

LAB ID 11642
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<000055> *QUALITY SYSTEM*

<005517A> The quality manual and related quality documentation do not include management arrangements for exceptionally permitting departures from standard operating procedures, policies or standard specifications. (Sec. 5.5.2.p. NELAC 2000).

CORRECTIVE ACTION (USGS ItemA): The Quality Management System (QMS) document (our quality manual) will be revised to address this issue. Our understanding of this finding was the need to set policy on permitting exceptions to standard practices that an analyst will likely be faced with. It is important to note that the Analytical Procedure SOP template does include a section for documenting deviations from the source method with a requirement to describe the rationale for the change. In addition, the NWQL has a custom proposal SOP to handle customer work for non-routine methods. These procedures and arrangements for handling exceptional departures will be addressed in the revision of the QMS.

Completion Date: November 30, 2003.

<000056> *PERSONNEL (SEC: 5. 6 NELAC 2000)*

<000566> Laboratory Management does not ensure that training records are kept up-to-date for all technical staff that include: (Sec. 5.6.2c NELAC 2000): evidence that the employee has read, understands and is using the latest version of the lab's in-house quality documentation. (Sec. 5.6.2c1 NELAC 2000), evidence that the employee has read, acknowledges and understands their personal & legal responsibilities including potential punishments & penalties for violations, (Sec. 5.6.2c3 NELAC 2000).

CORRECTIVE ACTION (USGS Item B): The new Quality Management System (QMS) document was approved for use just prior to the arrival of the audit team but staff training was not completed before the audit. Immediately after the audit, an uncontrolled copy of the document was posted on the laboratory's internal web page so that it would be readily available to all staff. In addition, supervisors of all laboratory units were provided paper copies of the uncontrolled document to be used for staff training. An email was sent to all laboratory staff on August 25, 2003 indicating the requirement to read the QMS. A training checklist was developed for unit chiefs to use to document that all staff had read and understood the QMS document. Unit chiefs have been instructed to ensure that all NWQL staff (Federal employees and Contract staff) read the QMS document by October 31, 2003.

The NWQL has taken several steps to address the requirement to provide evidence that all laboratory staff have read, acknowledge and understand their personal and legal responsibilities

including punishments and penalties for violation. These issues are addressed in the ethics training that each employee is required to take, in the QMS document that all staff have been instructed to read, and in the draft U.S. Department of Interior Code of Ethics that has been included as an appendix of the QMS. The ethics training that all employees specifically addressed the fact that data falsification was serious infraction that could result in a disciplinary action including termination of employment. The ethics training also addressed the fact that data falsification could result in an individual's criminal prosecution. The training checklist on the QMS reading assignment that requires signature by each laboratory staff person provides the evidence to address this standard.

In addition, after the DOI Code of Ethics is approved, forms will be distributed to all employees and contract staff for signature that specifically acknowledged that they have read and understood the DOI and NWQL code of ethics, the new QMS manual, and that they understand the penalties for violations outlined in our Ethic Training program. If the DOI Ethics Code is not approved by the Department by January 1, 2004, then the NWQL will move forward with this acknowledgement signoff without including that element. In the future, this acknowledgement will be a specific training item in the training checklist for the QMS document reading assignment.

Completion Date: October 31, 2003

<000569> The laboratory's management does not assure all sample acceptance criteria (Section 5.11) are verified and that samples are logged into the sample tracking system and properly labeled and stored. (Sec. 5. 6.2f NELAC 2000).

COMMENT: THIS REFERS TO PROPER TEMPERATURE REQUIREMENTS.

CORRECTIVE ACTION (USGS Item C): Exit meeting notes indicate that this finding specifically concerned alkalinity samples. The USGS method does not require chilling of this sample type. However, USGS policy is to report field measurements of alkalinity in the national database. Laboratory measurements are submitted as a gross QA check. As indicated during the audit, the NWQL is no longer seeking accreditation for this parameter. In addition, we will take steps to ensure that all alkalinity data reported to our customers are appropriately qualified.

Completion date: November 30, 2003.

<000059> *MEASUREMENTS TRACEABILITY AND CALIBRATION (SEC. 5.9 NELAC 2000)*

<005911> All support equipment is not calibrated annually, using NIST traceable references when available, over the entire range in which the equipment is used. (Sec. 5.9.4.1b NELAC 2000)

COMMENT: THIS REFERS TO THE 180-DEGREE OVEN THERMOMETER.

