# Quality Assurance Project Plan
# For the Interlaboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| BQR | Branch Quality Assurance Representative |
| CAS | Chemical Abstracts Service |
| CCV | Continuing Calibration Verification |
| COC | Chain-of-Custody |
| EPA | Environmental Protection Agency |
| ESD | Environmental Sciences Division, Las Vegas, NV |
| DI | Deionized |
| DQI | Data quality indicator |
| DQO | Data quality objective |
| GWERD | Ground Water and Ecosystem Restoration Division, Ada, OK |
| HF | Hydraulic fracturing |
| HPLC | High performance liquid chromatography |
| MCEARD | Microbiological & Chemical Exposure Assessment Research Division, Cincinnati, OH |
| MDL | Method detection limit |
| MS | Mass spectrometry |
| NERL | National Exposure Research Laboratory |
| NRMRL | National Risk Management Research Laboratory |
| ORD | Office of Research and Development |
| PARCC | Precision, accuracy, representativeness, completeness, and comparability |
| PI | Principal Investigator |
| QA | Quality assurance |
| QATS | Quality assurance tracking system |
| QC | Quality control |
| QAPP | Quality assurance project plan |
| RPD | Relative percent difference |
| RSD | Relative standard deviation |
| SOP | Standard operating procedure |
| TSA | Technical system audit |



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# SECTION A. PROJECT MANAGEMENT

## A3 Distribution List

| | |
|---|---|
| EPA, ORD, NERL, ESD | |
| Patrick DeArmond | (702) 798-2102 |
| Lantis Osemwengie | (702) 798-2513 |
| Brian Schumacher | (702) 798-2242 |
| George Brilis | (702) 798-3128 |
| Daniel Heggem | (702) 798-2278 |
| Maliha Nash | (702) 798-2201 |
| | |
| EPA, ORD, NERL, IO | |
| Michelle Henderson | (513) 569-7353 |
| | |
| EPA, Region 5 | |
| Lawrence Zintek | (312) 886-2925 |
| Angela Ockrassa | (312) 353-3521 |
| | |
| EPA, Region 3 | |
| Jennifer Gundersen | (410) 305-2835 |
| Cynthia Caporale | (410) 305-2732 |
| Fred Foreman | (410) 305-2629 |
| | |
| EPA, ORD, NRMRL, GWERD | |
| David Jewett | (580) 436-8560 |
| | |
| EPA, ORD, OSP | |
| Stephen Watkins | (202) 564-3744 |
| | |
| EPA, ORD, NERL, MCEARD | |
| Jody Shoemaker | (513) 569-7298 |
| Margie Vazquez | (513) 569-7182 |



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## A4 Project/Task Organization

The *Interlaboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry* study is a special project designed to determine the efficacy of a method developed by US EPA Region 3 for the determination of glycols in drinking waters derived from drinking water wells. This project is associated with the hydraulic fracturing study being conducted by the U.S. EPA. The special project will be managed and implemented by the Environmental Sciences Division (ESD) in Las Vegas, NV, of the EPA Office of Research and Development (ORD). Brian Schumacher is the Technical Research Lead. For the verification/validation of the method, a minimum of three analytical laboratories will participate in the analyses of a series of samples. It is anticipated that the following EPA laboratories will be participating in this study:

1. National Exposure Research Laboratory (NERL), Environmental Sciences Division, Las Vegas, NV,

2. National Exposure Research Laboratory, Microbiological & Chemical Exposure Assessment Research Division (MCEARD), Cincinnati, OH,

3. National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division (GWERD), Ada, OK,

4. Region 3 Environmental Science Center, Fort Meade, MD, and

5. Region 5 Chicago Regional Laboratory, Chicago, IL.

**Table 1** summarizes individual responsibilities for the special study activities. **Figure 1** illustrates the individual and organizational interactions of all involved parties.

## 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. One concern that has been identified associated with the hydraulic fracturing process is the potential for chemicals used during the hydraulic fracturing process to enter ground water aquifers that may be used as drinking water sources. Of concern for this special project are diethylene glycol (CAS #111-46-6), triethylene glycol (CAS #112-27-6), tetraethylene glycol (CAS #112-60-7), 2-butoxyethanol (CAS #111-76-2), and 2-methoxyethanol (CAS #109-86-4). In response to this concern, the US EPA Region 3 Environmental Science Center in Fort Meade, MD (to be referred to as Region 3) has developed a quick method for the determination and quantification of these compounds. This method needs to be verified to determine its efficacy in determining these compounds in laboratory and drinking water matrices.



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**Table 1. Main Study Activities and Responsible Organizations.**

| Study Activities | Responsible Party |
|---|---|
| Design, implementation, and management of the study | Brian Schumacher, ESD |
| Quality Assurance Project Plan (QAPP) Preparation | Lawrence Zintek, Region 5; Brian Schumacher, ESD |
| Drinking well water collection | David Jewett, GWERD |
| Water sample preparation and spiking | Lantis Osemwengie, ESD |
| Method testing | Patrick DeArmond, ESD; Lawrence Zintek, Region 5; Jennifer Gundersen, Region 3; Jody Shoemaker, MCEARD |
| Data review and data analysis; report development | Patrick DeArmond, ESD; Brian Schumacher, ESD; Maliha Nash, ESD |
| Data storage, management, and access | Patrick DeArmond, ESD |
| Ensure the quality assurance (QA) and quality control (QC) activities described in the QAPP are being implemented | George Brilis, ESD; Angela Ockrassa, Region 5; Margie Vazquez, MCEARD; Jill Bilyeu, Region 3 |
| Data QA and QC review | Participating Laboratory's Quality Assurance Manager |
| QA oversight, problem resolution assistance, and tracking corrective action | Michelle Henderson, NERL |



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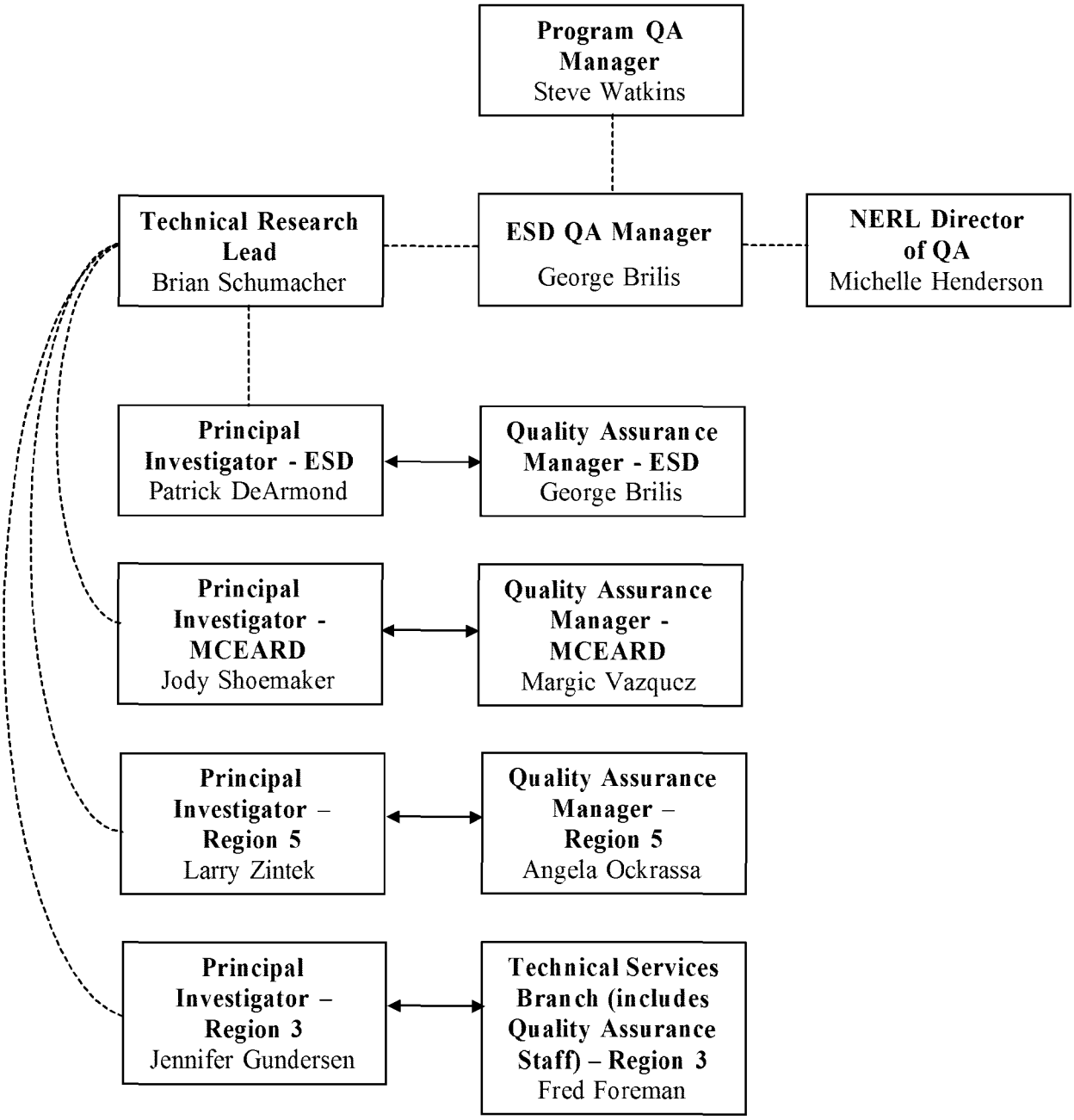


