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Author: Vicki Schlegel

Quality Assurance Manual

INTRODUCTION

In recent years, quality assurance and control (QA/QC) has become fundamental to the production of analytical data for scientific research. The purpose of this manual is to describe the quality assurance program employed at the Water Sciences Laboratory (WSL). The Water Sciences Laboratory strives to apply appropriate elements of this program to all research and analytical activities. This manual also provides Laboratory personnel and other interested parties with a description of our policies for maintaining analytical quality assurance. Quality Assurance Project Plans (QAPP) define project specific QA policies for research and services conducted through the Water Sciences Laboratory.

OBJECTIVES AND QUALITY POLICIES

The objective of the WSL Quality Assurance Program is to foster accurate, precise, and reliable analytical results for all procedures performed at the facility. Implementation of this program includes managerial, statistical, investigative, preventative, and corrective techniques to maximize data quality at the minimum additional cost. The program must be cost-effective, and at the same time enable the Water Sciences Laboratory to meet or exceed both project and non-project data quality standards. Specific objectives to promote quality assurance include:

- Development and utilization of rugged and proven analytical methods adapted from published and standardized procedures.
- Training of appropriate laboratory personnel in basic QA/QC measures and laboratory-specific methods.
- Establishment of performance standards to compare with routine data quality.
- Establishment of procedures for method/procedure modification to improve data quality.
- Monitoring and documenting routine analytical performance.
- Participation in appropriate performance evaluation programs.
- Establishment of performance standards for laboratory personnel.

In general, WSL policies emphasize the prevention of problems rather than detection and correction of problems after they occur. The WSL shall use published standardized methods and provide written procedures, including basic QA/QC requirements, to staff for all routine methods and activities influencing data quality. New methods will be verified using suitable test samples or reference materials, and compared to previous validated methods if possible. The WSL shall retain copies of all supporting documentation, including analytical results, for a time period specified by each project. If necessary, results are held indefinitely to verify the actions taken for each sample analyzed at the facility. A comprehensive calibration and maintenance program optimizes instrument performance and data

quality. Reagents and supplies shall be of appropriate grade for the procedure, and gravimetric and volumetric apparatus shall be of a suitable class and calibrated as necessary.

Analytical data quality objectives (DQO) for environmental research projects will define the confidence level required, and determine the level of reliability, precision, accuracy, detection limits, and validation methods. Although the level of reliability, precision, and accuracy required for most analyses varies according to the method and analyte, data quality is to be kept as high as practical on a day-to-day basis.

SAMPLE COLLECTION, HANDLING, AND LOGIN

In the past, sampling has been performed by field-trained Water Sciences Laboratory personnel following a sampling plan defining the objectives or purposes for sample collection and analysis. At present, the WSL does not employ a field collection specialist, so samples are collected by the submitting agency. The written plan provides QA documentation, describes guidelines, step-by-step sampling instructions, references to standard operating procedures (SOPs), and ensures that sampling is accomplished as planned. The sampling plan addresses the matrix to be sampled, collection method, statistical requirements, containers, preservation methods, and handling procedures. Specific instructions for identification of samples, information to be included on the containers, labeling, and frequency of field quality control (QC) samples are also included in the plan. Sampling handling and transport may also be referenced in an SOP. If chain-of-custody forms are used to document sample collection and transport, an example form is included in the plan. Finally, any special treatment, holding and disposal requirements, and routing of results are addressed in the sampling plan.

WSL staff accepting samples and field records are responsible for initiating the laboratory custody record and insuring that the handling and condition of each sample is documented. Samples suspected of being inferior will be noted and, at the discretion of the analyst or Laboratory Director, may be rejected for analysis. The sample collector is contacted to request a replacement sample. If an additional sample is unavailable, questionable samples may be analyzed but the results will be flagged and appropriate narrative provided.

Sample receipt and login includes assessment of a unique laboratory identification number. Samples receipt is currently recorded on hard-copy tracking forms, and all sample information is then entered onto a computer-based Laboratory Information Management System (WSLims). The WSLims computer program has been created in-house using Borland C++ (v.4.5) programming language, Object-Windows (v.2.5) graphical-user interface (GUI), and Borland Database Engine (v.2.0) for the database structure and code. WSLims assigns the unique Laboratory ID number used to identify and track samples throughout processing and analysis. Field samples are batched in groups no larger than twenty with four laboratory quality control (QC) samples added to each batch.