CORRECTIVE ACTION: (USGS Item D): A NIST traceable thermistor capable of checking temperatures in the 180 degree Celsius operational range of the Total Dissolved Solids oven has been ordered. The thermistor probe can be placed into the oven during operation to compare readings against the oven readout and the laboratory's continuous temperature monitoring system. The oven has been wired into the monitoring system, and as stated in our SOP, an annual calibration against the NIST traceable standard will be performed. It is expected that the NIST traceable thermistor will be delivered by mid-November. Verification of the TSD oven operation should be completed by November 30, 2003.

<05919a> Glass microliter syringes do not come with a certificate attesting to established accuracy or the accuracy initially demonstrated and documented by the laboratory.

CORRECTIVE ACTION: (USGS Item E): Calibration of syringes will be verified before use, or certified syringes will be purchased. Documentation of the verification process will be included in the quality management system document and in SOP OX0340.0.

Completion Date: December 9, 2003

<000510> *TEST METHODS AND SOPs (Sec. 5.10 NELAC 2000)*

<005101> The laboratory does not have SOPs for all test methods and laboratory activities. (Sec. 5.10.1.1 NELAC 2000).

COMMENT: THIS REFERS TO STANDARD AND QUALITY CONTROL SAMPLE PREPARATIONS FOR RADIOCHEMISTRY.

CORRECTIVE ACTION: (USGS Item F): The Quality Assurance Section will prepare an SOP describing preparation, validation, and acceptance criteria for blanks, standards, and QC samples for in-house radiochemical analyses. Completion Date: November 30, 2003

<005103> All instructions, standards, manuals and reference data relevant to the work of the laboratory are not maintained up-to-date and readily available to the staff. (Sec. 5.10.1b NELAC 2000).

COMMENT: THIS REFERS TO ORGANICS METHOD SOPs

CORRECTIVE ACTION: (USGS Item G): The SOP's for both sample preparation "(OP0393.0) and sample analysis (OM0389.0) have been approved and posted on the NWQL web page (7/13/03). Training for both the current analyst and sample preparation personnel has been completed. Completion Date: September 25, 2003

<005108> Each test method does not include or reference the following where applicable: (Sec. 5.10.1.2b NELAC 2000), definitions;

COMMENT: THIS REFERS TO NEED FOR MORE COMPLETENESS; pollution prevention, (Sec. 5.10.1.2b17 NELAC 2000).

CORRECTIVE ACTION: (USGS Item H): A team has been working to create a single document containing definitions to be used in all SOPs. The first version will be completed no later than January 1, 2004 with updates and additions thereafter as needed. The Business Development Team will review each SOP due for renewal and each new SOP to ensure that all definitions match the definitions document and that all needed definitions are included or referenced. Since all SOPs are reviewed at least once every 3 years, all SOPs will be corrected within 3 years.

A NWQL policy statement will be prepared to address pollution prevention. This policy is expected to be distributed by October 31, 2003 and will be included in the annual safety training requirement and be referenced in our QMS and all appropriate SOPs.

The Business Development Team will review each SOP due for renewal and each new SOP to ensure that this pollution prevention/waste minimization policy is included. Since all SOPs are reviewed at least once every 3 years, all SOPs will be corrected within 3 years.

Completion Date: January 1, 2004

<051023A> The laboratory does not establish Standard Operating Procedures addressing manual calculations including manual integrations. (Sec. 5.10.4.c NELAC 2000)

CORRECTIVE ACTION: (USGS Item I): Guidance regarding use of manual calculations and manual integrations will be incorporated into a new SOP. The SOP will be used to train the appropriate Analytical Services staff members.

Completion Date: December 9, 2003

<000511> *SAMPLE HANDLING (SEC 5.11 NELAC 2000)*

<005117> The laboratory does not have a written sample acceptance policy that clearly outlines the circumstances under which samples will be accepted. (Sec. 5.11.2 NELAC 1999)

COMMENT: SAMPLE ACCEPTANCE POLICY NEEDS TO REFLECT ELAP REQUIREMENTS FOR PRESERVATION AND HANDLING (ELAP ITEM 241 AND 242).

CORRECTIVE ACTION: (USGS Item J): The NWQL will revise the Log-In SOP to incorporate a documented sample acceptance policy for preservation and handling.

Completion Date: November 30, 2003.

<051118> The results of all sample acceptance and receipt checks are not recorded. (Sec. 5.11.3b NELAC 2000).

CORRECTIVE ACTION: (USGS Item K): All temperature checks are recorded on the Analytical Service Request form at the time samples are received. The temperature at receipt is then recorded in the Laboratory Information Management System (LIMS).