**Figure 1. Organizational Flowchart for Glycol Method Study.**



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## A6 Project/Task Description

The primary objectives of this study are to: 1) verify the performance of Region 3 Standard Operating Procedure (SOP) in multiple laboratories [Phase 1], 2) validate the Region 3 SOP in multiple laboratories [Phase 2], and 3) evaluate and, if appropriate, revise the SOP and/or quality control (QC) acceptance criteria in the method. This may or may not include any unforeseen communications regarding instrument parameters, supplies, and/or equipment.

Verification for this study (Phase 1) will be performed in different laboratories to ensure that each laboratory can perform/follow the SOP provided by Region 3 with the goal of obtaining the same level of results as identified in the Region 3 laboratory. The quality assurance/quality control (QA/QC) procedures for this phase of the project will follow the QA/QC specified in the Region 3 SOP. Verification testing will be performed in laboratory grade water.

Validation for this study (Phase 2) will be performed through the submission of multiple blind samples (spiked and unspiked) in multiple matrices (laboratory grade water and drinking water from a well) to each participating laboratory for analysis. The QA/QC procedures for this phase of the project will follow the QA/QC specified in the Region 3 SOP and in this Quality Assurance Project Plan (QAPP).

To ensure that these study objectives are met, all participating laboratories shall strictly adhere to the above Phases 1 and 2 requiring that:

- Each laboratory verify and optimize the liquid chromatography/mass spectrometry /mass spectrometry (LC/MS/MS) conditions used by Region 3 on their instrumentation to meet Region 3 reporting limits or determine the reporting limits on their LC/MS/MS systems.
- Each laboratory follows all analytical and quality control procedures in the Region 3 SOP and this QAPP (depending on phase of the study).
- Any laboratory that wishes to deviate from the procedures in the Region 3 SOP or this QAPP shall obtain prior approval of the changes from the Research Technical Lead and document those approved changes in detail.
- All data produced are capable of being verified by an independent person reviewing the analytical data package.
- Each laboratory must have a comprehensive quality assurance (QA) program in place and operating throughout the study. This QA program will ensure that the data produced are of appropriate and documented quality. The laboratory's quality management plans shall be made available to the technical research lead.

## A7 Quality Objectives and Criteria for Measurement Data

The Data Quality Objective for this study is that the results from three groups of samples must have their variance determined and the variance among the laboratories must agree to within 30% of the established average. If this criterion is met, then the method is considered to be robust, precise and acceptable for normal use. If the variance exceeds 40%, the method will need further evaluation for systematic errors.

Data quality indicators (DQIs) 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



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samples and duplicate un-spiked samples will be expressed as relative standard deviation (RSD) for replicates of three or more or as relative percent difference (RPD) for duplicates.

Accuracy refers to correctness of the data and is the difference between the population mean of the determination and the true value or assumed true value. Bias is the systematic error inherent in the method or caused by an artifact in the measurement process.

Representativeness expresses the degree to which data accurately and precisely represent a measured characteristic of a condition of a population or a process. For the validation phase of this study, representativeness will be ensured as only the ESD laboratory will prepare and send the samples to the participating laboratories for analysis.

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.

Comparability is the relative confidence that one data set can be compared to another. Comparability will be ensured by all the participating laboratories receiving the same samples (i.e., samples from the same source) and following the Region 3 SOP for the analysis of the samples.

The data quality indicators (DQIs) for precision, accuracy, and completeness for each major measurement parameter are summarized in **Table 2**.

## A8 Special Training/Certification

Special Training
To achieve the stated quality objectives, only analysts trained and experienced in the use of the liquid chromatography /tandem mass spectrometry will carry out measurements.

## A9 Documents and Records

Laboratory activities must be documented according to the appropriate record keeping policy of the laboratory performing the analyses. These policies generally 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.

Electronic copies of this QAPP, SOPs, and any associated audit reports, will be kept on the shared EPA O: drive as per the HF Quality Management Plan[1]; in the NERL Quality Assurance Tracking System (QATS) database; and on the EPA Hydraulic Fracturing website (http://epa.gov/hydraulicfracturing/ ) once finally approved and cleared.

The Technical Research Lead will be responsible for distribution of the current version of the QAPP, timely communications with all involved participants 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.



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**Table 2. Data Quality Indicators for Measurement Data.**

| QC Check | Frequency | Completeness | Precision | Accuracy | Corrective Action |
|---|---|---|---|---|---|
| 5-point initial calibration | Prior to sample analysis | 100% | RSD≤20% | $R^2 \geq 0.99$ | No samples will be run until calibration passes criteria. |
| 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 control sample [d] | One per batch of samples [a] | 100% | RPD≤30% [c] | ± 30% of known value | Check the system and reanalyze the standard. Re-prepare the standard if necessary. Recalibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be invalidated. |
| Laboratory fortified matrix (e.g., matrix spike) | One per batch of samples [a] | 100% | RPD≤30% [c] | Recovery between 70 and 130% of spike concentration | 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 replicate | One per batch of samples [a] | 100% | RSD≤30% [c] | N/A | Inspect the system, narrate discrepancy. Samples must be bracketed by acceptable QC or they will be invalidated. |
| Quality control check standard [e] | One per batch of samples [a] | 100% | RSD≤25% [c] | ± 20% of known value | Reanalyze, obtain new sample from Research Task Lead. 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. |
| Method detection limit | Each chemical | 100% | TBD for each HF chemical | TBD for each HF chemical | TBD for each HF chemical |

[a]Batch of samples not to exceed 20 samples.

[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. Laboratory replicates shall be performed in at least triplicate.

[d]The laboratory control sample will be an approximate mid-calibration concentration sample prepared by the participating laboratory using their current primary standard lot.

[e]The quality control check standard (QCCS) will be prepared by the ESD laboratory independent of the ESD analyst and will be prepared from a different lot of the primary standards. One QCCS will be supplied to each participating laboratory.



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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 each organizations record management policy. These records include, but are not limited to, recorded information such as the standard and sample preparation, blanks, calibration standards, and QC. Records will be retained in a laboratory notebook that is kept by the researchers. Separate, new hardbound laboratory notebooks specifically dedicated to this study are strongly encouraged. 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 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. Each participating laboratory Branch QA Representative (BQR), or equivalent, shall perform a documented review of laboratory and electronic recordkeeping. For example, after reviewing a laboratory notebook, the BQR shall initial and date that the review has been performed.

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 data and those who contribute shall be "Data Stewards." Data may be transferred to electronic spreadsheets for analysis and presentation. It is strongly recommended that a new e-folder be created for this study.

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 according to EPA Records Schedule 501 *Applied and Directed Scientific Research*.

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, and
- E-mails.

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

Emails will be kept in ECMS, where available.



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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 work papers and administrative correspondence

- Includes completed questionnaires or other documents used for data collection, drafts or copies of interim progress reports, and other work papers 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.