LABORATORY QUALITY CONTROL CHECKS

Quality control (QC) includes all procedures followed to ensure the accuracy of the data generated are known to a stated degree of probability. QC encompasses instrument calibration, personnel training, and use of pure reagents and certified standards. QC checks (samples) are used to monitor the performance of the analytical system. All QC samples, whether laboratory or field, are logged into the WSLims database

and assigned a unique laboratory ID number and laboratory batch number. Thus, during processing and analysis, QC samples are indistinguishable from other samples. Checks for laboratory quality control include the following in all routine standard analyses:

Table 2.1: Laboratory Quality Controls

Description	Abbreviation	Frequency
Laboratory Regent Blank	LRB	at least 5%
Laboratory Fortified Blank	LFB	at least 5%
Laboratory Duplicate	LD	at least 5%
Laboratory Fortified Matrix	LFM	up to 5%

For trace-level analysis, the following additional checks may be added:

Table 2.2: Additional Checks

Description	Frequency
Isotope/Internal standards	every sample
Surrogates	every sample
Reference/Certified standard	as available
Instrument replicates	at least 5%
Batch replicates	at least 5%
Solvent replicates	at least 5%
Spike check	at least 5%
Performance evaluation	as available

Depending on the project, the Water Sciences Laboratory also analyzes and evaluates field QC samples, including:

Table 2.3: Field QC Samples

Description	Abbreviation	Frequency
Field Duplicate samples	FD1	at least 5%
Field Reagent Blanks	FRB	at least 5%
External Laboratory Duplicates	FDX	up to 5%
Field Equipment Blanks	FEQ	up to 5%

Most analysis involve the generation of multilevel or multi-standard calibration curves immediately prior to sample analysis. The number of calibration levels range from two to ten-point, depending on the protocol, with a higher number of levels used in more critical trace-level analytical work. Samples with analyte concentrations above the calibration curve are normally rerun after adjusting either the sample concentration or the calibration range to produce a response falling within the calibration range. Calibrations are often checked using an externally prepared reference sample or certified standard.

Analytical precision and accuracy are monitored through the use of Shewhart statistical parameters (I, R, and P) and quality control charts. Control charts are usually generated to visually monitor duplicate ranges (R), spike recovery (P), and matrix-spike recovery (P).

$$R = |FD1 - FD2|$$

$$I = \frac{|FD1 - FD2|}{FD1 + FD2}$$

Upper control limits (UCL) for the range (R) of duplicate analyses is determined by:

$$UpperControlLimit(UCL) = D_4 \frac{\sum_{i=1}^{n} R_i}{n}$$

"R" values for duplicate analyses are generally calculated, tabulated, and graphed using WSLims or spreadsheet software (Excel, Microsoft Corporation).

Accuracy is monitored using perfect recovery (P) in fortified blanks (LFB; equation 2.4) and matrix spike (LFM; equation 2.5) samples, and may be checked using standard reference materials (SRM) and performance evaluation (PE) samples.

$$PercentRecovery_{LFB} = 100(\frac{measured}{known})$$

$$PercentRecovery_{LFM} = 100(\frac{measured - background}{spike})$$

Upper (equation 2.6) and lower control (equation 2.7) limits for recovery are determined by:

$$UCL = \frac{\sum_{i=1}^{n} P_i}{n} + 3\sqrt{\frac{\sum(P_i - \frac{\sum_{i=1}^{n} P_i}{n})^2}{n-1}}$$

$$LCL = \frac{\sum_{i=1}^{n} P_i}{n} - 3\sqrt{\frac{\sum(P_i - \frac{\sum_{i=1}^{n} P_i}{n})^2}{n-1}}$$

Qualitative identification and confirmation of contaminants, or absence thereof, is done by comparison of the results with those of a known amount of standard reference material or by comparison to a second well-characterized method. For assay and impurity tests, specificity is demonstrated by the resolution of the two closest eluting compounds. If impurities are available, it must be demonstrated that the assay is unaffected by the presence of spiked materials (impurities and/or excipients). If impurities are not available, the test results are compared to a second well-characterized procedure. This is further described in the specific analyte SOP.