Since pH verifications are performed in various sections of the laboratory (login, analytical lines, and chain of custody lab) it is not possible to include this information for each bottle type in the Analytical Service Request form. The Information technology Section will develop an application on the LIMS that will require appropriate sample acceptance checks before analysis. These records of sample acceptance and receipt checks, such as temperature and pH verification, will be recorded and filed electronically with the sample information in the LIMS.

Development of this LIMS application is one of the more complex issues to be addressed from the audit but will be planned for completion by December 31, 2003.

<0000d1> *CHEMICAL TESTING AND AIR TESTING DETAILED METHOD REVIEW (NELAC SEC. 5 APP. D.1)*

<00d118> The laboratory does not document procedures for determining the effect of the sample matrix on method performance.

CORRECTIVE ACTION: (USGS Item L): The NWQL supports the basis for the NELAC standards as outlined in the white paper prepared by the Environmental Laboratory Advisory Board (ELAB), a Federal Advisory Committee commissioned by EPA to advise them on laboratory accreditation issues. The white paper provides a comprehensive discussion about the use of matrix spikes and the responsibilities of project staff to identify matrix spike requirements that address their data quality objectives (DQO's). A copy of the ELAB white paper is attached.

This white paper provides the detailed reasoning behind the changes voted into Appendix D of the NELAC Quality Systems standard in May 2001. The most significant change is the elimination of matrix spikes as a required Positive Control for chemical testing. Matrix spikes are now identified as an element of "Sample Specific Controls" and the language in frequency of use specifies that this will be determined as part of a systematic planning process (DQO's) or as specified by a mandated test method. The white paper makes it clear that the DQO process is a responsibility of the field not the laboratory.

Where required as mandated by Drinking Water methods the NWQL does utilize Matrix Spike samples at a rate of one per set up to a maximum rate of 1 per 20 samples and this is documented in our SOPs.

The majority of the methods that the NWQL is seeking accreditation for do not have mandated Matrix Spike requirements. However, we have taken steps to facilitate the understanding and use of the Matrix Spike samples by our customers. The USGS has a Field QA/QC class for water quality projects that has been offered frequently since 1994. The NWQL has participated in the presentation of this class since its inception with an emphasis on the need for matrix spike samples. The USGS National Field Manual for the collection of Water-Quality data discusses the need for project staff to evaluate the need for matrix spike samples. To further customer understanding, recent NWQL Method Reports have emphasized the need for the projects to include matrix spike samples as part of their field QA.

The NWQL routinely offers its customers matrix spikes for Organic Methods. Inorganic spikes have been used infrequently and the NWQL sees the need to further educate customers on the need for inorganic matrix spikes. Although we report matrix spike results to its customers, the NWQL tracking and data management need improvement. A NWQL Technical Memorandum is being prepared to communicate with our USGS customers on processes to request and interpret matrix spike data to determine the effect of sample matrix on method performance. The memorandum should be distributed by December 9, 2003. Custom proposals clearly state that customers should consider matrix spike data for non-standard or unapproved methods and matrices.

During our Quality System Review scheduled for late fall, NWQL management will discuss and evaluate processes to use summaries of matrix spike data in an annual analytical method assessment.

Completion Date: December 9, 2003.

<00d120> The frequency of the analysis of matrix specific samples is not determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the required mandated test method.

CORRECTIVE ACTION: (USGS Item M): See response to item <00d118> above for background information. The frequency of matrix spikes needs to be determined by field project staff. The NWQL will provide technical assistance to the field to help them determine the appropriate level of field QC to be included in a project plan.

A NWQL Technical Memorandum is being prepared to communicate with our USGS customers on processes to request and interpret matrix spikes. This memorandum will provide information to help project staff assess the frequency of matrix spike sample submissions as part of their systematic planning process. The memorandum will reinforce information in the National Field Manual and the associated field QC course offered by the USGS. This document should be distributed by December 9, 2003.

<000d13> All essential quality control measures are not incorporated in the lab's method manual. (Sec. D NELAC)

COMMENT : THIS REFERS TO 515.1

CORRECTIVE ACTION: (USGS Item N): The method SOP will be updated to reflect that the free acid form of the chlorophenoxy acid herbicides is used in laboratory reagent spikes and laboratory matrix spikes.

Completion Date: December 15, 2003.

<000d17> Any affected samples are not associated with contaminated blank reprocessed for analysis or the results reported with appropriate data qualifying codes.

COMMENT: THIS REFERS TO 625.

