in Section D1 and D2, is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements.

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	At least once for each project	Performed by ESD QAM
PE	For each critical measurement, if an applicable PE is available	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	Throughout HF Research Progam as needed	Performed by ESD QAM and/or delegate.
ADQ	Approximately 50% of each critical measurement associated with a project	Performed by ESD QAM and/or the ECB QA representative.
Data usability assessment	Each data set associated with a project.	Performed by Key Investigator and supporting personnel
Data Verification	Each data set associated with a project	Performed by Key Investigator and supporting personnel

C2 Reports to Management

Any findings from an audit should be reported to the Research Technical Lead and Principal Investigator as soon as possible and within 5 business days of the review so that corrective actions can be made as quickly as possible. Formal written audit reports and responses, if necessary, will be made typically within 10 business days of the audit or review, depending upon the ESD QAM or ECB QA representative workload and availability. Audit reports will be provided by the Organization's QAM to the Program QA Manager and the Research Technical Lead. Results of the verification of corrective actions and audit closure will be monitored by the organization's QAM and reported to 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.

Verification of data is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method requirements. Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method or procedural compliance to determine the analytical quality of a specific data set. All verification and validation methods, described in Section D2, will be noted in the analysis provided in the final project report.

D2 Verification and Validation Methods

Data verification and validation will be performed following the guidance of the EPA document "Guidance on Environmental Data Verification and Data Validation" (EPA QA/G-8).[26] For data verification, generated data will be reviewed by the PI to verify how they were recorded, transformed, analyzed, and qualified. Analytical methods are examples of sources that can provide specifications for data collection, and data verification evaluates how closely the methods were followed during data generation. The data should be verified against applicable methods or SOPs, and any deviations of the criteria should be noted in the data verification documentation. Other records commonly used for data verification include, but are not limited to COC forms, refrigerator logs, sample preparation logs, certificates of standards, and instrument readouts. Verified data are data that have been checked for a variety of factors, including transcription errors, correct application of dilution factors, correct application of conversion factions, etc.

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:

$$\% \quad R100\% \times \frac{(S-U)}{C_{sa}}$$

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:

$$\% \quad R100\% \times \frac{C_m}{C_{srm}}$$

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 replicates, spike replicates, and replicate quality control samples.
For duplicates, the precision will be indicated by the Relative Percent Difference (RPD), to be calculated as follows:

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

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:

$$\%\text{RSD} = (s / \bar{x}) \times 100\%$$

Where:
%RSD = relative standard deviation
s = standard deviation
$\bar{x}$ = 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:

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

Where:
%C = percent completeness
V = number of measurements judged valid
n = total number of measurements.

D3.4 Method Detection Limit

Defined as follows for all measurements (40CFR 136 Part B):

$$\mathrm{MDL} = t_{(n\text{-}1,\ 1\text{-}\alpha = 99.0)} \times S$$

Where:
MDL = method detection limit
$t_{(n\text{-}1,\ 1\text{-}\alpha = 99.0)}$ = 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 and references in Appendix A taken from EPA/600/R-11/122/November 2011, *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*.[1]

Table A1. Chemicals found in hydraulic fracturing fluids.

Chemical Name	Use	Ref.
1-(1-naphthylmethyl)quinolinium chloride		39
1-(phenylmethyl)-ethyl pyridinium, methyl derive.	Acid corrosion inhibitor	28,29,34
1,1,1-Trifluorotoluene		27
1,1':3',1''-Terphenyl		37
1,1':4',1''-Terphenyl		37
1,1-Dichloroethylene		27
1,2,3-Propanetricarboxylic acid, 2-hydroxy-, trisodium salt, dihydrate		39,40
1,2,3-Trimethylbenzene		39, 40
1,2,4-Butanetricarboxylic acid, 2-phosphono-		39,40
1,2,4-Trimethylbenzene	Non-ionic surfactant	30,31,34,39,40
1,2-Benzisothiazolin-3-one		27,39,40
1,2-Dibromo-2,4-dicyanobutane		39,40
1,2-Ethanediaminium, N, N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'bis(2-hydroxyethyl)-N,N'-dimethyl-,tetrachloride		39
1,2-Propylene glycol		37,39,40
1,2-Propylene oxide		39
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol		39,40
1,3,5-Trimethylbenzene		39,40
1,4-Dichlorobutane		27
1,4-Dioxane		27,40
1,6 Hexanediamine	Clay control	34
1,6-Hexanediamine		37,39
1,6-Hexanediamine dihydrochloride		39
1-[2-(2-Methoxy-1-methylethoxy)-1-methylethoxy]-2-propanol		34
1-3-Dimethyladamantane		37
1-Benzylquinolinium chloride	Corrosion inhibitor	27,39,40
1-Butanol		27,39,40
1-Decanol		39
1-Eicosene		27,40
1-Hexadecene		27,40
1-Hexanol		39
1-Methoxy-2-propanol		27,39,40
1-Methylnaphthalene		28
1-Octadecanamine, N,N-dimethyl-		39
1-Octadecene		27,40
1-Octanol		39
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., chlorides, sodium salts		39
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., inner salts		27,39,40
1-Propanaminium, N-(3-aminopropyl)-2-hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., inner salts		27,39,40
1-Propanesulfonic acid, 2-methyl-2-[(1-oxo-2-propenyl)amino]-		27,40
1-Propanol	Crosslinker	31,39,40
1-Propene		34
1-Tetradecene		27,40
1-Tridecanol		39
1-Undecanol	Surfactant	34

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Chemical	Use	Ref.
2-(2-Butoxyethoxy)ethanol	Foaming agent	28
2-(2-Ethoxyethoxy)ethyl acetate		39,40
2-(Hydroxymethylamino)ethanol		39
2-(Thiocyanomethylthio)benzothiazole	Biocide	34
2,2'-(Octadecylimino)diethanol		39
2,2,2-Nitrilotriethanol		37
2,2'-[Ethane-1,2-diylbis(oxy)]diethanamine		39
2,2'-Azobis-{2-(imidazlin-2-yl)propane dihydrochloride		27,40
2,2-Dibromo-3-nitrilopropionamide	Biocide	27,28,29,31,38,39,40
2,2-Dibromopropanediamide		27,40
2,4,6-Tribromophenol		27
2,4-Dimethylphenol		33
2,4-Hexadienoic acid, potassium salt, (2E,4E)-		27,40
2,5 Dibromotoluene		27
2-[2-(2-Methoxyethoxy)ethoxy]ethanol		37
2-acrylamido-2-methylpropanesulphonic acid sodium salt polymer		39
2-acrylethyl(benzyl)dimethylammonium Chloride		27,40
2-bromo-3-nitrilopropionamide	Biocide	28,29
2-Butanone oxime		39
2-Butoxyacetic acid		37
2-Butoxyethanol	Foaming agent, breaker fluid	28,29,38,39,40
2-Butoxyethanol phosphate		37
2-Di-n-butylaminoethanol		39,40
2-Ethoxyethanol	Foaming agent	28,29
2-Ethoxyethyl acetate	Foaming agent	28
2-Ethoxynaphthalene		27,40
2-Ethyl-1-hexanol		30,39,40
2-Ethyl-2-hexenal	Defoamer	34
2-Ethylhexanol		38
2-Fluorobiphenyl		27
2-Fluorophenol		27
2-Hydroxyethyl acrylate		39,40
2-Mercaptoethanol		39
2-Methoxyethanol	Foaming agent	28
2-Methoxyethyl acetate	Foaming agent	28
2-Methyl-1-propanol	Fracturing fluid	34,39,40
2-Methyl-2,4-pentanediol		39,40
2-Methyl-3(2H)-isothiazolone	Biocide	34,39
2-Methyl-3-butyn-2-ol		27,40
2-Methylnaphthalene		28
2-Methylquinoline hydrochloride		27,40
2-Monobromo-3-nitrilopropionamide	Biocide	31,39,40
2-Phosphonobutane-1,2,4-tricarboxylic acid, potassium salt		39
2-Propanol, aluminum salt		39
2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, chloride		27,40
2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, chloride, homopolymer		27,40
2-Propenoic acid, polymer with sodium phosphinate		27,40
2-Propenoic acid, telomer with sodium hydrogen sulfite		27,40
2-Propoxyethanol	Foaming agent	28
2-Substituted aromatic amine salt		39,40
3,5,7-Triazatricyclo(3.3.1.1(superscript 3,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-		27,40
3-Bromo-1-propanol	Microbiocide	28