Method Detection Limit (MDL)

A method detection limit (MDL) is defined as the minimum concentration that can be measured with a 99% confidence that the concentration is greater than zero. MDLs are determined for all routine analytical methods from analysis of a prepared test sample in a matrix similar to typical unknown samples. The procedure used is taken directly from EPA Federal Register (1989) Pt. 136 Appendix B, Definition and procedure for the determination of the method detection limit – Rev. 1.11. All new or revised methods are subjected to MDL tests before use on unknown samples. MDLs for trace-level analyses are repeated annually, or more frequently if necessary, to confirm sensitivity. Reporting limits, or Quantitation Limits

(QL), are typically set at 3 to 5 times the concentrations obtained from method detection limit tests to compensate for additional uncertainty when handling unknown samples.

Microbiology samples are generally not processed by the Water Sciences Laboratory, and thus no specific parameters are in place for such samples.

ANALYTICAL PROCEDURES

All routine methods at the Water Sciences Laboratory are in the form of numbered standard operation procedures (SOPs). The written format for standard operating procedures is described in Part II General Methods. The format includes sections for method references, scope, basic principles, apparatus, safety, step-by-step procedures, calculations, statistics, quality assurance, and additional information helpful for utilizing the procedure. The list of SOPs continues to grow, and procedures are updated as needed to incorporate changes and improvements in our analytical methodology. In general, routine analytical methods must meet realistic objectives with respect to sensitivity, accuracy, reliability, precision, interferences, matrix effects, limitations, costs, and the time required.

Most of the analytical procedures used are based on published and standardized methods found in: *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998); *Methods for the determination of organic compounds in drinking water* (USEPA, 1988; 1992); *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846* (USEPA, 1986, and current updates), *Methods for chemical analysis of water and waste* (USEPA, 1983), *ASTM Annual Book of Standards* (ASTM, 1991), *Techniques of Water-Resources Investigations* (USGS, 1989), and *Methods of Soil Analysis* (ASA, 1986). When standardized methods are not available or are unsuitable, in-house methods are developed and often based on procedures found in scientific publications such as *Analytical Chemistry, Journal of the Association of Analytical Chemists, Journal of Chromatography,* and a wide variety of other peer-reviewed publications. Routine methods are validated using test samples and standards, compared to previously-used methods if applicable, and if found acceptable are described in a written SOP.

INSTRUMENT CALIBRATION AND MAINTENANCE

Instrumentation housed at the Water Sciences Laboratory include to light gas isotope ratio mass spectrometers and three high-vacuum preparation systems which are used for highly precise measurements of the variations in the amounts of stable isotopes of nitrogen in nitrate, as well as the stable isotopes of hydrogen and oxygen in water for tracing water movement in hydrologic systems. Two gas chromatograph/mass spectrometer (GC/MS) quadrupole systems are used for measuring trace levels of pesticides and degradation products of pesticides, gasoline oxygenates, organic acid derivatives, algal metabolites, and other volatile thermally-labile compounds. Other gas chromatographs, two ion chromatographs, and an HPLC system are used for measuring dissolved gases, dissolved ions, and polar organic compounds in ground and surface water. A liquid chromatograph (LC) interfaced with an ion trap tandem mass spectrometer (LC/MS/MS) provides the capability to determine explosives residues and RDX degradation products (MNX and TNX), acetamide degradation products, pharmaceutical compounds, and other polar organics that are not suitable for determination by GC/MS. A GC with a micro-electron capture detector interfaced with a vacuum extraction system is used in ultra-trace level determination of chlorofluorocarbons (CFCs) for ground water age-dating. An inductively coupled plasma mass spectrometry (ICP-MS) is used to determine water hardness and other metals, including isotope analysis.

Other analytical equipment includes a supercritical fluid extractor (SFE), carbon analyzers, and spectrophotometers, as well as some older radiochemical instrumentation used for naturally occurring isotopes. All of these analyses are under the management of this QA Manual. A list of applicable Standard Operating Procedures (SOPs) for current methods is provided in Appendix III.

Calibration frequency is a function of the instrument and the procedures, and the SOPs specify the minimum required. Calibration is required before running samples on any equipment with frequent (5%) calibration checks. Complete recalibration is recommended at the beginning of every run analyzing a maximum 2 complete batches, with more frequent recalibrations necessary if increased variability is observed. Results with the highest level of certainty require complete calibration before and after the analysis, and new calibration curves must be checked against previous curves to determine if the instrument and standards are giving acceptable and similar responses. Where possible, the calibration is checked against an independently prepared secondary or reference standard for additional verification. See each specific SOP for further clarification.