CORRECTIVE ACTION: (USGS Item O): Data are currently with raised reporting levels or qualified with an "E"(estimated concentration) code to distinguish data that may be compromised due to a sample process contamination. Recently, the USGS National Database was modified to allow use of a "v" data qualifier code to specifically identify data that may be influenced by process contamination. The NWQL will develop data reporting procedures in the Laboratory Information Management System (LIMS) to allow use of this data qualifier code for impacted samples.

Development of this LIMS reporting application should be completed by December 9, 2003.

<000d18> A method blank is not performed: a. One per 1 preparation batch, per matrix type; or b. in those instances for which there is no separate preparation method, the batch is not defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

COMMENT: THIS REFERS TO 200.7

CORRECTIVE ACTION: (USGS Item P): One matrix-matched blank is included in each batch of environmental samples to be digested (up to 180 sample bottles, the maximum determined by the digestion oven size). Because the digestions occur in closed containers, there is minimal possibility of cross-contamination, negating the need for multiple prepared blanks. Unprocessed matrix-matched blanks are analyzed at the rate of one per 10 environmental sample batch, as defined in the associated SOP.

For filtered samples, which do not require a separate preparation method, unprocessed matrix-matched blanks are also analyzed once per 10 environmental samples batch, as defined in the associated SOP.

The above is valid for both methods 200.7 and I - 4471 – 97, the latter being the USGS method for which we are seeking accreditation.

No corrective action is required.

<00d111> The source of contamination is not investigated and measures taken to minimize or eliminate the problem and the affected samples reprocessed; or the data appropriately qualified if: 1. The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the test method or by regulation, AND is greater than 1/10 of the amount measured in any sample. 2. The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.

COMMENT: THIS REFERS TO 625

CORRECTIVE ACTION: (USGS Item Q): The corrective action process outlined in the Organic Chemistry Program QA/QC Guidance manual will be used to investigate and take measures to minimize or eliminate the problem. This process will be implemented by November 30, 2003.

<00d112> An LCS (a sample matrix free of analytes of interest spiked with a verified known amount of analyte) is not performed at a frequency of 1 per preparation batch of 20 or less samples per matrix, per sample extraction or preparation method except for analytes for which spiking solutions are not available, OR in those instances for which there is no separate preparation method, the batch is not defined as environmental samples that are analyzed together with the same method and personnel using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

COMMENT: THIS REFERS TO 200.7

CORRECTIVE ACTION: (USGS Item R): Effective December 9, 2003, one matrix-matched NIST-traceable LCS will be included in each batch of environmental samples to be digested (up to 180 sample bottles, the maximum determined by the digestion oven size). During analysis, the LCS will be analyzed once, and one CCV will be analyzed at the rate of once per 10 environmental sample batch, as defined in the associated SOP. The CCV is composed of all constituents to be analyzed, prepared from the standards stock solution, spiked into matrix-matrix-matched de-ionized water.

For filtered samples, which do not require a separate preparation method, unprocessed LCSs will also be analyzed once per 10 environmental samples.

The above is valid for both methods 200.7 and I - 4471 – 97, the latter being the USGS method for which we are seeking accreditation.

<00d132> Sufficient raw data records are not retained to permit reconstruction of the initial calibrations using as appropriate, but not limited to: (Sec. D.1.3.b, 5.9.4.2.b, 5.9.4.2.2.c NELAC): instrument.

COMMENT: THIS REFERS TO 200.7.

CORRECTIVE ACTION: (USGS Item S): As of August 1, 2003, the analytical method, instrument ID, and analytical batch number are included in the reference data (raw data records) for the ICP-OES section.

<00d133> All initial calibrations are not verified with a standard obtained from a second source. (Sec. D.1.3.b,5.9.4.2.1 NELAC)

COMMENT: THIS REFERS TO 525, 625, 200.7, 353.2

CORRECTIVE ACTION: (USGS Item T): Appropriate third party check standards (NIST traceable where possible) will be purchased and run in every run to verify the initial calibration.

Completion Date: December 9, 2003

<00D143> The details of the continuing instrument calibration procedure, calculations and associated statistics are not included or referenced in the test method SOP. (Sec. D.1.3,b,5.9.4.2.2.a NELAC)

COMMENT: THIS REFERS TO 524.2

CORRECTIVE ACTION: (USGS Item U): The volatiles analysis SOP OW0279.0 will be updated to include the continuing calibration procedure. The SOP will be updated to reference calculations and statistics that are included in the method open filed report.

Completion Date: December 9, 2003

<00d160> All procedures used to determine detection limits are not documented including the matrix type and all supporting data is not retained. (Sec. D.1.4. NELAC)

COMMENT: THIS REFERS TO 507, 508

CORRECTIVE ACTION: (USGS Item V): The MDL studies exist for these methods, however new MDL studies are to be completed in conjunction with the QCS and NYSDOH samples scheduled to be received in the laboratory on 10/6/2003. The new MDL's for these

methods are expected to be complete by 12/15/2003. A copy of these new MDL's will be provided to QAS for inclusion in the method history file.