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# SECTION B. MEASUREMENT

## B1 Sampling Design

For the verification phase of this study, each participant laboratory will be sent a copy of the Region 3 SOP. The conditions in the SOP will be used as a starting point in order to optimize each instrument for the list of analytes on the participant laboratory's LC/MS/MS systems. If the reporting limits can be met in the participant laboratories, the laboratory will perform precision and accuracy tests in reagent water at the reporting limit, lowest level of calibration curve, and at the midpoint of the calibration curve. If the laboratory cannot meet the Region 3 reporting limits, then the reporting limit may be raised and calibration curve adjusted after consulting with the Technical Research Lead and Principal Investigators (PIs). This discrepancy may be caused by the different sensitivities of the LC/MS/MS systems used. All LC and MS conditions will be documented by the individual laboratories. All method parameters and recovery data for the target analytes and surrogates will be sent to the Technical Research Lead in spreadsheet format (to be provided ). At least seven replicates at each level shall be used in order to determine precision and accuracy and an MDL for each analyte in each laboratory (40CFR 136 Part B). The participating laboratory shall prepare the samples in deionized laboratory water using whatever water purification system is available at the laboratory.

For the validation phase of this study, three sets of seven "replicates" of water samples will be prepared by ESD-LV for a total of 21 blind samples. Samples for laboratory validation phase of the study will be prepared by an independent scientist (i.e., one not involved with the glycol method verification/validation study) at ESD-LV. ESD-LV shall not divulge the concentration to the participant laboratories. ESD-LV may discuss the appropriate spike concentrations with the Technical Research Lead and Project Quality Assurance Manager to ensure appropriate spike levels. Seven samples will be laboratory reagent water spiked at an unknown concentration. Seven samples will be drinking water from a drinking water wells at a selected field site. The seven samples from a drinking water well at a selected field site will be spiked at a known concentration of each compound.

## B2 Sampling Methods

Bulk samples from drinking water wells will be acquired by NRMRL-Ada. Collection of 4 gallons is anticipated to be sufficient for this project. The bulk samples will be collected in clean, capped amber glass containers and labeled with the source and date of sampling.

Deionized (DI) water at ORD-ESD will be generated on site using a Barnstead NANOpure system. The cartridges for the system are changed when the resistivity is $\leq 14.0$ MΩ·cm.

Information to be provided with the bulk sample shall include:

- a unique identification number as decided by NRMRL-Ada
- Sample location (longitude, latitude, altitude [where applicable])
- Brief description of sample source
- Date and time of acquisition
- Volume or weight of sample (approximations acceptable)
- Filtered or unfiltered sample with the micron unit of the filter provided
- Comments describing any unusual aspects of the sample or its acquisition.



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## B3 Sample Handling and Custody

All sample shipments will use the NRMRL Chain-of-Custody (COC) form shown in Appendix B.

As quickly as possible, NRMRL-Ada will ship the drinking well water samples to ESD-LV. Samples should be shipped on ice via overnight courier for arrival the following morning. Samples shall not be collected and shipped on a Thursday or Friday.

Samples prepared and submitted during the validation phase of the study shall follow chain-of-custody procedures with documentation describing:

(1) The project name,
(2) Sample receipt date and time,
(3) Condition of samples received,
(4) Sample numbers received,
(5) Signatures of individual(s) receiving the samples, and
(6) If applicable, the air bill or other shipping number.

Proper documentation will be maintained and analyst procedures documented. Samples will be properly labeled and stored in refrigerators maintained at 4° C ± 2° C. The refrigerators shall be monitored with temperatures recorded.

Immediately after sample shipment (i.e., as soon as samples are in the custody of the carrier), the bulk water sampling team from GWERD will inform ESD of the shipment and provide information on the shipment, including sample numbers, numbers of coolers, and courier and bill number. ESD will confirm that samples have arrived in good condition and as scheduled. If necessary, the GWERD will implement tracking activities to locate any lost shipment(s) or resend samples due to loss in shipment. Once the samples are received, ESD will prepare the samples and send them to the participating laboratories within 2 days.

Similarly, immediately after sample shipment (i.e., as soon as samples are in the custody of the carrier) of the validation phase samples , ESD will inform the participating laboratories of the shipment and provide information on the shipment, including sample numbers, numbers of coolers, and courier and bill number. The participating laboratories will confirm that samples have arrived in good condition and as scheduled. If necessary, the ESD will implement tracking activities to locate any lost shipment(s) or resend samples due to loss in shipment. Once the samples are received, the participating laboratories shall analyze within a time frame to meet the 14 day holding time for the glycol samples.

Because glycol ethers are ubiquitous in the environment, including laboratories, the sample laboratories must judiciously guard against sample contamination. Glycol and glycol ether free glassware and cleaning processes shall be used in all applications by all laboratories during this study.

## B4 Analytical Methods

The analytical method to be used for this study will be provided as an SOP from U.S. EPA Region 3.



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## B5 Quality Control

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

For the verification phase of this study, QC criteria presented in the Region 3 SOP shall be followed. The results of verification testing will be used to identify and quantify (1) the sources of significant variability in method performance, (2) probable systematic error, or method bias, (3) the usable dynamic range and limits of detection for method measurements, (4) method sensitivity, and (5) method ruggedness, the relative stability of method performance for small variations in critical method parameter values.

For the validation phase of this study, the QC criteria presented in the Region 3 SOP shall be followed as well as the QC criteria specified in Table 2 of this QAPP. Should there be a difference between the Region 3 SOP and the criteria in Table 2, the criteria in Table 2 shall be followed. Table 2 provides details of the QC samples to be performed, the minimum required frequency of analysis, the anticipated precision and accuracy numbers, and corrective actions to be taken should an acceptance criterion not be met.

The equations to be used for the calculation of the PARCC parameters and MDL are given in Section D3 of this QAPP.

Method Detection Limits

An estimation of the method detection limit (MDL) for individual analytes identified from the glycol list will be made according to procedures as outlined in 40CFR 136 Part B.

## B6 Instrument/Equipment Testing, Inspection, and Maintenance

Preventative maintenance will be scheduled as needed and may be triggered by criteria in Table 2 (section A7). An instrument maintenance log book shall be 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 all critical instrumental parameters is required.

## B7 Instrument Calibration and Frequency

Various mass spectrometers will be used for obtaining mass spectra of the glycols. All of the mass spectrometers have distinctly different analyzers and operating conditions. Initial conditions will be based on the conditions specified in the SOP submitted by Region 3. Initial and continuing calibration shall follow the procedures specified in the SOP.

## B9 Non-Direct Measurements

Not applicable.



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## B10 Data Management

Data will be managed according to participating laboratories' data management policies and policies specified in the HF Quality Management Plan. For example, ESD-LV will follow the NERL IIQMP, Section 8 and Appendix 6.[1] A daily laboratory notebook will be maintained to document all experiments carried out, principal 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).



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# SECTION C. ASSESSMENT AND OVERSIGHT

## C1 Assessments and Response Actions

This project will have a Technical Systems Audit (TSA) performed during the laboratory validation phase of the study. The findings of the TSA will be reported to the Research Technical Lead, NERL Director of Quality Assurance, and Program QA Manager (QAM).

After the laboratory verification and the laboratory validation phase of the project are completed, the critical target analytes, selected by the participating organization's QA manager or delegate, will undergo an Audit of Data Quality (ADQ). NRMRL has an SOP for this activity that will be used by the participating organization's QA Manager and/or delegate.

A schedule of the applicable audits is listed in **Table 3**.

If corrective actions are identified in any of these audits, the participating laboratory's QA Manager must inform the Program QAM, NERL Director of Quality Assurance, and Research Technical Lead.

**Table 3. Schedule of Audits.**

| Type of Audit | Frequency | Details |
|---|---|---|
| TSA | Conducted at each stage of method testing and development (e.g., during optimization of instrumental parameters, during optimization of method, etc.) | Performed by participating organization's QAM |
| Surveillance audit | Conducted once during laboratory validation phase | Performed by participating organization's QAM |
| ADQ | Conducted after method verification and validation once data has been collected. | Performed by participating organization's QAM |

## C2 Reports to Management

Audit reports will have a 5 business day turnaround time in order to have effective corrective action due to the short duration of this project. Audit reports will be provided by the Organization's QAM to the Program QA Manager, NERL Director of Quality Assurance, and 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 and NERL Director of Quality Assurance.