Table continued on next page

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Chemical	Use	Ref.
4-(1,1-Dimethylethyl)phenol, methyloxirane, formaldehyde polymer		27,40
4-Chloro-3-methylphenol		33
4-Dodecylbenzenesulfonic acid		27,39,40
4-Ethyloct-1-yn-3-ol	Acid inhibitor	30,39,40
4-Methyl-2-pentanol		39
4-Methyl-2-pentanone		30
4-Nitroquinoline-1-oxide		27
4-Terphenyl-d14		27
(4R)-1-methyl-4-(prop-1-en-2-yl)cyclohexene		30,39,40
5-Chloro-2-methyl-3(2H)-isothiazolone	Biocide	34,39,40
6-Methylquinoline		37
Acetaldehyde		39,40
Acetic acid	Acid treatment, buffer	29,30,31,38,39,40
Acetic acid, cobalt(2+) salt		39,40
Acetic acid, hydroxy-, reaction products with triethanolamine		40
Acetic anhydride		30,38,39,40
Acetone	Corrosion Inhibitor	29,30,39,40
Acetonitrile, 2,2',2''-nitrilotris-		39
Acetophenone		39
Acetylene		38
Acetylenic alcohol		39
Acetyltriethyl citrate		39
Acrolein	Biocide	34
Acrylamide		27,39,40
Acrylamide copolymer		39
Acrylamide-sodium acrylate copolymer		27,40
Acrylamide-sodium-2-acrylamido-2-methlypropane sulfonate copolymer	Gelling agent	27,39,40
Acrylate copolymer		39
Acrylic acid/2-acrylamido-methylpropylsulfonic acid copolymer		39
Acrylic copolymer		39
Acrylic polymers		39,40
Acrylic resin		40
Acyclic hydrocarbon blend		39
Adamantane		37
Adipic acid	Linear gel polymer	29,39,40
Alcohol alkoxylate		39
Alcohols		39,40
Alcohols, C11-14-iso-, C13-rich		27,40
Alcohols, C9-C22		39
Alcohols; C12-14-secondary		39,40
Aldehyde	Corrosion inhibitor	31,39,40
Aldol		39,40
Alfa-alumina		39,40
Aliphatic acids		27,39,40
Aliphatic alcohol glycol ether		40
Aliphatic alcohol polyglycol ether		39
Aliphatic amine derivative		39
Aliphatic hydrocarbon (naphthalenesulfonic acide, sodium salt, isopropylated)	Surfactant	34
Alkaline bromide salts		39
Alkalinity		34
Alkanes, C10-14		39
Alkanes, C1-2		33
Alkanes, C12-14-iso-		40
Alkanes, C13-16-iso-		39
Alkanes, C2-3		33

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Chemical	Use	Ref.
Alkanes, C3-4		33
Alkanes, C4-5		33
Alkanolamine/aldehyde condensate		39
Alkenes		39
Alkenes, C>10 .alpha.-		27,39,40
Alkenes, C>8		39
Alkoxylated alcohols		39
Alkoxylated amines		39
Alkoxylated phenol formaldehyde resin		39,40
Alkyaryl sulfonate		39
Alkyl alkoxylate		39,40
Alkyl amine		39
Alkyl amine blend in a metal salt solution		39,40
Alkyl aryl amine sulfonate		39
Alkyl aryl polyethoxy ethanol		27,40
Alkyl esters		39,40
Alkyl hexanol		39,40
Alkyl ortho phosphate ester		39
Alkyl phosphate ester		39
Alkyl quaternary ammonium chlorides		39
Alkyl* dimethyl benzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 2.5% C18 2.5% C10 and trace of C8)	Corrosion inhibitor	27
Alkylaryl sulfonate		27,39,40
Alkylaryl sulphonic acid		39
Alkylated quaternary chloride		39,40
Alkylbenzenesulfonate, linear	Foaming agent	29,30,39
Alkylbenzenesulfonic acid		38,39,40
Alkylethoammonium sulfates		39
Alkylphenol ethoxylates		39
Almandite and pyrope garnet		39,40
Alpha-C11-15-sec-alkyl-omega-hydroxypoly(oxy-1,2-et hanediyl)		39
Alpha-Terpineol		37
Alumina	Proppant	39,34,40
Aluminium chloride		27,39,40
Aluminum	Crosslinker	29,33,39,40
Aluminum oxide		39,40
Aluminum oxide silicate		39
Aluminum silicate	Proppant	34,40
Aluminum sulfate		39,40
Amides, coco, N-[3-(dimethylamino)propyl]		39,40
Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with chloroacetic acid, sodium salts		39
Amides, coco, N-[3-(dimethylamino)propyl], N-oxides		27,39,40
Amides, tall-oil fatty, N,N-bis(hydroxyethyl)		27,40
Amides, tallow, n-[3-(dimethylamino)propyl],n-oxide s		39
Amidoamine		39
Amine		39,40
Amine bisulfite		39
Amine oxides		39
Amine phosphonate		39
Amine salt		39
Amines, C14-18; C16-18-unsaturated, alkyl, ethoxylated		39
Amines, C8-18 and C18-unsatd. alkyl	Foaming agent	30
Amines, coco alkyl, acetate		39
Amines, coco alkyl, ethoxylated		40

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Chemical	Use	Ref.
Amines, polyethylenepoly-, ethoxylated, phosphonomethylated		39
Amines, tallow alkyl, ethoxylated, acetates (salts)		39,40
Amino compounds		39
Amino methylene phosphonic acid salt		39
Aminotrimethylene phosphonic acid		39
Ammonia		35,38,39,40
Ammonium acetate	Buffer	30,31,39,40
Ammonium alcohol ether sulfate		27,39,40
Ammonium bifluoride		38
Ammonium bisulfite	Oxygen scavenger	32,38,39,40
Ammonium C6-C10 alcohol ethoxysulfate		39
Ammonium C8-C10 alkyl ether sulfate		39
Ammonium chloride	Crosslinker	28,29,31,39,40
Ammonium citrate		27,40
Ammonium fluoride		39,40
Ammonium hydrogen carbonate		39,40
Ammonium hydrogen difluoride		39,40
Ammonium hydrogen phosphonate		40
Ammonium hydroxide		27,39,40
Ammonium nitrate		27,39,40
Ammonium persulfate	Breaker fluid	28,29,38
Ammonium salt		39,40
Ammonium salt of ethoxylated alcohol sulfate		39,40
Ammonium sulfate	Breaker fluid	29,30,39,40
Amorphous silica		38,39,40
Anionic copolymer		39,40
Anionic polyacrylamide		39,40
Anionic polyacrylamide copolymer	Friction reducer	29,30,39
Anionic polymer		39,40
Anionic polymer in solution		39
Anionic surfactants	Friction reducer	29,30
Anionic water-soluble polymer		39
Anthracene		33
Antifoulant		39
Antimonate salt		39,40
Antimony		27
Antimony pentoxide		39
Antimony potassium oxide		39,40
Antimony trichloride		39
Aromatic alcohol glycol ether		39
Aromatic aldehyde		39
Aromatic hydrocarbons		34,40
Aromatic ketones		39,40
Aromatic polyglycol ether		39
Aromatics		28
Arsenic		33
Arsenic compounds		40
Ashes, residues		40
Atrazine		37
Attapulgite	Gelling agent	34
Barium		33
Barium sulfate		30,39,40
Bauxite	Proppant	34,39,40
Bentazone		37
Bentone clay		40