Completion Date: December 15, 2003.

ICP/MS 200.8

<S018> The instrument is not stable within a standard deviation of 5% for all analytes on 5 replicate analysis of the tuning solution.

CORRECTIVE ACTION: (USGS Item W): The USGS methods do not use the criterion of a standard deviation of +/- 5% for all analytes on 5 replicates of the tuning solution. The USGS methods use internal standards to minimize the effects of instrument drift and use the results to monitor variability of measurements throughout the day.

No corrective action is necessary.

<S021> The high calibration standard s not prepared in two parts, with Silver and Barium introduced separately into the ICP-MS.

CORRECTIVE ACTION: (USGS Item X): EPA method 200.8, Revision 5.4, Section 7.4 states that a separate solution for barium and silver is “suggested”, not required. The NWQL has been combining these elements in calibration standard solutions successfully for many years

No corrective action is necessary

<S025> All of the values for the Quality Control Sample do not agree within +/- 10% of the true values.

CORRECTIVE ACTION: (USGS Item Y): EPA method 200.8, Revision 5.4, Section 9.2.3 states the following: “If the QCS is used for determining acceptable on-going instrument performance, analysis of the QCS prepared to a concentration of 100 ug/L must be within +/- 10% of the stated value or within acceptance limits listed in table 8, whichever is the greater.” The acceptance limits listed in table 8 include “calculated as average recovery +/- 3 standard deviations.” The NWQL has been using a +/- 3 standard deviation criterion for more than 10 years

<S035> Multi element calibration standards are not prepared every two weeks.

CORRECTIVE ACTION: (USGS Item Z): The ICP – MS SOP will be updated to state an expiration date for multi-element calibration standards of 2 months, as supported by QC data. The completion date is November 14, 2003.

<0000D4> *RADIOCHEMICAL ANALYSIS DETAILED METHOD REVIEW*

<00d446> The Initial Demonstration is not performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel or method.

CORRECTIVE ACTION: (USGS Item AA): Demonstration of Capability documentation will be compiled for all analysts and instruments as per NELAC standards and Quality Management System requirement by November 15, 2003.

<R949> RADON IN WATER - EPA METHOD 913.0

<R951> SAMPLING

<R952> Samples are not collected using techniques that avoid headspace after collection.

CORRECTIVE ACTION: (USGS Item BB): The USGS NWQL has never followed the collection technique described in EPA Method 913.0. We also have never sought accreditation for radon analysis by EPA Method 913.0. The radon method followed at the NWQL is ASTM Method D5072. This method does not require that the sample be collected using techniques that avoid headspace after collection.

The Quality Assurance Section will revise the radon analysis SOP to reflect the correct methodology.

The SOP will be revised, reviewed, and approved by November 30, 2003.

THE FOLLOWING DEFICIENCIES RELATE TO PENDING APPROVAL METHODS

TDS USGS-1-1750-85

<C1528> Filter discs other than glass fiber filter discs - (without organic binder) are used.

COMMENT: THERE IS NO RECORD OF METHOD-SPECIFIED FILTER. NOTE: METHOD I DOES NOT SPECIFY FILTRATION PROCEDURE OR APPARATUS. SEND A COPY OF FILTRATION PROCEDURE FOR DISSOLVED SOLIDS.

CORRECTIVE ACTION: (USGS Item CC): USGS Method I-1750-85 does not indicate that the type and lot number of the filters need to be documented. District personnel follow the USGS National Field Manual <http://water.usgs.gov/owq/Fieldprocedures.html> - Chapter A5 for protocols to collect the samples. The USGS National Field Manual requires samples to be filtered through a 0.45-micrometer (µm) disposable capsule filter. See section 5.2.1 in the field manual for specific directions for filtering samples.

No corrective action is required

<C1526> Samples are not cooled to 4oC immediately after collection and analyzed within 7 days.

CORRECTIVE ACTION: (USGS Item DD): NWQL customers follow the USGS National Field Manual Chapter A-5 for protocols to preserve samples for the USGS residue on Evaporation Method. Please see section 5.2.1 for specific directions for preserving and filtering samples <http://water.usgs.gov/owq/Fieldprocedures.html> for detail. For this method the sample is required to be filtered through a 0.45-micrometer disposable capsule filter.