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# 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.

Data packages submitted by the participating laboratories shall include the following:

- Summary level data in spreadsheet format; (format to be provided);
- Individual results (in µg/L), including results for all target compounds found in all blanks.
- **Note**: Laboratories will not be allowed to average results or perform other data manipulations beyond those described in Region 3 SOP. When results are below the minimum level of quantitation but are detected, laboratories will be required to report the actual calculated result, regardless of its value;
- A list of the composition and concentrations of target compounds in the calibration, QA/QC, all samples analyzed, and a run chronology;
- Saved at participant lab - not reported unless asked by Technical Research Lead or Program QAM: Copies of all raw data, including chromatograms, quantitation reports, spectra, bench sheets, and laboratory notebooks showing weights, volumes, and other data that will allow verification of the calculations performed and will allow the final results reported to be traced to the raw data. Details and raw data from all runs may be requested and reviewed for determination as to whether further testing is required;
- A written report that details any problems associated with analysis of samples or standard solutions. The written report also must provide comments on the performance of any part of Region 3 SOP;
- A detailed description of any modifications to the procedures specified in Region 3 SOP;
- Laboratories also will be instructed to use the following rules in reporting results:
    - Quantitative results above or at the MDL - report value;
    - Quantitative results below the MDL - report value but "U" flag with footnote giving the MDL;
    - Nonquantitative results - report as less than the MDL value and state the MDL value;
    - ND (not detected) – use when no peaks associated with the compound are identified on the chromatogram;
    - The terms zero or trace are not to be used.

For the verification phase of the study, the participating laboratories shall have until March 22, 2012 (tentatively) to submit the data package to the Technical Research Lead. The Technical Research Lead and Principal Investigators will have 4 days from the receipt of the data to evaluate and report the findings. A conference call will be conducted after this phase with the participating laboratories to ensure the success of the multi-lab verification process.

For the validation phase of the study, the participating laboratories shall have until April 19, 2012 (tentatively) to submit the data package to the Technical Research Lead. The Technical Research Lead and Principal Investigators will have 5 days from the receipt of the data to evaluate and report the findings. A conference call will be conducted after this phase with the participating laboratories to ensure the success of the multi-lab validation process.



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## D2 Verification and Validation Methods

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

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

## D3 Calculation of Data Quality Indicators

The calculation of data quality indicators will be based on the following equations[2]:

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:

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

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

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

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

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



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Precision

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

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

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

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

$$\%\text{RSD} = (s / \overline{y}) \times 100\%$$

Where:
%RSD = relative standard deviation
$s$ = standard deviation
$y$ = mean of replicate analyses.

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:

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

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

Method Detection Limits

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

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

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



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## REFERENCES

1. Quality Management Plan – Plan to Study the Potential impacts of Hydraulic Fracturing on Drinking Water Resources. December 2011.

2. Simes, G.F. 1991. Preparation Aids for the Development of Category I Quality Assurance Project Plans. EPA/600/8-91/003.



EPAPAV0133321

# Appendix A

# Region 3 SOP



EPAPAV0133322

# Glycol Analysis of Aqueous Samples by Direct Injection HPLC/MS/MS

Effective Date: March 2012

EPA Region 3
Office of Analytical Services and Quality Assurance
701 Mapes Road
Fort Meade, Maryland 20755

Approved by:

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Peer-Reviewer, Laboratory Branch

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## Updates Table

**Peer reviewer's initials indicate that changes meet the NELAC and regulatory requirements described in Section 9.4 in SOP R3-QA060**

| Responsible Person | Date | Description of Change | Peer Reviewer | Date |
|---|---|---|---|---|
| | | New SOP | | |
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## 1 Scope and Application

1.1 This Standard Operating Procedure (SOP) documents and provides a descriptive method to perform glycol analysis by HPLC/MS/MS on liquid matrices.

1.2 This SOP is based on EPA SW-846 Method 8321B, 8000C and ASTM D7731-11[E1] and applies to the measurement of glycols listed in Table 1.

Table 1: Analyte List

| Analyte | CAS # | MDL (aqueous, ug/l) | NQL (aqueous, ug/l) |
|---|---|---|---|
| Diethylene glycol | 111-46-6 | In prep | 25 |
| Triethylene glycol | 112-27-6 | In prep | 25 |
| Tetraethylene glycol | 112-60-7 | In prep | 25 |
| 2-Butoxyethanol | 111-76-2 | In prep | 5 |
| 2-Methoxyethanol | 109-86-4 | In prep | 10 |

## 2 Summary of the Method

2.1 The method employs high performance liquid chromatography (HPLC) coupled with positive electrospray ionization (ESI+) tandem mass spectrometry (MS/MS) for the determination of a suite of glycols in aqueous matrices.

2.2 A sample aliquot is directly injected into the HPLC/MS/MS system without extraction or derivitization. Concentration of each identified analyte is performed through linear, external standard calibration.

2.3 Target compounds are identified by retention time and one or more MRM (Multiple Reaction Monitoring) transition.

## 3 Definitions

3.1 Refer to the ESC Quality Manual for applicable definitions

3.1.1 MRM: Multiple Reaction Monitoring is the application of selected reaction monitoring to multiple product ions from one or more precursor ions.

## 4 Interferences

4.1 Suspended solids in the sample can clog frits in the sample management system and on the column. If site history suggests, samples may be filtered prior to introduction to the

HPLC/MS/MS system.

4.2 Matrix interferences may be caused by contaminants in the sample.

4.3 All reusable glassware must be cleaned according to procedures for cleaning glassware used in organic compound analyses per R3QA-054 Glassware Preparation for Organic Analyses.

## 5 Safety

5.1 Before beginning any procedures, refer to the Chemical Hygiene Plan (CHP) in the OASQA Quality Assurance Manual for general safety precautions and guidelines.

5.2 All sample prep work should be conducted in a fume hood.

5.3 The toxicity or carcinogenicity of each reagent used in this method may not have been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

5.4 Material Safety Data Sheets (MSDS) must be maintained in the facility for all reagents used in the laboratory. This information must be made available to all personnel prior to the performance of this SOP and upon staff request. The MSDS (hard copies) are currently located in the library as well as electronically on CD-ROM and online.

5.5 All applicable safety and compliance guidelines set forth by the EPA and by federal, state, and local regulations must be followed during the performance of this SOP. In addition, all procedures outlined in the OASQA Chemical Hygiene Plan must be adhered to. Stop all work in the event of a known or potential compromise to the health and safety of any person and immediately notify the Safety Officer, and other appropriate personnel as outlined in the CHP.

5.6 All laboratory waste must be handled in accordance with guidelines established in the CHP and the appropriate waste disposal procedures identified in Section 15.0 (Waste Management).

5.7 Analysts must be cognizant of all instrumental hazards (i.e. dangers from electrical shock, heat or explosion etc.).

5.8 All chemicals used in the performance of this SOP, as well as the samples, should be handled with caution. Adequate protective gear should be worn. At a minimum, this includes ANSI approved safety glasses and a lab coat to protect from chemical splashes, and powderless gloves made from acid resistant materials such as nitrile, latex, neoprene, butyl or PVC.

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5.9 Spill procedures: Follow the procedures outlined in the ESC Occupant Emergency Plan (OEP), Hazardous Material Spills section. For minor spills (which can be handled by the analyst) wear safety glasses, lab coat, and gloves to clean up the material. For significant spills, immediately contact the SHEM Manager.

## 6 Equipment and Supplies

6.1 HPLC/MS/MS system: Analytical instrument and accessories suitable for automated injection of samples onto analytical HPLC columns and fragmentation and detection by a tandem mass spectrometer.

6.2 System used at R3-ESC: Waters (Milford, MA) TQD HPLC/MS/MS system: equipped with a 1 to 50 µL or 1 to 100 µL loop injector and electrospray (ESI) tandem mass spectrometer (MS/MS) capable of multiple reaction monitoring (MRM) and negative and positive ion mode.