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Chemical	Use	Ref.
Bentonite	Fluid additives	29,30,39,40
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex		40
Benzalkonium chloride		40
Benzene	Gelling agent	28,39,40
Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated, sodium salts		40
Benzene, C10-16-alkyl derivs.		39
Benzenesulfonic acid, (1-methylethyl)-, ammonium salt		27,40
Benzenesulfonic acid, C10-16-alkyl derivs.		39,40
Benzenesulfonic acid, C10-16-alkyl derivs., potassium salts		39,40
Benzo(a)pyrene		33
Benzoic acid		38,39,40
Benzyl chloride		39
Benzyl-dimethyl-(2-prop-2-enoyloxyethyl)ammonium chloride		37
Benzylsuccinic acid		37
Beryllium		35
Bicarbonate		27
Bicine		39
Biocide component		39
Bis(1-methylethyl)naphthalenesulfonic acid, cyclohexylamine salt		39
Bis(2-methoxyethyl) ether	Foaming Agent	28
Bishexamethylenetriamine penta methylene phosphonic acid		39
Bisphenol A		37
Bisphenol A/Epichlorohydrin resin		39,40
Bisphenol A/Novolac epoxy resin		39,40
Blast furnace slag	Viscosifier	34,40
Borate salts	Crosslinker	32,39,40
Borax	Crosslinker	28,29,39,40
Boric acid	Crosslinker	28,29,38,39,40
Boric acid, potassium salt		39,40
Boric acid, sodium salt		38,39
Boric oxide		27,39,40
Boron		33
Boron sodium oxide		39,40
Boron sodium oxide tetrahydrate		39,40
Bromide (-1)		27
Bromodichloromethane		27
Bromoform		27
Bronopol	Microbiocide	29,30,39,40
Butane		30
Butanedioic acid, sulfo-, 1,4-bis(1,3-dimethylbutyl) ester, sodium salt		39
Butyl glycidyl ether		39,40
Butyl lactate		39,40
C.I. Pigment orange 5		40
C10-C16 ethoxylated alcohol	Surfactant	34,39,40
C-11 to C-14 n-alkanes, mixed		39
C12-14-tert-alkyl ethoxylated amines		27,40
Cadmium		33
Cadmium compounds		34,40
Calcium		33
Calcium bromide		40
Calcium carbonate		39,40
Calcium chloride		27,38,39,40
Calcium dichloride dihydrate		39,40
Calcium fluoride		39
Calcium hydroxide	pH control	34,39,40

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Chemical	Use	Ref.
Calcium hypochlorite		39,40
Calcium oxide	Proppant	34,38,39,40
Calcium peroxide		39
Calcium sulfate	Gellant	34,40
Carbohydrates		30,39,40
Carbon		40
Carbon black	Resin	34,40
Carbon dioxide	Foaming agent	29,30,39,40
Carbonate alkalinity		27
Carbonic acid calcium salt (1:1)	pH control	34,39
Carbonic acid, dipotassium salt		39,40
Carboxymethyl cellulose		37
Carboxymethyl guar gum, sodium salt		39
Carboxymethyl hydroxypropyl guar		38,39,40
Carboxymethylguar	Linear gel polymer	29
Carboxymethylhydroxypropylguar	Linear gel polymer	29
Cationic polymer	Friction reducer	29,30
Caustic soda		34,40
Caustic soda beads		34,40
Cellophane		39,40
Cellulase enzyme		39
Cellulose		27,39,40
Cellulose derivative		39,40
Ceramic		34,40
Cetyl trimethyl ammonium bromide		39
CFR-3		40
Chloride		33
Chloride (-1)		40
Chlorine	Lubricant	34
Chlorine dioxide		27,39,40
Chlorobenzene		33
Chlorodibromomethane		27
Chloromethane		27
Chlorous ion solution		39
Choline chloride		38,39,40
Chromates		39,40
Chromium	Crosslinker	35
Chromium (III) acetate		39
Chromium (III), insoluble salts		29
Chromium (VI)		29
Chromium acetate, basic		34
Cinnamaldehyde (3-phenyl-2-propenal)		38,39,40
Citric acid	Iron control	32,38,39,40
Citrus terpenes		27,39,40
Coal, granular		39,40
Cobalt		27
Coco-betaine		27,40
Coconut oil acid/diethanolamine condensate (2:1)		39
Collagen (gelatin)		39,40
Common White		40
Complex alkylaryl polyo-ester		39
Complex aluminum salt		39
Complex organometallic salt		39
Complex polyamine salt		38
Complex substituted keto-amine		39

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Chemical	Use	Ref.
Complex substituted keto-amine hydrochloride		39
Copolymer of acrylamide and sodium acrylate		39,40
Copper		30,39
Copper compounds	Breaker fluid	
Copper sulfate		27,39,40
Copper(I) iodide	Breaker fluid	29,30,39,40
Copper(II) chloride		27,39,40
Coric oxide		40
Corn sugar gum	Corrosion inhibitor	
Corundum		40
Cottonseed flour		34,40
Cremophor(R) EL		27,39,40
Crissanol A-55		27,40
Cristobalite		39,40
Crotonaldehyde		39,40
Crystalline silica, tridymite		39,40
Cumene		27,39,40
Cupric chloride dihydrate		27,38,39
Cuprous chloride		39,40
Cured acrylic resin		39,40
Cured resin		38,39,40
Cured silicone rubber-polydimethylsiloxane		39
Cured urethane resin		39,40
Cyanide		35
Cyanide, free		27
Cyclic alkanes		39
Cyclohexane		38,39
Cyclohexanone		39,40
D-(-)-Lactic acid		39,40
Dapsone		39,40
Dazomet	Biocide	34,38,39,40
Decyldimethyl amine		27,40
D-Glucitol		27,39,40
D-Gluconic acid		39
D-Glucose		39
D-Limonene		27,30,38
Di(2-ethylhexyl) phthalate		27,39
Diatomaceous earth, calcined		39
Diatomaceus earth	Proppant	34,40
Dibromoacetonitrile		27,39,40
Dibutyl phthalate		33
Dicalcium silicate		39,40
Dicarboxylic acid		39
Didecyl dimethyl ammonium chloride	Biocide	39,34
Diesel		28,29,39
Diethanolamine	Foaming agent	28,29,39,40
Diethylbenzene		27,39,40
Diethylene glycol		30,38,39,40
Diethylene glycol monobutyl ether		37
Diethylene glycol monoethyl ether	Foaming agent	28
Diethylene glycol monomethyl ether	Foaming agent	28,39,40
Diethylenetriamine	Activator	31,39,40
Diisopropylnaphthalene		27,40
Diisopropylnaphthalenesulfonic acid		27,39,40
Dimethyl glutarate		39,40

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Chemical	Use	Ref.
Dimethyl silicone		39,40
Dinonylphenyl polyoxyethylene		40
Dipotassium monohydrogen phosphate		30
Dipropylene glycol		27,39,40
Di-secondary-butylphenol		39
Disodium dodecyl(sulphonatophenoxy)benzenesulphonat e		39
Disodium ethylenediaminediacetate		39
Disodium ethylenediaminetetraacetate dihydrate		39
Dispersing agent		39
Distillates, petroleum, catalytic reformer fractionator residue, low-boiling		39
Distillates, petroleum, hydrodesulfurized light catalytic cracked		39
Distillates, petroleum, hydrodesulfurized middle		39
Distillates, petroleum, hydrotreated heavy naphthenic		30,39,40
Distillates, petroleum, hydrotreated heavy paraffinic		39,40
Distillates, petroleum, hydrotreated light	Friction reducer	30,31,38,39,40
Distillates, petroleum, hydrotreated light naphthenic		39
Distillates, petroleum, hydrotreated middle		39
Distillates, petroleum, light catalytic cracked		39
Distillates, petroleum, solvent-dewaxed heavy paraffinic		39,40
Distillates, petroleum, solvent-refined heavy naphthenic		39
Distillates, petroleum, steam-cracked		39
Distillates, petroleum, straight-run middle		39,40
Distillates, petroleum, sweetened middle		39,40
Ditallow alkyl ethoxylated amines		27,40
Docusate sodium		39
Dodecyl alcohol ammonium sulfate		39
Dodecylbenzene		27,40
Dodecylbenzene sulfonic acid salts		39,40
Dodecylbenzenesulfonate isopropanolamine		27,39,40
Dodecylbenzene sulfonic acid, monoethanolamine salt		39
Dodecylbenzene sulphonic acid, morpholine salt		39,40
Econolite Additive		40
Edifas B	Fluid additives	30,40
EDTA copper chelate	Breaker fluid, activator	29,30,31,39,40
Endo- 1,4-beta-mannanase, or Hemicellulase		40
EO-C7-9-iso; C8 rich alcohols		40
EO-C9-11-iso; C10 rich alcohols		39,40
Epichlorohydrin		39,40
Epoxy resin		39
Erucic amidopropyl dimethyl detaine		27,39,40
Essential oils		39
Ester salt	Foaming agent	28
Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl) oxy]-, chloride		40
Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl) oxy]-,chloride, polymer with 2-propenamide		39,40
Ethane		30
Ethanol	Foaming agent, non-ionic surfactant	28,29,31,39,40
Ethanol, 2,2'-iminobis-, N-coco alkyl derivs., N-oxides		39
Ethanol, 2,2'-iminobis-, N-tallow alkyl derivs.		39
Ethanol, 2-[2-[2-(tridecyloxy)ethoxy]ethoxy]-, hydrogen sulfate, sodium salt		39
Ethanolamine	Crosslinker	28,29,39,40
Ethoxylated 4-nonylphenol		34
Ethoxylated alcohol/ester mixture		40
Ethoxylated alcohols		30,34,38,39,40