No Corrective Action Required

CHLORIDE AND SULFATE BY IC USGS 1-2057-85 (USGS ONLY)

<C1736> Stock standards are not stored at 4oC and/or not kept longer than one month.

CORRECTIVE ACTION: (USGS Item EE): We will arrange to have all standards kept in a refrigerator at 4° C. We will prepare a reagent/standards preparation logbook and record the receipt and preparation of all standards, and reagents

<00d131> The SOPs or the test method SOP do not reference the details of the initial calibration procedures, including calculations, integrations and acceptance criteria associated statistics. (Sec. D.1.3.b,5,9,4.2.1a NELAC)

CORRECTIVE ACTION: (USGS Item FF): We will modify the SOP to address the initial calibration procedures, including calculations, integrations and acceptance criteria.

The point-to point calibration will continue to be used. However the continuity of the cal curve will be evaluated using a quadratic curve fit, with a required R2 value of 0.995. The accuracy of the curve will be evaluated by analyzing two third-party check-standards, one at a concentration of 150 mg/L and one at 1.5 mg/L. The calibration will be deemed acceptable if the analysis of these standard solutions produces results that are within statistically determined control limits.

Completion Date: December 1, 2003

<00d134> The criteria for the acceptance of an initial calibration is not established (correlation coefficient or relative percent difference). Sec. D. (1.3.b,5.9.4.2.1e NELAC)

CORRECTIVE ACTION: (USGS Item GG): We will modify the SOP to address the initial calibration procedures, including calculations, integrations and acceptance criteria.

The point-to point calibration will continue to be used. However the continuity of the cal curve will be evaluated using a quadratic curve fit, with a required R2 value of 0.995. The accuracy of the curve will be evaluated by analyzing two third-party check-standards, one at a concentration of 150 mg/L and one at 1.5 mg/L. The calibration will be deemed acceptable if the analysis of these standard solutions produces results that are within statistically determined control limits.

Completion Date: December 1, 2003

<051028> The records of reagent and standard preparation do not indicate traceability to purchased stocks or neat compounds, reference to method of preparation, date of preparation, expiration date and preparer's initials. (Sec. 5.10.5c NELAC 2000)

CORRECTIVE ACTION: (USGS Item HH): A logbook will be established, which will address the traceability of reagents and standards, reference to method of preparation, date of preparation, expiration date and preparer's initials.

Completion Date: December 1, 2003

OIL AND GREASE 1664A

<Y005A> The amount of acid added to the sample bottle before sampling is not determined by lowering the pH of a separate aliquot to <2.

CORRECTIVE ACTION: (USGS Item II): NWQL customers follow USGS Field Manual protocols to collect and preserve the Oil and Grease samples. The field manual requires preservation to be done by adding 2mL of concentrated sulfuric acid to the sample. The requirement to collect a separate aliquot to determine the amount of sulfuric acid required to lower the pH to less than 2 is not mentioned in that text. This requirement will be forwarded to the editor of the Field Manual by October 31, 2003.

<Y006> The pH is not checked without introducing either probes or pH paper directly into the sample.

CORRECTIVE ACTION: (USGS Item JJ): The NWQL will start checking the pH of Oil & Grease samples by the using a glass rod to test the pH of the sample in order to be in compliance with the method and SOP.

Completion Date: November 15, 2003

<Y025A> The pH of the sample is not verified at <2 by use of a glass rod and pH paper at the time of the analysis.

CORRECTIVE ACTION: (USGS Item KK): The NWQL will start checking the pH of Oil & Grease samples by the using a glass rod to test the pH of the sample in order to be in compliance with the method and SOP.

Completion Date: November 15, 2003

PHENOLS SM18 5530 (USGS ONLY)

The stock standard is not standardized according to the method (titrated with 0.025M sodium thiosulfate titrant).

CORRECTIVE ACTION: (USGS Item LL): Standard Method 5530C, paragraph 3a., indicates that the direct weighing yields a standard solution; if extreme accuracy is required, standardize with 0.025M sodium thiosulfate. We are following the preparation procedure in the method, however extreme accuracy is not required.

No corrective action required

TKN AND TOTAL PHOSPHATE USGS I-4515-91, USGS I-4610-91

<051223> The strip charts, tabular printouts, computer data files, analytical notebooks and run logs do not include: (Sec. 5.12.3.3 NELAC 2000): sample preparation including cleanup & separation protocols, ID codes, volumes, weights, instrument printouts, meter readings, calculations & reagents used. COMMENT: THIS REFERS TO RECORD OF DIGESTION REAGENT AND DIGESTION PREPARATION RECORD.