6.3 HPLC column: Waters (Milford, MA) Atlantis dC18 3µm , 2.1 x 150mm. Other columns may be used if they provide sufficient retention and separation of the target analytes.

6.4 Data System: Computer system with software capable of accepting and processing raw detector data from the HPLC/MS/MS. The system must have the following capabilities:

Integrate peaks from raw data.
Provide peak height and peak area information.
Calculate and store calibration information.
Identify peaks of interest by retention time.
Quantitate peaks of interest using calibration obtained.
Produce chromatograms.
Allow overlay and comparison of chromatograms.
Produce reports with quantitation information.
Provide a vehicle for storing data.
Define manually integrated data on report.
The current system for operation and processing is Waters Empower2 (current revision)

6.5 Disposable 0.45um syringe tip filters, Teflon, if needed to remove suspended solids.

6.6 Disposable luer tip syringes, sized as appropriate, if needed to remove suspended solids.

6.7 Volumetric flasks - Class A glass: sized as appropriate

6.8 Micro syringes or Class A graduated (to deliver) pipets, sized as appropriate

6.9 Autosampler vials- Glass, 2 mL crimp top or screw top with Teflon-lined septum

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6.10 Graduated cylinders, sized as appropriate

6.11 Disposable Pasteur pipets

## 7 Reagents and Standards

### 7.1 Reagents

7.1.1 Acetonitrile - HPLC grade or equivalent. Optima grade is preferred.

7.1.2 Organic-free, deionized water: ASTM Type III water provided and monitored in-house according to R3-QA065 (current revision) and further polished at a point of use Millipore unit to a resistivity of 18 MΩ-cm and a total organic carbon of less than 50 ppb.

7.1.3 Nitrogen gas, provided by liquid nitrogen dewars

7.1.4 Argon gas, provided by liquid argon dewars

7.1.5 Formic Acid, reagent grade.

7.1.6 Sodium Cesium Iodide, NaCsI. For instrument tuning. Provided annually by manufacturer with system preventive maintenance (PM) kit.

7.1.7 Mobile phase: Reservoir A1: H2O with 0.1% formic acid, Reservoir B1: Acetonitrile with 0.1% formic acid.

### 7.2 Standards

7.2.1 All standards are to be labeled with the Element standard number and the preparer's initials. This is a unique identifier and all standard information is referenced in Element. Other information may include: expiration date, concentration, and manufacturer.

7.2.2 Standards must be stored in glass containers at 4 +/-2°C.

7.2.3 Stock standard solution 100 mg/L (ppm) glycol mix – This solution can be purchased commercially as a certified standard. Stock standards should be stored at 4-6°C or according to manufacturer's suggestions until manufacturer's expiration. Expiration dates should be clearly specified on the label.

7.2.4 Intermediate standard solution (1.0 and 10 mg/L glycol mix) – Prepared by dilution of stock standard solution to 10 or 100 mL with reagent water. Intermediate standards may be stored at 4±2 °C for a period of up to 6 months. Expiration dates should be clearly specified on the label.

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7.2.5 Calibration standards – Prepare dilutions of the intermediate standard solution to prepare five calibration standards Due to the varied responses of the analytes, recommended standard concentrations for establishing a calibration curve are: 5, 10, 25, 50, 100, 200, and 400µg/L (ppb). This range may be extended provided that the linear response can be adequately verified through satisfaction of all calibration criteria and quality control requirements. The low standard must be equivalent to or below the lowest result to be reported. All reported results must be within the calibration range.

**Sample Collection, Preservation and Storage**

8.1 This SOP does not describe sample collection procedures; however, the following guidelines are followed once samples are received at the laboratory.

8.2 Samples must be stored in tightly sealed glass at 4 +/- 2°C in a designated sample refrigerator. Recommended sample container is 40mL vial with Teflon septa without the use of acid preservation.

8.3 Analyze samples within 14 days of collection.

8.4 Samples extracted outside of holding time should be noted in the case narrative and qualified according to the lab QM.

## 9 Quality Control

9.1 Batch QC. The following are relevant QC criteria for this method taken from the OASQA Laboratory Quality Manual (current revision).

| NELAC Requirement | Minimum Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| **Method Blank – BLK** (clean matrix **processed**) | One per sample preparation batch[1] | Fails if the concentration of a targeted analyte in the blank is at or above the reporting limit, AND is greater than 1/10 of the amount measured in any sample. Criteria do not apply to sample results reported as less than values and mandated methods that require correction for blanks. | If outside acceptance criteria reprep affected samples or qualify sample results. |
| **Laboratory Control Sample** (LCS) – **BS** (clean matrix spiked with analytes of interest) | One per sample preparation batch [1] | ±20% of expected value for aqueous samples. As per 8000C. LCS/BS is equivalent to CCV because there is no extraction. Sec 11.7.6 | If outside acceptance criteria, first re-analyze the failed QC to verify difficulty. If still failing, perform corrective actions and reprep. affected |

| NELAC Requirement | Minimum Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| | | | samples or qualify results. |
| **Matrix Spike – MS** (spiked or fortified sample) | One per 20 samples per matrix<br>Selection of sample [3] | ±30% of expected value for aqueous samples. This is a conservative /demanding limit based on acceptance criteria for spikes into clean matrix (LCS-BS) per 8000C Section 9.5.4.. | If outside acceptance criteria, qualify the sample associated with failing QC results. |
| **Matrix Spike Duplicate –MSD** (analysis of second fortified aliquot, processed) | One per 20 samples per matrix and site<br>Selection of sample [3] | Relative percent difference: 25, as per Method 8000C. ±30% of expected value for aqueous samples. As per Method 8000C, Sec 9.5.4. RPD≤25 | If outside acceptance criteria, qualify the sample associated with failing QC results. Re-analyze the sample (holding time and sample volume permitting). If MS/MSD recoveries are high, first examine raw ion data for possible interference. If the problem is confirmed by re-analysis, include explanation in analytical report. If the MS/MSD recover problems are not confirmed and recoveries from the second analysis are within the QC limits, then report the second analysis and reject the first. |
| **Initial Calibration –** | At least five calibration standards with one at the Level of Quantitation (not to include the blank) | $r^2 \geq 0.99$ as per Method 8000C Sec 9.3.2. Minimum of 5 concentrations Method 8000C Sec 9.4.1.1 | If the initial instrument calibration results are outside established acceptance criteria, corrective actions must be performed. Results associated with an unacceptable initial instrument calibration must be qualified. Results of samples not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty. |
| **Second Source Quality Control Standard** (QCS) – **SCV** (material is from a second source; **source independent** of calibration standards, not processed) | One per initial calibration | ±20% of expected value as per Method 8000C. Sec 9.3.6. | If outside acceptance criteria, first re-analyze or reprep. the failed QC to verify difficulty. If still out, correct problem then recalibrate or qualify results. |
| **Continuing Instrument** | One at beginning, end and | ±20% of expected value as per | If outside acceptance criteria, |

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| NELAC Requirement | Minimum Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| **Calibration Verification – CCV** | every 20 samples (analytical batch). | Method 8000C. Sec 1.1.7.6 | first re-analyze or reprep the failed QC to verify difficulty. If reanalysis passes the first time, then continue run. If reanalysis fails but routine corrective actions correct the problem, then there must be two consecutive passing QCs before continuing the run. If it still fails, then recalibrate and reanalyze all samples since the last acceptable CCV or stop analysis (additional analyses shall not occur) and if any samples in the batch cannot be re-analyzed report data specifying the direction of the bias if clearly indicated. |
| **Selectivity – Retention Time** | All chromatography methods | All analytes in initial calibration standards, LCS-BS, SCV and CCV within windows established per method or in-house limits. The Empower software processing method currently sets the retention time window at ±5% of the analyte's retention time in the mid-point calibration curve. | If outside acceptance criteria, first re-analyze or reprep the failed QC to verify difficulty. If still out, correct problem then recalibrate or qualify results. |
| **Surrogate – SUR** | Organic only - All samples, standards, QC (Surrogate compounds as per SOP and mandated methods). Not currently used, may be added at a future date. | Not currently used, may be added at a later date. | If outside acceptance criteria, qualify results associated with failing QC. |
| **Tuning** | Mass spectrometry methods - before each analytical batch [1] ASTM D7731-11 states that tuning should be done according to manufacturer's directions. Because hardware tuning is done with NaCsI, tuning is recommended to be done yearly with the PM so that salts do not build up on the quadrupole. | According to manufacturer's directions. | Perform instrument maintenance and rerun tuning standard. Data associated with an unacceptable tune shall not be reported. |