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Chemical	Use	Ref.
Ethoxylated alkyl amines		39,40
Ethoxylated amine		39,40
Ethoxylated fatty acid ester		39,40
Ethoxylated fatty acid, coco		40
Ethoxylated fatty acid, coco, reaction product with ethanolamine		40
Ethoxylated nonionic surfactant		39
Ethoxylated nonylphenol		37,39,40
Ethoxylated propoxylated C12-14 alcohols		39,40
Ethoxylated sorbitan trioleate		27,40
Ethoxylated sorbitol esters		39,40
Ethoxylated undecyl alcohol		39
Ethoxylated, propoxylated trimethylolpropane		27,40
Ethylacetate		38,39,40
Ethylacetoacetate		39
Ethyllactate		27,40
Ethylbenzene	Gelling Agent	28,38,39,40
Ethylcellulose	Fluid Additives	34
Ethylene glycol	Crosslinker/ Breaker Fluids/ Scale Inhibitor	28,29,38,39,40
Ethylene glycol diethyl ether	Foaming Agent	28
Ethylene glycol dimethyl ether	Foaming Agent	28
Ethylene oxide		27,39,40
Ethylene oxide-nonylphenol polymer		39
Ethylenediaminetetraacetic acid		39,40
Ethylenediaminetetraacetic acid tetrasodium salt hydrate		27,39,40
Ethylenediaminetetraacetic acid, diammonium copper salt		40
Ethylene-vinyl acetate copolymer		39
Ethylhexanol		40
Fatty acid ester		39
Fatty acid, tall oil, hexa esters with sorbitol, ethoxylated		39,40
Fatty acids		39
Fatty acids, tall oil reaction products w/acetophen one, formaldehyde & thiourea		40
Fatty acids, tall-oil		27,39,40
Fatty acids, tall-oil, reaction products with diethylenetriamine		39
Fatty acids, tallow, sodium salts		27,40
Fatty alcohol alkoxylate		39,40
Fatty alkyl amine salt		39
Fatty amine carboxylates		39
Fatty quaternary ammonium chloride		39
FD & C blue no. 1		39
Ferric chloride		27,39,40
Ferric sulfate		39,40
Fluorene		28
Fluoride		27
Fluoroaliphatic polymeric esters		39,40
Formaldehyde polymer		39
Formaldehyde, polymer with 4-(1,1-dimethyl)phenol, methyloxirane and oxirane		39
Formaldehyde, polymer with 4-nonylphenol and oxirane		39
Formaldehyde, polymer with ammonia and phenol		39
Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide		40
Formalin		27,39,40
Formamide		27,39,40
Formic acid	Acid Treatment	28,29,38,39,40
Formic acid, potassium salt		27,39,40

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Chemical	Use	Ref.
Fuel oil, no. 2		39,40
Fuller's earth	Gelling agent	34
Fumaric acid	Water gelling agent/ linear gel polymer	28,29,39,40
Furfural		39,40
Furfuryl alcohol		39,40
Galactomannan	Gelling agent	34
Gas oils, petroleum, straight-run		39
Gilsonite	Viscosifier	39,40
Glass fiber		27,39,40
Gluconic acid		38
Glutaraldehyde	Biocide	32,38,39,40
Glycerin, natural	Crosslinker	27,31,39,40
Glycine, N-(carboxymethyl)-N-(2-hydroxyethyl)-, disodium salt		39
Glycine, N,N'-1,2-ethanediylbis[N-(carboxymethyl)-, disodium salt		27,39,40
Glycine, N,N-bis(carboxymethyl)-, trisodium salt		27,39,40
Glycine, N-[2-[bis(carboxymethyl)amino]ethyl]-N-(2- hydroxyethyl)-, trisodium salt		39
Glycol ethers		38,39
Glycolic acid		27,39,40
Glycolic acid sodium salt		27,39,40
Glyoxal		39
Glyoxylic acid		39
Graphite	Fluid additives	34
Guar gum		38,39,40
Guar gum derivative		39
Gypsum		34,40
Haloalkyl heteropolycycle salt		39
Heavy aromatic distillate		39
Heavy aromatic petroleum naphtha		34,40
Hematite		39,40
Hemicellulase		30,39,40
Heptane		30,39
Heptene, hydroformylation products, high-boiling		39
Hexane		30
Hexanes		39
Hydrated aluminum silicate		39,40
Hydrocarbons		39
Hydrocarbons, terpene processing by-products		27,39,40
Hydrochloric acid	Acid treatment, solvent	28,29,31,38,39,40
Hydrogen fluoride (Hydrofluoric acid)	Acid treatment	39
Hydrogen peroxide		27,39,40
Hydrogen sulfide		27,39
Hydrotreated and hydrocracked base oil		39
Hydrotreated heavy naphthalene		30
Hydrotreated light distillate		40
Hydrotreated light petroleum distillate		40
Hydroxyacetic acid ammonium salt		27,40
Hydroxycellulose	Linear gel polymer	29
Hydroxyethylcellulose	Gel	32,39,40
Hydroxylamine hydrochloride		27,39,40
Hydroxyproplyguar	Linear gel polymer	29
Hydroxypropyl cellulose		37
Hydroxypropyl guar gum	Linear gel delivery, water gelling agent	28,29,31,39,40
Hydroxysultaine		39

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Chemical	Use	Ref.
Igepal CO-210		27,39,40
Inner salt of alkyl amines		39,40
Inorganic borate		39,40
Inorganic particulate		39,40
Inorganic salt		39
Instant coffee purchased off the shelf		39
Inulin, carboxymethyl ether, sodium salt		39
Iron	Emulsifier/surfactant	34
Iron oxide	Proppant	34,39,40
Iron(II) sulfate heptahydrate		27,39,40
Iso-alkanes/n-alkanes		39,40
Isoascorbic acid		27,39,40
Isomeric aromatic ammonium salt		27,39,40
Isooctanol		30,39,40
Isooctyl alcohol		39
Isopentyl alcohol		39
Isopropanol	Foaming agent/ surfactant, acid corrosion inhibitor	28,29,38,39,40
Isopropylamine		39
Isoquinoline, reaction products with benzyl chloride and quinoline		40
Isotridecanol, ethoxylated		27,39,40
Kerosine, petroleum, hydrodesulfurized		27,39,40
Kyanite	Proppant	39,34,40
Lactic acid		39
Lactose		27,40
Latex 2000		34,40
L-Dilactide		39,40
Lead		33,39
Lead compounds		40
Lignite	Fluid additives	34
Lime		40
Lithium		27
L-Lactic acid		39
Low toxicity base oils		39
Lubra-Beads coarse		40
Maghemite		39,40
Magnesium		33
Magnesium aluminum silicate	Gellant	34
Magnesium carbonate		39
Magnesium chloride	Biocide	39,34
Magnesium chloride hexahydrate		40
Magnesium hydroxide		39
Magnesium iron silicate		39,40
Magnesium nitrate	Biocide	39,34,40
Magnesium oxide		39,40
Magnesium peroxide		39
Magnesium phosphide		39
Magnesium silicate		39,40
Magnetite		39,40
Manganese		33
Mercury		35
Metal salt		39
Metal salt solution		39
Methanamine, N,N-dimethyl-, hydrochloride		30,39,40