CORRECTIVE ACTION: (USGS Item MM): Logbooks to document digestion reagent and digestion preparation records for these procedures will be set up.

Completion Date: December 9, 2003

<00d133>All initial calibrations are not verified with a, standard obtained from a second source. (Sec. D.1.3.b,5.9.4.2.1 NELAC)

CORRECTIVE ACTION: (USGS Item NN): Appropriate third party check standards (NIST traceable where possible) will be purchased and used in every analytical run to verify the initial calibration.

Completion Date: December 9, 2003.

AUTOMATED NITRATE, NITRITE, AMMONIA, ORTHO-PHOSPHATE

<00d133> All initial calibrations are not verified with a standard obtained from a second source. (Sec. D.1.3.b,5.9.4.2.1 NELAC)

CORRECTIVE ACTION: (USGS Item OO): Appropriate third party check standards (NIST traceable where possible) will be purchased and used in every analytical run to verify the initial calibration.

Completion Date: December 9, 2003.

Gregory B. Mohrman

LABORATORY DIRECTOR

SIGNATURE

DATE

ELAB ATTACHMENT:

MEMORANDUM

To: Jim Pearson, Chair of the NELAC Board of Directors

CC: Jeanne Hankins, NELAP Executive Director
Joe Slayton, Chair, Quality Systems Committee

From: Environmental Laboratory Advisory Board

RE: Recommendations for Changes to Appendix D of Chapter 5 of the NELAC Standards

Date: May 11, 2000

The Environmental Laboratory Advisory Board (ELAB) strongly requests NELAC to consider revising Appendix D of Chapter 5 of the NELAC standards as summarized in the enclosed attachment. We would request these changes be voted on this year, with an immediate effective date.

ELAB believe the current language provides onerous requirements for laboratories, unnecessarily increasing the cost for environmental monitoring; is in conflict with several EPA regulations; perpetuates the confusion about the appropriate role of matrix quality control samples, and does not adequately describe an essential element for laboratory accreditation.

ELAB has formed a subcommittee for this issue, and offers the energy of this subcommittee over the next few months to work with the Quality Systems committee to resolve any differences prior to the July, 2000 Conference. The changes ELAB is proposing are only an interim measure; ELAB believes Appendix D needs a more thorough revision, using language in the enclosed attachments as a basis.

Attached is the suggested changes to Appendix D shown in revision/strikeout mode (Attachment 1), a white paper on this topic developed by the ELAB subcommittee (**Attachment 2**), and background supporting information on this topic published by EPA and the US Army Corps of Engineers (Attachment 3) which should be considered as the Quality Systems committee considers future revisions.

Attachment 2

THE APPROPRIATE USE OF MATRIX-SPECIFIC QUALITY CONTROL SAMPLES

Essential Data Assessment Tools for Environmental Analyses

Prepared By:

ELAB Quality Control Sample Subcommittee

Members:

Harry Gearhart, DuPont Engineering

Deborah Loring, STL Laboratories

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For many years there has been confusion in the environmental community over the respective functions of **laboratory** quality control (QC) samples and those QC samples used for other purposes, defined in this document as **matrix-specific** (QC) samples (Carlberg). Unfortunately, this confusion has been compounded by some of the language in Appendix D.1 of Chapter 5 of the NELAC standards. The primary function of **laboratory** QC samples generated in the laboratory, such as the LCS and the method blank, should be to demonstrate that the laboratory is performing the method effectively at a particular point in time. In contrast, the primary function of the **matrix-specific** QC samples, such as surrogate spikes, matrix spikes, matrix duplicates, and field blanks should be to demonstrate how effective the method was when applied to the matrix at a particular site (Parr). This distinction does not exist in Appendix D.1.

While the analysis of laboratory QC samples can be considered an essential requirement for a quality system, and thus should be evaluated as part of a laboratory accreditation program, requirements to analyze matrix-specific QC samples should not be linked to accreditation requirements. Although these samples provide a valuable tool to assess the quality of environmental data, their use should be based on data user needs; as part of laboratory accreditation, laboratories need to demonstrate their ability to perform these analyses, when required by their customers.

Control of the analytical process is maintained using the batch principle, and a number of different batches may be identified. These include the sampling batch (a group of samples collected together), the preparation batch (a group of samples prepared together), and the analysis batch (a group of samples analyzed together). These latter two terms have been appropriately defined in the NELAC glossary. It is important to note that many laboratories combine samples collected from various sites into one preparation or analysis batch. Any given sampling batch may, or may not, include matrix-specific QC samples.