[1] ***Batch:*** *environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A* ***preparation batch*** *is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An* ***analytical batch*** *is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical*

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*batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)*

[2] *The components to be spiked shall be as specified by the mandated test method. Any permit specified analytes, as specified by regulation or client requested shall also be included. If there are no specified components, the laboratory shall spike per the following:*
*For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.*
*For those test methods that have extremely long lists of analytes, a representative number may be chosen using the following criteria for choosing the number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included over a two year period.*
*For methods that include 1-10 targets, spike all components.*
*For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater.*
*For methods that include 21 or more targets, spike at least 16 components.*
*(NELAC, Section D.1.1.3.1c)*

[3] *The selected sample shall be rotated among client samples so various matrix problems may be noted and/or addressed.*

## 10 Calibration and Standardization

10.1 Refer to the Batch QC table for calibration criteria.

10.2 While many mass spectrometry methods require daily tuning to assure proper mass identification prior to each sample batch, ASTM Method D7731-11 states that tuning/mass calibration should be according to manufacturer's directions. According to the TQD Operator Manual, unless problems are noted, this system is only required to be tuned for proper mass identification annually with the system PM. Tuning is done with a NaCsI solution and repeated introduction of NaCsI can cause buildup of salt in the system and result in reduced sensitivity and will necessitate frequent cleaning.

10.3 Tuning to determine the correct system settings (cone voltage, desolvation temperature, source temperature etc) for a particular analyte is done as needed and according to manufacturer's directions. Representative settings for the analytes in this method are listed in Section 11.

10.4 Records of the annual system PM are maintained in the instrument maintenance log.

10.5 Suggested concentrations for the initial calibration levels are 5.0 to 400.0 ppb. If a wider calibration range is needed, more standard levels should be added provided the calibration curve remains linear. Suggested 5-point calibration levels is 5, 10, 25, 50, 100.

10.6 Linear calibration may be used if the $r^2 \geq 0.99$ and all continuing calibrations and calibration verifications pass. If linear calibration fails, calibration must be re-run.

10.7 The average of the retention times of the mid-level concentrations is to be used in the

processing method as the analyte retention time.

10.8 Certificates of analysis are stored in G201.

## 11 Procedure

### 11.1 Sample Preparation

11.1.1 Transfer sample to an autosampler vial using a glass Pasteur pipet. If necessary, filter the sample through a 0.45µm syringe tip filter and dispense into autosampler vial.

11.1.2 Prepare matrix spike samples in a 10.0 mL volumetric flask. Fill to about 50% with sample; add an appropriate volume of spike solution to achieve the needed concentration. The volume of spike added should not be more than 100-200ul (1-2% of the total sample volume) or it could affect the concentration in the source sample. Fill the volumetric flask to the mark with sample and mix by inverting several times. If necessary, filter the sample through a 0.45µm syringe tip filter and dispense into autosampler vial.

11.2 HPLC/MS analysis

11.2.1 Calibrate the HPLC/MS/MS with NaCsI, according to manufacturer's directions, during annual preventive maintenance. More frequent calibration with NaCsI can leave residue on the quadrupoles and should only be done following significant instrument repair.

11.2.2 Appropriate MRMs were determined during method development (see 11.2.6 below) but can be reevaluted as needed, by tuning with authentic, individual standards to determine the most abundant MRMs. Tuning may be done via the Waters Intellistart™ automated tuning program or manually through the tune page.

11.2.3 Mobile phases.

11.2.3.1 For 2-methoxyethanol, isocratic elution at 0.3ml/min at 98% A1 and 2% B1 is used.

11.2.3.2 For the other analytes a gradient is used.

| Time (min) | Flow rate ml/min | % A1 | % B1 | Curve |
|---|---|---|---|---|
| Initial | 0.4 | 98 | 2 | Linear |
| 3.0 | 0.4 | 98 | 2 | Linear |
| 10.5 | 0.4 | 85 | 15 | Linear |
| 12.5 | 0.4 | 85 | 15 | Linear |
| 13 | 0.4 | 98 | 2 | Linear |
| 13-19 | 0.4 | 98 | 2 | Equilibration before next injection |

11.2.4 The typical injection volume is 30 µL.

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11.2.5 The gradient may be modified to achieve separation of target analytes in one run.

11.2.6 The following MRMs are monitored but may be adjusted depending on instrument response. The MRM marked * has a higher response and is used as the primary MRM for calibration and quantitation. The second MRM may be monitored and for supplementary confirmation but due to the lower response, cannot be used to confirm concentrations at the lower portions of the calibration curve. ASTM D7731-11 uses only one MRM per analyte.

Diethylene Glycol, Time: 0-5min, span: 0.2 Da, retention time (RT): 1.8min

| Precursor (Da) | Product (Da) | Dwell (sec) | Cone voltage (V) | Collision energy V) |
|---|---|---|---|---|
| 106.94 | 44.9* | 0.2 | 18 | 48 |
| 106.94 | 88.4 | 0.2 | 18 | 22 |

Triethylene Glycol, Time:0-5min, span 0.2 Da, RT: 2.9min

| Precursor (Da) | Product (Da) | Dwell (sec) | Cone voltage (V) | Collision energy V) |
|---|---|---|---|---|
| 150.97 | 45.10* | 0.2 | 24 | 26 |
| 150.97 | 89.00 | 0.2 | 24 | 24 |

Tetraethylene Glycol: Time 5-13min, span 0.2 Da, RT: 5.6 min

| Precursor (Da) | Product (Da) | Dwell (sec) | Cone voltage (V) | Collision energy V) |
|---|---|---|---|---|
| 195.05 | 45.10* | 0.2 | 22 | 22 |
| 195.05 | 89.00 | 0.2 | 22 | 20 |

2-Butoxyethanol: Time, 5-13min, span 0.2 Da, RT: 10.6min

| Precursor (Da) | Product (Da) | Dwell (sec) | Cone voltage (V) | Collision energy V) |
|---|---|---|---|---|
| 118.93 | 57.10 | 0.2 | 16 | 20 |
| 118.93 | 63.00* | 0.2 | 16 | 14 |

2-Methoxyethanol: Time 0-4min, span 0.2 Da, RT: 2.6min

| Precursor (Da) | Product (Da) | Dwell (sec) | Cone voltage (V) | Collision energy V) |
|---|---|---|---|---|
| 76.91 | 59.10* | 0.2 | 12 | 8 |

11.2.7 MS/MS settings may be adjusted to meet quantitation limit requirements but are generally as follows:

| | 2-methoxyethanol | All other analytes |
|---|---|---|
| Desolvation temperature | 350°C | 400°C |
| Source temperature | 150°C | 150°C |
| Collision gas flow (Argon) | 0.1ml/min | 0.1ml/min |
| Cone gas | 25 L/hr | 25 L/hr |
| Desolvation gas | 600 L/hr | 800 L/hr |
| Ion Mode | Electrospray positive (ESI+) | Electrospray postive (ESI+) |

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| | | |
|---|---|---|
| Column temperature | 30°C | 30°C |
| Sample chamber | 4°C | 4°C |
| Inter-channel delay | 0.005s | 0.005s |
| Inter-scan delay | 0.005s | 0.005s |
| | | |

## 12 Data Analysis and Calculations

12.1 Refer to the current version of the Laboratory QM for Quality Control related equations and the policy on reporting significant figures.

12.2 Refer to R3QA-067 (current revision) for policies on manual integration.

12.3 Identify and confirm the presence of target analytes in the samples by matching the retention time of the MRM.

Compare the retention time of the MRM with the retention time determined during the initial calibration. The retention times should not be more than 5% different from the initial calibration average.