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Chemical	Use	Ref.
Methane		30
Methanol	Acid corrosion inhibitor	28,29,31,38,39,40
Methenamine		39,40
Methyl bromide		27
Methyl ethyl ketone		33
Methyl salicylate		38
Methyl tert-butyl ether	Gelling agent	28
Methyl vinyl ketone		
Methylcyclohexane		39
Methylene bis(thiocyanate)	Biocide	34
Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched		40
Mica	Fluid additives	29,30,39,40
Microbond expanding additive		40
Mineral		39,40
Mineral filler		39
Mineral oil	Friction reducer	32,40
Mixed titanium ortho ester complexes		39
Modified alkane		39,40
Modified cycloaliphatic amine adduct		39,40
Modified lignosulfonate		39
Modified polysaccharide or pregelatinized cornstarch or starch		37
Molybdenum		27
Monoethanolamine		40
Monoethanolamine borate		39,40
Morpholine		39,40
Muconic acid		37
Mullite		39,40
N,N,N-Trimethyl-2[1-oxo-2-propenyl]oxy ethanaminimum chloride		27,40
N,N,N-Trimethyloctadecan-1-aminium chloride		39
N,N'-Dibutylthiourea		39
N,N-Dimethyl formamide	Breaker	32,40
N,N-Dimethyl-1-octadecanamine-HCl		39
N,N-Dimethyldecylamine oxide		27,39,40
N,N-Dimethyldodecylamine-N-oxide		37
N,N-Dimethylformamide		30,39,40
N,N-Dimethyl-methanamine-n-oxide		27,40
N,N-Dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-benzenemethanaminium chloride		27,40
N,N-Dimethyloctadecylamine hydrochloride		39
N,N'-Methylenebisacrylamide		39,40
n-Alkanes,C10-C18		33
n-Alkanes,C18-C70		33
n-Alkanes,C5-C8		33
n-Butanol		38
Naphtha, petroleum, heavy catalytic reformed		30,39,40
Naphtha, petroleum, hydrotreated heavy		27,39,40
Naphthalene	Gelling agent, non-ionic surfactant	28,31,38,39,40
Naphthalene derivatives		39
Naphthalenesulphonic acid, bis (1-methylethyl)-methyl derivatives		39
Naphthenic acid ethoxylate		40
Navy fuels JP-5		27,39,40
Nickel		33
Nickel sulfate	Corrosion inhibitor	34
Nickel(II) sulfate hexahydrate		39
Nitrazepam		37

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Chemical	Use	Ref.
Nitrilotriacetamide	scale inhibiter	38,39
Nitrilotriacetic acid		39,40
Nitrilotriacetic acid trisodium monohydrate		39
Nitrobenzene		37
Nitrobenzene-d5		27
Nitrogen, liquid	Foaming agent	29,30,39,40
N-Lauryl-2-pyrrolidone		39
N-Methyl-2-pyrrolidone		40
N-Methyldiethanolamine		37
N-Oleyl diethanolamide		39
Nonane, all isomers		39
Non-hazardous salt		39
Nonionic surfactant		39
Nonylphenol (mixed)		39
Nonylphenol ethoxylate		37,39,40
Nonylphenol, ethoxylated and sulfated		39
N-Propyl zirconate		39
N-Tallowalkyltrimethylenediamines		39,40
Nuisance particulates		39
Nylon fibers		39,40
Oil and grease		33
Oil of wintergreen		39,40
Oils, pine		39,40
Olefinic sulfonate		39
Olefins		39
Organic acid salt		39,40
Organic acids		39
Organic phosphonate		39
Organic phosphonate salts		39
Organic phosphonic acid salts		39
Organic salt		39,40
Organic sulfur compound		39
Organic surfactants		39
Organic titanate		39,40
Organo-metallic ammonium complex		39
Organophilic clays		27,39,40
O-Terphenyl		27,40
Other inorganic compounds		39
Oxirane, methyl-, polymer with oxirane, mono-C10-16 -alkyl ethers, phosphates		39
Oxiranemethanaminium, N,N,N-trimethyl-, chloride, homopolymer		27,40
Oxyalkylated alcohol		39,40
Oxyalkylated alkyl alcohol		39
Oxyalkylated alkylphenol		27,39,40
Oxyalkylated fatty acid		39
Oxyalkylated phenol		39
Oxyalkylated polyamine		39
Oxylated alcohol		30,39,40
P/F resin		40
Paraffin waxes and hydrocarbon waxes		39
Paraffinic naphthenic solvent		39
Paraffinic solvent		39,40
Paraffins		39
Pentaerythritol		37
Pentane		30
Perlite		40

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Chemical	Use	Ref.
Peroxydisulfuric acid, diammonium salt	Breaker fluid	28,29,39,40
Petroleum		39
Petroleum distillates		39,40
Petroleum gas oils		39
Petroleum hydrocarbons		27
Phenanthrene	Biocide	28,29
Phenol		33,39,40
Phenolic resin	Proppant	34,38,39,40
Phosphate ester		39,40
Phosphate esters of alkyl phenyl ethoxylate		39
Phosphine		39,40
Phosphonic acid		39
Phosphonic acid (dimethlamino(methylene))		39
Phosphonic acid, (1-hydroxyethylidene)bis-, tetrasodium salt		39,40
Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-	Scale inhibitor	34,39
Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, sodium salt		27,40
Phosphonic acid, [nitrilotris(methylene)]tris-, pentasodium salt		39
[[(Phosphonomethyl)imino]bis[2,1-ethanediylnitrilob is(methylene)]]tetrakis phosphonic acid ammonium salt		27,40
Phosphoric acid ammonium salt		39
Phosphoric acid Divosan X-Tend formulation		39
Phosphoric acid, aluminium sodium salt	Fluid additives	39,34
Phosphoric acid, diammonium salt	Corrosion inhibitor	34
Phosphoric acid, mixed decyl and Et and octyl esters		39
Phosphoric acid, monoammonium salt		40
Phosphorous acid		39
Phosphorus		27
Phthalic anhydride		39
Plasticizer		39
Pluronic F-127		39,40
Poly (acrylamide-co-acrylic acid), partial sodium salt		40
Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-ome ga-hydroxy-, phosphate		39,40
Poly(oxy-1,2-ethanediyl), .alpha.-(octylphenyl)-ome ga-hydroxy-, branched		39
Poly(oxy-1,2-ethanediyl), alpha,alpha'-[[(9Z)-9-oct adecenylimino]di-2,1-ethanediyl]bis[.omega.-hydroxy-		39,40
Poly(oxy-1,2-ethanediyl), alpha-sulfo-.omega.-hydro xy-, C12-14-alkyl ethers, sodium salts		39,40
Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy		39
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexylo xy)-ammonium salt		39,40
Poly(oxy-1,2-ethanediyl), alpha-tridecyl-omega-hydr oxy-		39,40
Poly-(oxy-1,2-ethanediyl)-alpha-undecyl-omega-hydro xy		39,40
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy	Acid corrosion inhibitor, non-ionic surfactant	27,34,39,40
Poly(sodium-p-styrenesulfonate)		39
Poly(vinyl alcohol)		39
Poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexan ediyl]	Resin	34
Polyacrylamide	Friction reducer	29,32,34,39,40
Polyacrylamides		39
Polyacrylate		39,40
Polyamine		39,40
Polyamine polymer		40
Polyanionic cellulose		39

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Chemical	Use	Ref.
Polyaromatic hydrocarbons	Gelling agent/ bactericides	28,29,34
Polycyclic organic matter	Gelling agent/ bactericides	28,29,34
Polyethene glycol oleate ester		27,40
Polyetheramine		39
Polyethoxylated alkanol		27,40
Polyethylene glycol		30,38,39,40
Polyethylene glycol ester with tall oil fatty acid		39
Polyethylene glycol mono(1,1,3,3-tetramethylbutyl)p henyl ether		27,39,40
Polyethylene glycol monobutyl ether		39,40
Polyethylene glycol nonylphenyl ether		27,39,40
Polyethylene glycol tridecyl ether phosphate		39
Polyethylene polyammonium salt		39
Polyethyleneimine		40
Polyglycol ether	Foaming agent	28,29,34
Polyhexamethylene adipamide	Resin	34
Polylactide resin		39,40
Polymer		40
Polymeric hydrocarbons		40
Polyoxyalkylenes		38,39
Polyoxylated fatty amine salt		27,39,40
Polyphosphoric acids, esters with triethanolamine, sodium salts		39
Polyphosphoric acids, sodium salts		39,40
Polypropylene glycol	Lubricant	34,39
Polysaccharide		38,39,40
Polysaccharide blend		40
Polysorbate 60		40
Polysorbate 80		27,40
Polyvinyl alcohol	Fluid additives	34,39,40
Polyvinyl alcohol/polyvinylacetate copolymer		39
Portland cement clinker		40
Potassium		27
Potassium acetate		27,39,40
Potassium aluminum silicate		30
Potassium borate		27,40
Potassium carbonate	pH control	31,32,34
Potassium chloride	Brine carrier fluid	28,29,34,38,39,40
Potassium hydroxide	Crosslinker	28,29,34,39,40
Potassium iodide		39,40
Potassium metaborate		30,39,40
Potassium oxide		39
Potassium pentaborate		39
Potassium persulfate	Fluid additives	39,34
Propane		30
Propanimidamide, 2,2''-azobis[2-methyl-, dihydrochbride		39,40
Propanol, 1(or 2)-(2-methoxymethylethoxy)-		37,39,40
Propargyl alcohol	Acid corrosion inhibitor	28,29,34,38,39,40
Propylene carbonate		39
Propylene glycol		40
Propylene pentamer		39
p-Xylene		39,40
Pyridine, alkyl derivs.		39