Troubleshooting and repair procedures are performed with an instrument malfunctions. Diagnostic procedures are usually found in the instrument manual, notebook, or may be obtained from the instrument manufacturer. All repairs and maintenance are performed by trained and qualified personnel from the instrument manufacturer, university instrument shops, or the Water Sciences Laboratory.

Calibration runs and instrumental maintenance are documented in the same bound instrument notebooks. The instrument notebook should contain all pertinent instrument identification information on the first page, including manufacturer, model and serial numbers, UNLID numbers, installation date, warranty information, room and building numbers, and any other relevant information. Calibration record entries include the date and time, the sample batch, instrument identification and location, calibration procedure used, the instrument operator and the results of the calibration. All maintenance work, whether preventative or unscheduled, is documented in the instrument notebook. Maintenance record entries include the date and time, symptoms, maintenance or repair details, date repair completed, parts replaced, name or initials of the person who performed the work, and any other relevant information. The current instrument notebook is to remain stationed with the appropriate instrument for continuous reference and updating.

NONCONFORMITY AND CORRECTIVE ACTION

QC nonconformity may indicate an analytical problem requiring corrective action. Laboratory corrective action occurs at several levels. The most common and efficient corrective action involves the action of the technician or analyst in charge of analyzing a batch of samples. In most analytical procedures, nonconformity may be signaled by significant deviations in instrument response, variability in replicate analyses of a standard or sample, atypical blank responses, or other unusual characteristics. The technician or analyst then may attempt to locate the cause of the nonconformity and effect correction prior to calibrating and running the samples. Results of QC samples may also signal nonconformity and can also trigger corrective action. Although variations in accuracy and precision reflected in QC samples are typically determined well after a batch of samples has been run, the analyst or technician may also note unusual responses for some blanks, replicates, or reference samples that may immediately be brought to the attention of the Laboratory Director for more immediate corrective action.

The following guidelines are used to evaluate nonconformity in trace organic QC samples, method or calibration blanks, or surrogates:

1. Upper Control Limits (UCL) exceeded for Range (R) and Recovery (P)
2. Lower Control Limits (LCL) exceeded for Recovery (P)
3. Blanks exceeding Reporting Limits (QL)
4. Failure of Performance Evaluation (PE) sample analysis

If corrective action is necessary, the analyst and Laboratory Director will take some or all of the following steps to remedy the problem:

1. Check methodology to verify preparation and analytical SOPs were followed.
2. Check calculations and measurement data.
3. Check instruments to ensure proper calibration and operation.
4. Check reagents and laboratory conditions for contamination.
5. Reanalyze all samples run at the time the problem was detected and compare original re-run values to verify matrix effects or contamination.
6. If the problem is not resolved, seek assistance from instrument manufacturer.

The following guidelines are used if the nonconformity is the instrument tune or calibration:

1. Check the maintenance logs and associated instrumentation and columns. Perform maintenance if required.
2. Check expiration dates and integrity of standards. Re-prepare standards as necessary.
3. Determine if sample results are affected.
4. Re-calibrate instrument to meet specifications and re-analyze samples.

Reports of quality control results are prepared annually, or more frequently if problems arise, and submitted to the Laboratory Director. These reports consist of a summary of quality control calculations for the year, and a comparison to the previous year's results. Any changes in control limits, analytical variability, or other problems will be noted in the report together with recommendations for improvements or modifications to the analytical process.

DATA REDUCTION, VALIDATION AND REPORTING

The technician or analyst in charge of the analysis is responsible for verifying and tabulating raw data into a form containing the Lab ID#, field identifier, collection date, project, protocol, batch number, analysis date, and results of analysis. The analyst reviews the tabulated results to verify that sample preparation/analysis documentation is correct and complete, the appropriate SOP was followed, QC results are within control limits, and that any special sample preparation/analysis requirements have been met. The WSL standard operating procedure Batch Accept and Report lists general acceptance and reporting procedures.

Any problems with sample analysis will be communicated verbally and in writing to the supervisor, together with an explanation of how the problem was resolved. Calculations for data reduction are included in the method's standard operating procedure. Results are typically entered or transferred electronically to a computer spreadsheet for performing calculations and reporting, although handwritten results are acceptable. The data package is then initialed, dated, and passed on for review.