12.4 Linear (external) calibration may be used if the $r^2 \geq 0.99$.

12.5 Water samples

$$\text{Final result } (\mu g/L\ ClO_4^-) = (C)(D)$$

Where:
C = Concentration or calibration curve (µg/L analyte) D = Dilution factor (if needed)

## 13 Method Performance

13.1 Method performance is evaluated based on the criteria in Table 2.

13.2 DOC accuracy and precision data and MDL study data are maintained in the OASQA Central QS files.

13.3 NQLs are listed in Section 1. There are no problematic compounds associated with this method.

## 14 Pollution Prevention

14.1 This method has been developed to generate 10 mL or less of waste per aqueous sample. As this SOP is routinely performed, the analyst will consider other methods to reduce the use and generation of hazardous chemicals/waste.

14.2 Resource Management: Water Conservation. Laboratory personnel should be mindful

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of water consumption, and whenever possible, employ practices that minimize water use.

## 15 Waste Management

15.1 *Waste type code*: Will vary with sample. Record the WO # on sample waste containers.

15.2 All laboratory waste must be handled in accordance with guidelines established in the ESC Chemical Hygiene Plan (current revision).

15.3 The waste flow chart is on file with the SHEM Office.

15.4 *Amount of waste per sample*: Approximately 1[illegible]mL [illegible]rless of waste will be generated per sample.

## 16 References

16.1 SW-846 Method 8321B,Solvent-extractable nonvolatile compounds by high-performance liquid chromatography/thermospray mass spectrometry or ultraviolet detection (rev 2, Feb 2007)

16.2 SW-846 Method 8000C, Determinative Chromatographic Procedures. (rev 3, March 2003)

16.3 ASTMD7731-11[E1], Standard Test Method for Determination of Dipropylene Glycol Monobutyl Ether in Sea Water by Liquid Chromatography/Tandem Mass Spectrometry. (August 2011)

16.4 Waters ACQUITY TQD Empower 2154 customer Familiarization Guide. Waters Corp. (2008) Milford MA.

16.5 EPA Region 3 OASQA Laboratory Quality Manual (QM), Current Revision.

16.6 EPA Region 3 OASQA Chemical Hygiene Plan, Current Revision.

16.7 EPA Region 3 OAS[illegible]A [illegible]ccupant Emergency Plan, Current Revision.

16.8 EPA Region 3 OAS[illegible]A, Laboratory Notebook Policy, Current Revision.

16.9 TQD Maintenance logbook: SNB 357.

16.10 Waters TQD System Run Log: PNB 207

16.11 Certificates of analysis notebook: SNB 114

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16.12 R3-QA067. Procedures for Manual Integration, Current revision.

16.13 R3-QA054. Glassware Preparation for Organic Analyses. Current revision.

16.14 R3-QA065. Calibration, Verification and Maintenance of Laboratory Support Equipemt. Current revision.

16.15 NELAC Standard. Current revision

## 17 Tables, Diagrams, Flowcharts and Validation Data

17.1 Waste handling flow chart is on file with the SHEM office.

17.2 QA/QC data is on file with the OASQA Quality Assurance Officer.

17.3 Attachment 1. EPA Internal Technical Review Checklist

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Attachment 1: **Glycols by LC/MS (R3-QA239) Technical Review Checklist (TRC) Checklist**

*For Internal Use Only*

Site Name:_____WO#_____
Analyst: _____ Date given to Reviewer:_____
Matrix (circle): Aqueous / Other _____
Program (circle): Superfund / RCRA / WPD (NPDES) / SDWA / Other: _____

**The signature below indicates the following:**
- This data meets the needs of the customer according to the request.
- The analysis was performed as per the SOP, or exceptions documented.
- All documentation needed to recreate the analyses has been reviewed.
- Data Review status set to Peer Reviewed in Element.

Peer Reviewer signature _____ Date accepted_____
If any data for this case is stored with another case file, give Site Name and WO#_____

**Peer Reviewer Completes Section Below:**

**General:**

| | YES | NO | N/A Comments |
|---|---|---|---|
| Raw data is identified with sample IDs, site name, WO#, analyst name, date of analysis. | ____ | ____ | ____ |

**Quality Control:**

| | Yes | No | n/a | comments |
|---|---|---|---|---|
| NaCsI cal according to mfg recommendation within year | | | | |
| Initial calibration: $r^2 \geq 0.99$ | | | | |
| Holding time: 14 days to analysis | | | | |
| | | | | |
| | | | | |
| Method Blank < NQL | | | | |
| SCV ~~(old term: LVM)~~ (±20%) | | | | |
| CCV (old:CLC) (±20% mid-range) | | | | |
| BS Blank spike (±20% mid range) | | | | |
| Reported + results for samples met RT requirement for primary MRM fragment? | | | | |
| Reported + results for samples met RT requirement for 2ndary MRM fragment or explained in narrative. | | | | |
| Manual integration as per R3QA067 | | | | |
| Matrix spike/dup: ±30% aq, 25% mid range spike | | | | |

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**Calculations/Report:**

Calculations and transcriptions checked. _____ ____ ____ _____
Element Draft Report reviewed. _____ ____ ____ _____
Deviations and problems documented. _____ ____ ____ _____

Additional Comments by Peer Reviewer:

_____
_____
_____
_____

**Analyst ensures that the data case file is complete and accurate as per SOP R3QA-066:**

____ Bench sheet or Work Order list
____ Sample Prep logs
____ Instrument run log
____ Standard/Reagent Prep log
____ Raw data
____ Data status set to analyzed
____ Appropriate TV sheets / Certificates of Analysis
____ Element Peer Review report

Additional Comments by Analyst on data issues:

_____
_____
_____
_____
_____
_____
_____

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# Appendix B

# NRMRL Chain of Custody Form



EPAPAV0133340

USEPA, ORD, NRMRL

# Sample Analysis Request and Chain of Custody (COC) Record



| | |
|---|---|
| Project:<br><br>Location:<br>Project Manager/Phone: | Lab Name:<br>Address:<br><br>Contact Name/Phone: |
| Shipping Method:<br><br>Shipping Tracking Number: | Shipping Date:<br><br>Total Number of Shipping Containers: |

| Sample Number | Sample Matrix/Description | Date/Time Collected | Container Type | Preservation | Number of Containers | Requested Parameters | | | | | | Special Instructions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
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***Relinquished By:*** Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

***Received By:*** Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

***Comments:***

***Relinquished By:*** Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

***Received By:*** Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

***Comments:***

*Pink copy - Field Custodian, Yellow copy - Lab Custodian, White copy - Project Manager*

EPA-442 (CIN) (09/08)

# Appendix C

## NRMRL SOP for *Performing Audits of Data Quality (ADQs)*



EPAPAV0133342

| STANDARD OPERATING PROCEDURE<br>NRMRL | Category | QA |
|---|---|---|
| | Document No. | LSAS-QA-02-0 |
| | Effective Date | 5/9/11 |
| | Revision Date | Not Applicable |
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| | Page No. | 1 of 8 |
| | Approval: | |

## TITLE: Performing Audits of Data Quality (ADQs)

### 1.0 Purpose

ADQs are used to verify that reported data are of acceptable quality for their intended use. The ADQ is an examination of data after they have been collected and verified by project personnel. It is conducted to determine how well the measurement system performed with respect to the data quality indicator (DQI) goals specified in the QA project plan (QAPP) and whether the data were accumulated, transferred, reduced, calculated, summarized, and reported correctly. This procedure describes the process used to perform and document ADQs in support of NRMRL research activities.

### 2.0 Revision History

History of document changes

| Date | Revision No. | Change | Ref. Section |
|---|---|---|---|
| 01/03/11 | 0 | New Procedure | Not Applicable |

### 3.0 Persons Affected

This SOP applies to QA Managers (or designees) who perform ADQs and Technical Lead Persons (TLPs) who have data subjected to ADQs.

### 4.0 Policy

The NRMRL Quality Management Plan (QMP) requires that ADQs be performed by the QA Manager (or designee) for all QA Category 1 and 2 research projects. ADQs may also be performed for QA Category 3 and 4 research projects when specifically requested by management, when dictated by program requirements, or as determined to be necessary by the TLP or QA Manager. ADQs are performed by QA Managers or their designees.