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Chemical	Use	Ref.
Pyridinium, 1-(phenylmethyl)-, Et Me derivs., chlorides	Acid corrosion inhibitor, corrosion inhibitor	28,29,34,39,40
Pyrogenic colloidal silica		39,40
Quartz	Proppant	29,30,34,39,40
Quartz sand	Proppant	32,34
Quaternary amine		37
Quaternary amine compounds		39
Quaternary ammonium compound		37,39
Quaternary ammonium compounds, (oxydi-2,1-ethanediyl)bis[coco alkyldimethyl, dichlorides		27,40
Quaternary ammonium compounds, benzylbis(hydrogenated tallow alkyl)methyl, salts with bentonite	Fluid additives	29,30,34
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides		39
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with bentonite		40
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with hectorite	Viscosifier	34
Quaternary ammonium compounds, dicoco alkyldimethyl, chlorides		39
Quaternary ammonium compounds, trimethyltallow alkyl, chlorides		39
Quaternary ammonium salts		37,39,40
Quaternary compound		39
Quaternary salt		39,40
Radium (228)		9
Raffinates (petroleum)		30
Raffinates, petroleum, sorption process		39
Residual oils, petroleum, solvent-refined		30
Residues, petroleum, catalytic reformer fractionator		39,40
Resin		40
Rosin		39
Rutile		39
Saline	Brine carrier fluid, breaker	30,31,34,39,40
Salt		40
Salt of amine-carbonyl condensate		40
Salt of fatty acid/polyamine reaction product		40
Salt of phosphate ester		39
Salt of phosphono-methylated diamine		39
Salts of alkyl amines	Foaming agent	28,29,34
Sand		40
Saturated sucrose		27,39,40
Secondary alcohol		39
Selenium		27
Sepiolite		40
Silane, dichlorodimethyl-, reaction products with silica		40
Silica	Proppant	32,34,39,40
Silica gel, cryst.-free		40
Silica, amorphous		39
Silica, amorphous precipitated		39,40
Silica, microcrystalline		34
Silica, quartz sand		40
Silicic acid (H4SiO4), tetramethyl ester		39
Silicon dioxide (fused silica)		39,40
Silicone emulsion		39
Silicone ester		40

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Chemical	Use	Ref.
Silver		27
Silwet L77		39
Soda ash		40
Sodium		33
Sodium 1-octanesulfonate		27,40
Sodium 2-mercaptobenzothiolate	Corrosion inhibitor	34
Sodium acetate		27,39,40
Sodium alpha-olefin Sulfonate		40
Sodium aluminum oxide		39
Sodium benzoate		27,40
Sodium bicarbonate		30,38,39,40
Sodium bisulfite, mixture of NaHSO3 and Na2S2O5		27,39,40
Sodium bromate	Breaker	34,39,40
Sodium bromide		27,38,39,40
Sodium carbonate	pH control	32,34,39,40
Sodium chlorate		39,40
Sodium chlorite	Breaker	27,31,34,39,40
Sodium chloroacetate		27,40
Sodium cocaminopropionate		39
Sodium decyl sulfate		39
Sodium diacetate		39
Sodium dichloroisocyanurate	Biocide	34
Sodium erythorbate		27,39,40
Sodium ethasulfate		39
Sodium formate		40
Sodium hydroxide	Gelling agent	27,34,38,39,40
Sodium hypochlorite		27,39,40
Sodium iodide		40
Sodium ligninsulfonate	Surfactant	34
Sodium metabisulfite		39
Sodium metaborate		27,39,40
Sodium metaborate tetrahydrate		39
Sodium metasilicate		39,40
Sodium nitrate	Fluid additives	34
Sodium nitrite	Corrosion inhibitor	34,39,40
Sodium octyl sulfate		39
Sodium oxide (Na2O)		39
Sodium perborate		39
Sodium perborate tetrahydrate	Concentrate	27,31,34,39,40
Sodium persulfate		30,38,39,40
Sodium phosphate		39,40
Sodium polyacrylate		27,39,40
Sodium pyrophosphate		30,39,40
Sodium salicylate		39
Sodium silicate		39,40
Sodium sulfate		27,39,40
Sodium sulfite		40
Sodium tetraborate decahydrate	Crosslinker	28,29,34
Sodium thiocyanate		39
Sodium thiosulfate		27,39,40
Sodium thiosulfate, pentahydrate		39
Sodium trichloroacetate		39
Sodium xylenesulfonate		38,39
Sodium zirconium lactate		39
Sodium α-olefin sulfonate		27

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Chemical	Use	Ref.
Solvent naphtha, petroleum, heavy aliph.		40
Solvent naphtha, petroleum, heavy arom.	Non-ionic surfactant	30,31,34,39,40
Solvent naphtha, petroleum, light arom.	Surfactant	34,39,40
Sorbitan, mono-(9Z)-9-octadecenoate		27,39,40
Stannous chloride dihydrate		39,40
Starch	Proppant	39,40
Starch blends	Fluid additives	29
Steam cracked distillate, cyclodiene dimer, dicyclopentadiene polymer		39
Steranes		33
Stoddard solvent		27,39,40
Stoddard solvent IIC		27,39,40
Strontium		27
Strontium (89&90)		34
Styrene	Proppant	34
Substituted alcohol		39
Substituted alkene		39
Substituted alkylamine		39
Sugar		40
Sulfamic acid		27,39,40
Sulfate		27,33,39,40
Sulfite		27
Sulfomethylated tannin		30
Sulfonate acids		39
Sulfonate surfactants		39
Sulfonic acid salts		39
Sulfonic acids, C14-16-alkane hydroxy and C14-16-alkene, sodium salts		27,39,40
Sulfonic acids, petroleum		39
Sulfur compound		39
Sulfuric acid		38,39,40
Surfactant blend		40
Surfactants		38,39
Symclosene		37
Synthetic organic polymer		39,40
Talc	Fluid additives	29,30,34,38,39,40
Tall oil, compound with diethanolamine		39
Tallow soap		39,40
Tar bases, quinoline derivatives, benzyl chloride-quaternized		27,39,40
Tebuthiuron		37
Terpenes		39
Terpenes and terpenoids, sweet orange-oil		27,39,40
Terpineol, mixture of isomers		27,39,40
tert-Butyl hydroperoxide (70% solution in water)		39,40
tert-Butyl perbenzoate		39
Tetra-calcium-alumino-ferrite		39,40
Tetrachloroethylene		27
Tetradecyl dimethyl benzyl ammonium chloride		39
Tetraethylene glycol		39
Tetraethylenepentamine		39,40
Tetrakis(hydroxymethyl)phosphonium sulfate		27,38,39,40
Tetramethylammonium chloride		27,38,39,40
Thallium and compounds		27
Thiocyanic acid, ammonium salt		27,40
Thioglycolic acid	Iron Control	34,39,40
Thiourea	Acid corrosion inhibitor	28,29,34,39,40
Thiourea polymer		39,40

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Chemical	Use	Ref.
Thorium		36
Tin		28
Tin(II) chloride		39
Titanium	Crosslinker	33
Titanium complex		39,40
Titanium dioxide	Proppant	34,39,40
Titanium(4+) 2-[bis(2-hydroxyethyl)amino]ethanolate propan-2-olate (1:2:2)		39
Titanium, isopropoxy (triethanolaminate)		39
TOC		27
Toluene	Gelling agent	28,39,40
trans-Squalene		37
Tributyl phosphate	Defoamer	34
Tricalcium phosphate		39
Tricalcium silicate		39,40
Triethanolamine		30,39,40
Triethanolamine hydroxyacetate		27,40
Triethanolamine polyphosphate ester		39
Triethanolamine zirconium chelate		39
Triethyl citrate		39
Triethyl phosphate		39,40
Triethylene glycol		30,39,40
Triisopropanolamine		39,40
Trimethyl ammonium chloride		38,40
Trimethylamine quaternized polyepichlorohydrin		30,39,40
Trimethylbenzene	Fracturing fluid	34,39
Tri-n-butyl tetradecyl phosphonium chloride		27,39,40
Triphosphoric acid, pentasodium salt		39,40
Tripropylene glycol monomethyl ether	Viscosifier	34
Tris(hydroxymethyl)amine		27
Trisodium citrate		27,40
Trisodium ethylenediaminetetraacetate		39,40
Trisodium ethylenediaminetriacetate		39
Trisodium phosphate		27,39,40
Trisodium phosphate dodecahydrate		39
Triterpanes		33
Triton X-100		27,39,40
Ulexite		39,40
Ulexite, calcined		40
Ultraprop		40
Undecane		27,40
Uranium-238		36
Urea		27,39,40
Vanadium		28
Vanadium compounds		40
Vermiculite	Lubricant	34
Versaprop		40
Vinylidene chloride/methylacrylate copolymer		40
Wall material		39
Walnut hulls		39,40
Water	Water gelling agent/ foaming agent	28,40
White mineral oil, petroleum		39,40
Xylenes	Gelling agent	28,39,40
Yttrium		28
Zinc	Lubricant	34