Data review and validation may be performed by both a supervising chemist and Laboratory Director and includes calculation of quality control statistics (range and recovery). Data review includes a check of calibration data, QC results, completeness of supporting documentation and results, and determination if results are ready for release in the form of a final report. If concentrations are not already in standard units, results are converted to mg/L or µg/L for liquid samples, µg/g or ng/g for solid samples, and µL/L or nL/L for gaseous samples, with method sensitivity determining the appropriate range. Results falling below the most recent reporting limits are converted to "<reporting limit" unless the project or individual requesting the analyses specifies uncensored results. A disclaimer is added to uncensored results indicating that concentrations below reporting limits are indeterminate and cannot be verified.

Quality control results falling outside control limits are immediately subjected to corrective action as discussed in the previous section. If corrective action does not resolve the nonconformity, and the source of a problem cannot be identified, the results for the affected sample batch are reported with a footnote describing the quality control issue. If the source of the problem can be identified, but cannot be corrected, the results may be discarded and the sampler or other responsible party will be contacted to determine whether re-sampling or other alternatives can be arranged in order to provide valid results. Issues that affect data quality are included in the cover letter or narrative that is produced with the sample results.

DOCUMENTATION AND RECORDS

The most recent versions of the quality assurance manual, standard operating procedures, and other relevant documents are distributed to affected laboratory staff, and a complete set of documents is available at all times in the Water Sciences Laboratory Box cloud storage. A revision number is indicated in the 3-digit code included in the document or method number. The Laboratory Manager will be responsible for ensuring that the most recent versions of all documents are used by laboratory staff, and that the most recent versions of documents are available in the Water Sciences Laboratory Box folder. Other records include, and are not limited to, personnel records, QA corrective action files, laboratory notebooks and worksheets, batch sheets, maintenance logs, standard logs, and laboratory sample log-in files. Sample log-in information is held in the WSLims as noted below. Records are stored in designated file drawers or electronically and are retained for 5 years, or as specified by contract, to allow for access to raw data information.

Holding times are calculated from the collection and preparation dates and stored in the WSLims. Samples are typically stored until results are verified and reported, and are held for four weeks after the results have been released and delivered to ensure that reanalysis will not be required. Results for samples prepared and analyzed after the maximum holding times have expired will be flagged. Results and supporting documentation may be held indefinitely at the Water Sciences Laboratory, although data older than five years may not be verifiable. Raw results are held in files, notebooks, and other standard forms. Electronic raw results and data are archived on the Water Sciences Laboratory Box cloud storage. Electronic records are secured through a digital signature. WSL staff are assigned unique names and each person choses an individual password. To log into laboratory computers, both the unique name and password are required.

LABORATORY ORGANIZATION AND RESPONSIBILITY

The WSL Quality Assurance Program is primarily the responsibility of the Laboratory Director. The manager is responsible for designing, equipping, and monitoring the laboratory quality assurance program including operating procedures, laboratory records, statistical techniques, calibration, and equipment maintenance.

The Laboratory Director will manage and provide oversight for the Quality Assurance Programs. The Laboratory Director does not perform the sample analysis and is independent from data generating groups. All corrective action is approved by the Laboratory Director, and he/she has final authority to stop work or make substantial changes to any method or procedure. The Laboratory Director monitors QC activities and results, determines conformity of procedures and results, and makes appropriate recommendations for corrections and improvements. The Laboratory Director seeks out new ideas and current developments in the field of quality control and makes recommendations for possible improvements where appropriate. The Laboratory Director is responsible for periodic review of the quality assurance manual to ensure that it reflects the current needs and operating conditions of the WSL. Revisions to the quality assurance program may become necessary following internal audits, assessments, inspections, or site visits.

Most laboratory staff hold degrees in environmental sciences, chemistry or laboratory technology. The minimum educational level of professional level staff is a bachelor's degree with experience, or a master's degree. Technical staff may possess a bachelor's degree (Grade III) or an Associate's Degree (Grade II). Laboratory technicians are typically recruited with Environmental Laboratory degrees as well as experience in an analytical laboratory. New personnel are given a concise summary of their job responsibilities, trained and tested in specific analytical methods and basic quality assurance/control procedures by experienced staff members before handling and analyzing samples.

PROCUREMENT

Purchased equipment, supplies, reagents, standards and other testing materials must be of sufficient quality so as not to adversely affect analytical results. Scientific vendors are regarded as resources or extensions of the analytical laboratory (Ratliff, 1990), and thus must adhere to the same standards of quality. The WSL has access to and experience with a wide variety of scientific manufacturers, both directly and indirectly through the University Purchasing Department. The Laboratory also is fortunate in most, if not all, cases to have the final word in choosing a supplier.