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| STANDARD OPERATING PROCEDURE<br>*NRMRL* | Category | QA |
|---|---|---|
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## 5.0 Definitions

5.1 Audit of Data Quality (ADQ) - a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the reported data are of acceptable quality for their intended use.

5.2 Data Quality Indicators - quantitative statistics and qualitative descriptors that are used to interpret the degree of acceptability or utility of data to the user. The principal data quality indicators are precision, accuracy, comparability, completeness, and representativeness.

5.3 Technical Lead Person (TLP) – the NRMRL employee who is responsible for all technical aspects of a research project. For extramural projects, the Contracting Officer Representative (COR) or Project Officer (PO) is the TLP.

5.4 Deficiency – an identified deviation that impacts the quality of the reported results.

5.5 Finding – a deficiency that has a significant effect on the quality of the reported results.

5.6 Observation - a deficiency that does not have a significant effect on the quality of the reported results.

## 6.0 Procedures

6.1 The need for an ADQ is identified early in the project planning process based on the QA category; ADQs are required for QA Category 1 and 2 projects. (The requirement for an ADQ and associated responsibilities must be included in the quality assurance project plan (QAPP) for these projects.) Other projects may be identified as needing an ADQ (see Section 4.0) early in the project planning process or at some other time during project implementation. When the need for an ADQ is identified, the TLP must coordinate audit activities with the QA Manager.

6.2 The TLP notifies the QA Manager when data packages that have already been verified by project personnel are available (if possible, advance notice should be given). For some projects, minimal data packages may be generated, while other



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projects may generate multiple data packages. The identification of specific data packages for review is made by the QA Manager to focus on the more critical parameters and to provide the best representation of the data generated. The QA Manager may use discretion in the review process as to the amount of data that will be reviewed for a specific project.

Note: ADQs must begin as soon as possible after data generation begins (when initial data packages and data summaries are available) to ensure that any problems are identified and resolved in a timely manner. ADQs must then continue throughout a project as determined to be appropriate by the QA Manager.

6.3 The TLP provides summaries of results for reporting and complete project data packages to the QA Manager. In the case of extramural support, the need for this documentation must be identified in the procurement documentation. A complete data package consists of the following:

6.3.1 Sample information: a list of each sample by unique number; date of sampling; method of sampling; analysis required for each sample; matrix/preservation; chain of custody documentation, if applicable.

6.3.2 Method information: identification of reference method(s) or laboratory SOPs used, including sample preparation if applicable; any modifications to the stated methods.

6.3.3 Summary of results: sample results for reporting; reporting units; reporting basis (e.g. dry weight); reporting limits; QC results (e.g., blanks, surrogates, spikes, replicates).

6.3.4 Raw data: dates of sample preparation and analysis, sample preparation initial and final masses/volumes; raw data including sample analysis sheets, logs, copies of laboratory notebooks, or raw data from instrumentation; instrument checks; calibration documentation; and calculations and/or spreadsheets used to reduce data.

6.3.5 Data Qualifiers: any problems or issues with receipt, storage, handling, or analysis of samples including resolution; deviations from project/method requirements; QC requirements not met; impact to reported results.



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**Note:** If any of the above is not provided for review, the QA Manager must evaluate the impact of the missing information on performing the ADQ. If necessary, the QA Manager will inform the TLP of the need for the missing information.

6.4 The QA Manager or designee prepares a checklist based on the type of data generated, such as the example checklist provided in Attachment 1 for measurement projects (additional items for review may be needed depending on the data being reviewed or a different checklist may be needed for non-measurement project types). The QAPP or other planning documents will be needed to identify data quality indicator requirements and goals. Multiple sections to the checklist may be needed if the data involves multiple sample matrices/analyte classes (e.g., air samples for metals, water samples for VOCs).

6.5 The QA Manager reviews the data packages(s) against the checklist. A representative set of the data is traced in detail from raw data and instrument readouts through data transcription or transference through data manipulation (either manually or electronically by commercial or customized software) through data reduction to summary data, data calculations, and final reported data. Particular attention is paid to the use of QC data in evaluating and reporting.

**Note:** For each data package reviewed, all calibration and QA/QC data must be reviewed. In addition, a percentage of input values for software program-generated calculations and hand calculations must be verified, as determined to be appropriate by the QA Manager. If problems are identified, additional verification is needed.

6.6 The QA Manager identifies deficiencies if present, and designates them as findings or observations.

6.7 The QA Manager documents the results of the ADQ in a report. The draft report must included the following at a minimum:

- **Introduction** to include audit information (e.g., TLP, project title, laboratory (organization), data package identifications, sample matrices/analyte classes, date, QA reviewer);
- **Summary** of findings and observations and a summary statement regarding the adequacy of the data for its intended use;
- **Individual finding/observation discussions** including a description of the



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deficiency and any effect on data quality and the recommended corrective action.

6.8 The QA Manager shall distribute the report to the TLP and the TLP's supervisor.

6.9 If the audit report contains findings, the TLP must respond in writing to the QA Manager (with a copy to the TLP's supervisor) with a plan for corrective actions. If the audit report contains observations only, the TLP is strongly encouraged to address the issues and provide a documented response to the QA Manager, but no additional QA review is needed.

6.10 For ADQ findings, the QA Manager reviews the ADQ corrective actions and provides documentation to the TLP and the appropriate supervisor regarding the acceptability of these corrective actions. The results cannot be used or reported until any needed corrective actions are determined to be acceptable.

6.11 Any required revisions to reported results must be made and submitted to the QA Manager for verification prior to the use or reporting of the results.

6.12 The TLP must maintain the ADQ report and any responses in the project files. The QA Manager must maintain the ADQ report and any responses in the QA files.

## 7.0 References

7.1 EPA QA/G-7, Guidance on Technical Audits and Related Assessments for Environmental Data Operations, EPA/600/R-99/080, January 2000

7.2 NRMRL Quality Management Plan, current edition

Prepared by: ETAVOS/MH
LSAS/LMD



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**ATTACHMENT 1**

**EXAMPLE ADQ CHECKLIST**

**GENERAL INFORMATION**

EPA Technical Lead Person (TLP):
Project Title:
Laboratory (Organization):
Report Identification/Date:
Sample Type(s)/Analyte(s):
QA Reviewer: ADQ Date:

**ITEMS REVIEWED**

| | Yes | No | NA | Comments |
|---|---|---|---|---|
| **Sample Information** | | | | |
| Are samples uniquely identified and correctly transcribed throughout the data package to the summary of results? | | | | |
| Does sample collection documentation indicate that samples were collected as described in the QAPP? | | | | |
| If calculations were used for sample collection information (e.g., air volumes), are these calculations correct? | | | | |
| Does sample collection documentation indicate appropriate preservation? | | | | |
| If applicable, is chain-of-custody documentation complete? | | | | |
| | | | | |



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| | Approval: | |

| | Yes | No | NA | Comments |
|---|---|---|---|---|
| **Sampling and Analysis Method Information** | | | | |
| Were methods specified in QAPP used? | | | | |
| If method modifications were used, are these modifications appropriate and well documented? | | | | |
| Were sample preparation and analytical method holding times met? | | | | |
| | | | | |
| **Summary Of Results** | | | | |
| Are the correct units reported? | | | | |
| Are reported results correct (verify any calculations performed[1])? | | | | |
| Were QC samples (blanks, second source checks, surrogates, spikes, replicates) analyzed at the frequency specified in the QAPP? | | | | |
| Did QC results meet the requirements specified in the QAPP? | | | | |
| | | | | |
| **Raw Data** | | | | |
| Were instruments calibrated as described in the QAPP? | | | | |
| Were calibration criteria met for initial and continuing checks? | | | | |
| Were reported results analyzed within calibration range? | | | | |
| Were instrument outputs correctly transcribed to data summary? | | | | |



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| | Yes | No | NA | Comments |
|---|---|---|---|---|
| | | | | |
| **Data Qualifiers** | | | | |
| If QC requirements were not met, were corrective actions performed? | | | | |
| If necessary, were data qualified appropriately? | | | | |
| | | | | |

[1]A percentage of input values for software program-generated calculations and hand calculations must be verified, as determined to be appropriate by the QA Manager. If problems are identified, additional verification is needed.



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