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Chemical	**Use**	**Ref.**
Zinc carbonate	Corrosion inhibitor	34
Zinc chloride		39
Zinc oxide		39
Zirconium		27
Zirconium complex	Crosslinker	30,31,39,40
Zirconium nitrate	Crosslinker	28,29
Zirconium oxide sulfate		39
Zirconium oxychloride	Crosslinker	39,34
Zirconium sodium hydroxy lactate complex (sodium zirconium lactate)		39
Zirconium sulfate	Crosslinker	28,29
Zirconium, acetate lactate oxo ammonium complexes		40
Zirconium,tetrakis[2-[bis(2-hydroxyethyl)amino-kN]e thanolato-kO]-	Crosslinker	31,39,40
α-[3.5-Dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-p oly(oxy-1,2-ethandiyl)		27,40

Table A2. Chemicals identified in flowback/produced water

Chemical	Ref.
1,1,1-trifluorotoluene	27
1,2-Bromo-2-nitropropane-1,3-diol (2-bromo-2-nitro-1,3-propanediol or bronopol)	34
1,-3-Dimethyladamantane	34
1,4-dichlorobutane	27
1,6-Hexanediamine	34
1-Methoxy-2-propanol	34
2-(2-Methoxyethoxy)ethanol	34
2-(Thiocyanomethylthio) benzothiazole	34
2,2,2-Nitrilotriethanol	34
2,2-Dibromo-3-nitrilopropionamide	34
2,2-Dibromoacetonitrile	34
2,2-Dibromopropanediamide	34
2,4,6-tribromophenol	27
2,4-dimethylphenol	33
2,5-dibromotoluene	27
2-butanone	33
2-Butoxyacetic acid	34
2-Butoxyethanol	34
2-Butoxyethanol phosphate	34
2-Ethyl-3-propylacrolein	34
2-Ethylhexanol	34
2-fluorobiphenyl	27
2-fluorophenol	27
3,5-Dimethyl-1,3,5-thiadiazinane-2-thione	34
4-nitroquinoline-1-oxide	27
4-terphenyl-d14	27
5-Chloro-2-methyl-4-isothiazolin-3-one	34
6-Methylquinoline	34
Acetic acid	34
Acetic anhydride	34
Acrolein	34
Acrylamide (2-propenamide)	34
Adamantane	34
Adipic acid	34
aluminum	33
ammonia	35
ammonium nitrate	34
ammonium persulfate	34
anthracene	33
antimony	27
arsenic	33

Chemical	Ref.
Atrazine	34
barium	33
Bentazon	34
benzene	33
benzo(a)pyrene	33
bicarbonate	27
bis(2-ethylhexyl)phthalate	27,35
bisphenol a	34
boric acid	34
boric oxide	34
boron	27,33
bromide	27
bromoform	27
Butanol	34
cadmium	33
calcium	33
carbonate alkalinity	27
Cellulose	34
chloride	33
chlorobenzene	33
chlorodibromomethane	27
Chloromethane	27
chrome acetate	34
Chromium	35
chromium hexavalent	
citric acid	34
cobalt	27
copper	33
cyanide	27,35
decyldimethyl amine	34
decyldimethyl amine oxide	34
diammonium phosphate	34
dichlorobromomethane	27
didecyl dimethyl ammonium chloride	34
diethylene glycol	34
diethylene glycol monobutyl ether	34
dimethyl formamide	34
dimethyldiallylammonium chloride	34
di-n-butylphthalate	33
dipropylene glycol monomethyl ether	34
dodecylbenzene sulfonic acid	34
Eo-C7-9-iso-, C8-rich alcohols	34
Eo-C9-11-iso,C10-rich alcohols	34

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Chemical	Ref.
ethoxylated 4-nonylphenol	34
ethoxylated nonylphenol	34
ethoxylated nonylphenol (branched)	34
ethoxylated octylphenol	34
ethyl octynol	34
ethylbenzene	33,34
ethylcellulose	34
ethylene glycol	34
ethylene glycol monobutyl ether	34
ethylene oxide	34
ferrous sulfate heptahydrate	34
fluoride	27
formamide	34
formic acid	34
fumaric acid	34
glutaraldehyde	34
glycerol	34
hydroxyethylcellulose	34
hydroxypropylcellulose	34
iron	33
isobutyl alcohol (2-methyl-1-propanol)	34
isopropanol (propan-2-ol)	34
lead	33
limonene	
lithium	27
magnesium	33
manganese	33
mercaptoacidic acid	34
mercury	35
methanamine,N,N-dimethyl-,N-oxide	34
methanol	34
methyl bromide	27
methyl chloride	27
methyl-4-isothiazolin	34
methylene bis(thiocyanate)	34
methylene phosphonic acid (diethylenetriaminepenta[methylenephosphonic] acid)	34
modified polysaccharide or pregelatinized cornstarch or starch	34
molybdenum	27
monoethanolamine	34
monopentaerythritol	34
m-terphenyl	34
muconic acid	34

Chemical	Ref.
N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy ethanaminium chloride	34
n-alkanes, C10-C18	33
n-alkanes, C18-C70	33
n-alkanes, C1-C2	33
n-alkanes, C2-C3	33
n-alkanes, C3-C4	33
n-alkanes, C4-C5	33
n-alkanes, C5-C8	33
naphthalene	33
nickel	33
Nitrazepam	34
Nitrobenzene	34
nitrobenzene-d5	27
n-methyldiethanolamine	34
oil and grease	33
o-terphenyl	27,34
oxiranemethanaminium, N,N,N-trimethyl-, chloride, homopolymer	34
p-chloro-m-cresol	33
petroleum hydrocarbons	27
phenol	33
phosphonium, tetrakis(hydroxymethly)-sulfate	34
phosphorus	27
polyacrylamide	34
polyacrylate	34
polyethylene glycol	34
polyhexamethylene adipamide	34
polypropylene glycol	34
polyvinyl alcohol [alcotex 17f-h]	34
potassium	27
propane-1,2-diol	34
propargyl alcohol	34
pryidinium, 1-(phenylmethyl)-, ethyl methyl derivatives, chlorides	34
p-terphenyl	34
quaternary amine	34
quaternary ammonium compound	34
quaternary ammonium salts	34
radium (226)	33
radium (228)	33
selenium	27
silver	27
sodium	33
sodium carboxymethylcellulose	34
sodium dichloro-s-triazinetrione	34
sodium mercaptobenzothiazole	34

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Chemical	**Ref.**
squalene	34
steranes	33
strontium	27
sucrose	34
sulfate	27,33
sulfide	27
sulfite	27
tebuthiuron	34
terpineol	34
tetrachloroethene	35
tetramethyl ammonium chloride	34
tetrasodium ethylenediaminetetraacetate	34
thallium	27
thiourea	34
titanium	33
toluene	33
total organic carbon	27
tributyl phosphate	34
trichloroisocyanuric acid	34
trimethylbenzene	34
tripropylene glycol methyl ether	34
trisodium nitrilotriacetate	34
triterpanes	33
urea	34
xylene (total)	33
zinc	33
zirconium	27

Table A3. Naturally occurring substances mobilized by fracturing activities

Chemical	Common Valence States	Ref.
aluminum	III	28
antimony	V,III,-III	28
arsenic	V, III, 0, -III	28
barium	II	28
beryllium	II	28
boron	III	28
cadmium	II	28
calcium	II	28
chromium	VI, III	28
cobalt	III, II	28
copper	II, I	28
hydrogen sulfide	N/A	36
iron	III, II	28
lead	IV, II	28
magnesium	II	28
molybdenum	VI, III	28
nickel	II	28
radium (226)	II	36
radium (228)	II	36
selenium	VI, IV, II, 0, -II	28
silver	I	28
sodium	I	28
thallium	III, I	28
thorium	IV	36
tin	IV, II, -IV	28
titanium	IV	28
uranium	VI, IV	36
vanadium	V	28
yttrium	III	28
zinc	II	28

APPENDIX B: Quality Assurance Project Plan Deviation Report

QAPP TITLE AND DATE: Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing

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, Technical Research Lead Date

_____ __ _____
Ed Heithmar, ECB QA Representative Date

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

References

1. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, EPA/600/D-11/22, November 2011, Office of Research and Development, US EPA, Washington, DC.

2. EPA Method 8032A, SW-846 Online: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, http://www.epa.gov/osw/hazard/testmethods/sw846/pdf_s/8032a.pdf.

3. EPA Method 8316, SW-846 Online: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, http://www.epa.gov/osw/hazard/testmethods/sw846/pdf_s/8316.pdf.

4. EPA Method 8015C, SW-846 Online: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, http://www.epa.gov/osw/hazard/testmethods/sw846/pdf_s/8015c.pdf.

5. EPA Method 160.1, Methods for the Chemical Analysis of Water and Wastes (MCAWW) (EPA/600/4-79/020), https://www.nemi.gov/apex/f?p=237:38:44670331898396__14:::P38_METHOD_ID:5212 .

6. EPA Method 160.2, Methods for the Chemical Analysis of Water and Wastes (MCAWW) (EPA/600/4-79/020), https://www.nemi.gov/apex/f?p=237:38:44670331898396__14:::P38_METHOD_ID:5213 .

7. EPA Method 900.0, Prescribed Procedures for Measurement of Radioactivity in Drinking Water (EPA/600/4-80-032), August 1980, http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_900_0.pdf.

8. EPA Method 200.7, Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), https://www.nemi.gov/apex/f?p=237:38:64676173054781__62:::P38_METHOD_ID:4690 .

9. EPA Method 6020A, SW-846 Online: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Inductively Coupled Plasma-Mass Spectrometry, http://www.epa.gov/osw/hazard/testmethods/sw846/pdf_s/6020a.pdf.

10. Munch, J. W. and Bassett, M.V., METHOD 521: Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS). U.S. Environmental Protection Agency, 2005, http://www.epa.gov/microbes/m_521.pdf .

11. Domino, M.M. et al., Method 552.3: Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatrography with Electron Capture Detection. U.S. Environmental Protection Agency, 2003, http://www.epa.gov/ogwdw/methods/pdfs/methods/met55_2_3.pdf.

12. Munch, J.W. Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/ Mass Spectrometry, Revision 4.1, 1995, https://www.nemi.gov/apex/f?p=237:38:26839555724665__83:::P38_METHOD_ID:4803 .

13. EPA Method 551.1, Methods for the Determination of Organic Compounds in Drinking Water - Supplement III (EPA/600/R-95-131), https://www.nemi.gov/apex/f?p=237:38:26839555724665 83:::P38_METHOD_ID:4809 .

14. EPA Method 8315A, SW-846 Online: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, http://www.epa.gov/osw/hazard/testmethods/sw846/pdf s/8315a.pdf.

15. Region 3 Standard Operating Procedure, "Glycol Analysis of Aqueous Samples by Direct Injection HPLC/MS/MS", March 2012.

16. Brilis, G.M., Lyon, J.G., Standard Operating Procedure for Quality Assurance in Analytical Chemistry Methods Development, EPA/600/R-04/189, October 2004.

17. Quality Management Plan: Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, January 2012. http://www.epa.gov/hfstudy/HF-QMP-1-19-2012.pdf [URL accessed October 10, 2012].

18. The NERL Quality Management Plan (QMP) Appendix 6 "NERL Scientific Record Keeping Policy", February 2012. http://intranet.epa.gov/nerlintr/qa/qs.html [URL accessed August 6, 2012].

19. ORD Policies and Procedures Manual, Section 13.2 "Paper Laboratory Records" signed in to policy December of 2006, last accessed in June 2009: Section 13.2: Paper Laboratory Records [URL accessed August 24, 2011].

20. Cold Storage Unit Monitoring Standard Operating Procedure, ECB-008.1, 2012.

21. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. http://www.epa.gov/epawaste/hazard/testmethods/sw84 6/online/index.htm [URL accessed July 15, 2011].

22. Youden, W. J., Steiner, E. H., "Statistical Manual of the Association of Official Analytical Chemists," AOAC, Arlington, VA, 1975.

23. *Validation of Testing/Measurement Methods*, EPA 600/X-83-060, by Llewellyn R. Williams, Environmental Monitoring Systems Laboratory, Las Vegas, NV, U.S. Environmental Protection Agency, September 1983.

24. Cole, T. F., Degner, K. B., Rust, S. W., Warner, J. S., *Single-Laboratory Method Validation Protocol*, prepared for U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, under EPA Contract No. 68-03-3234, September 6, 1985.

25. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., Budde, W.L., *Trace Analyses for Wastewaters,* Environ. Sci. Technol., 1981, 15, 1426-1435.

26. US EPA, *Guidance on Environmental Data Verification and Data Validation (QA/G-8)*, EPA/240/R-02/004, November 2002, http://www.epa.gov/quality/qs-docs/g8-final.pdf [URL accessed October 10, 2012].

27. New York State Department of Environmental Conservation. (2009, September). *Supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program (draft).*

Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs. Albany, NY: New York State Department of Environmental Conservation. Retrieved January 20, 2010, from ftp://ftp.dec.state.ny.us/dmn/download/OGdSGEISFull .pdf

28. Sumi, L. (2005). *Our drinking water at risk. What EPA and the oil and gas industry don't want us to know about hydraulic fracturing.* Durango, CO: Oil and Gas Accountability Project/Earthworks. Retrieved January 21, 2011, from http://www.earthworksaction.org/pubs/ DrinkingWater AtRisk.pdf.

29. US Environmental Protection Agency. (2004). *Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs.* No. EPA/816/R-04/003. Washington, DC: U.S. Environmental Protection Agency, Office of Water.

30. Material Safety Data Sheets; EnCana Oil & Gas (USA), Inc.: Denver, CO. Provided by EnCana upon U.S. EPA Region 10request as part of the Pavillion, WY, ground water investigation.

31. Material Safety Data Sheets; Halliburton Energy Services, Inc.: Duncan, OK. Provided by Halliburton Energy Services during an on-site visit by EPA on May 10, 2010.

32. Ground Water Protection Council & ALL Consulting. (2009). *Modern shale gas development in the United States: A primer.* Contract DE-FG26-04NT15455. Washington, DC: United States Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory. Retrieved January 19, 2011, from http://www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pd f

33. Veil, J. A., Puder, M. G., Elcock, D., & Redweik, R. J. (2004). *A white paper describing produced water from production of crude oil, natural gas, and coalbed methane.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, contract W-31-109-ENG-38. Argonne, IL: Argonne National Laboratory. Retrieved August 24, 2011 from http://www.evs.anl.gov/pub/doc/ProducedWatersWP0401 .pdf

34. US Environmental Protection Agency. (2010). *Expanded site investigation analytical report: Pavillion Area groundwater investigation.* Contract No. EP-W-05-050. Retrieved September 7, 2011, from http://www.epa.gov/region8/superfund/wy/pavill ion/PavillionAnalyticalResultsReport.pdf.

35. Alpha Environmental Consultants, Inc., Alpha Geoscience, & NTS Consultants, Inc. (2009). *Issues related to developing the Marcellus Shale and other low-permeability gas reservoirs.* Prepared for the New York State Energy Research and Development Authority, contract nos. 11169, 10666, and 11170. Albany, NY: New York State Energy Research and Development Authority.

36. Sumi, L. (2008). *Shale gas: Focus on the Marcellus Shale*. Durango, CO: Oil and Gas Accountability Project/Earthworks. Retrieved January 21, 2011, from http://www.earthworksaction.org/pubs/OGAPMarcellusS haleReport-6-12-08.pdf

37. US Environmental Protection Agency. (2010). *Region 8 analytical lab analysis.*

38. Bureau of Oil and Gas Management. (2010). *Chemicals used in the hydraulic fracturing process in Pennsylvania.* Pennsylvania Department of Environmental Protection. Retrieved September 12, 2011,

from http://assets.bizjournals.com/cms_media/pittsb urgh/datacenter/DEP_Frac_Chemical_List_6-30-10.pdf.

39. US House of Representatives Committee on Energy and Commerce Minority Staff (2011). *Chemicals used in hydraulic fracturing.*

40. Submitted non-Confidential Business Information by Halliburton, Patterson and Superior. Available on the Federal Docket, EPA-HQ-ORD-2010-0674.