As noted in Appendix D.1, a method blank and LCS must be processed with each extraction batch. These samples are used to evaluate and control laboratory performance and are appropriate. However, Appendix D.1 also requires that the laboratory analyze matrix-specific QC samples as well. This requirement leads directly to two problems. The first is that the matrix QC results then tend to be used for laboratory control rather than evaluation of the site matrix

effect on the analytical process. The second, much more serious issue, is that site investigators do not define the appropriate level of matrix-specific QC analyses since they know that the laboratory must perform some type of generic approach. This saves the site investigator money but has a very detrimental effect on overall data quality since the matrix-specific QC that the laboratory performs and reports will many times be on samples from a completely unrelated site.

As shown in Attachment 3, various matrix-specific QC samples have been defined (Wentworth). Only two of these QC samples, matrix spikes, and matrix spike duplicates (MS/MSD) and surrogate spikes (SS) are included in the Appendix D.1 requirements. The discussion below focuses only on MS/MSD analyses, as the requirements in NELAC for these samples are the most onerous. The suggested revisions to Appendix D include changes related to other types of matrix-specific QC samples as well.

WHAT DO MS/MSD RESULTS SHOW?

MS/MSD results are used to estimate the accuracy and precision of a measurement (i.e., the uncertainty in the measurement) for the sample which was spiked. If related samples from the site have similar physical and chemical characteristics, the MS results may, with caution, be used to extrapolate the expected uncertainty of the measurement to these other samples. The percent recovery is calculated for the MS/MSD, and the mean recovery can be used to estimate accuracy of the method on the site matrix. The Relative Percent Difference (RPD) is calculated for the MS/MSD, and can be used to estimate the precision of the method on the site matrix.

Some site matrices can show a significant bias. For example, in samples with high organic content, MS/MSD recoveries can often be significantly low (<50%) for organics. A low bias evident in the MS/MSD can often be extended to other samples at the site that are of a similar matrix. In this specific case, it would be appropriate to flag data from samples of that same matrix type at that site as being biased low, recognizing that target analytes reported at that site are likely to be underestimated. This information is crucial in risk assessment. Where contaminants of concern are detected at a site and are close to action levels, knowing that the data is biased low allows the data user to make responsible decisions with regards to actions taken based on the known bias of data close to action levels. Alternatively, if it is critical to obtain more accurate results, another more accurate method may be more appropriate.

Some site matrices can show a high bias. For example, highly complex organic matrices subjected to GC/ECD analyses for Pesticides, even with appropriate clean-up measures, can show a high bias, evident in MS/MSD recoveries. If this is the case, and target analytes detected at the site are close to or above action levels, it may be valuable to investigate the use of an analytical procedure less likely to be subject to these interferences, such as GC/MS.

CAN MS/MSD DATA BE EXTRAPOLATED TO OTHER SAMPLES AT THE SAME SITE?

Extrapolating the results of the MS/MSD to other samples at a given site should be performed carefully. However, it can be done in some cases, and assignment of qualifiers to indicate the measurement uncertainty is possible and appropriate and often performed as part of data

assessment. Physical characteristics, such as particle size, porosity, percent moisture, etc. can be evaluated. Visual inspection of the samples is also valuable. Inspection of raw analytical data, such as chromatograms is also useful in determination of bias and its extension to other samples at the site. If for example, other samples show relatively the same types, levels and patterns of contaminants and exhibit, in the case of organics analyses, similar surrogate recoveries, bias determination can be appropriately extended. Examination of the patterns and interferences in raw data, such as evaluation of chromatograms is helpful in assessing whether an MS/MSD bias can be extended to affect other samples at the site. There presently exists no appropriate mathematical model to correct results for bias based on MS/MSD results for samples other than those which were spiked. All of the above mentioned indicators, however, should be assessed, as it cannot be assumed that all samples at one site are of a “similar” matrix.

HOW DO THE RESULTS OF THE MS/MSD REFLECT LABORATORY CONTROL?

The laboratory uses the results of the Laboratory Control Sample (LCS) and Method Blank to show that the method is in “control”, i.e. that the laboratory processed the batch of samples within the expected performance of the method. These QC samples are analyzed with every laboratory batch. If the results of the LCS or method blank are out of control, the laboratory must take action, which most often will include reprocessing the entire batch of samples, but can include qualifying the results.

The MS/MSD results do not show whether the laboratory processed a batch within control guidelines. The laboratory generally does not, and should not take action (i.e. re-analyze MS/MSD, re-prepare and/or reanalyze batch, etc.) based on the MS/MSD results. The MS/MSD results do not show anything about the batch of samples with which they are processed. Laboratory batches may consist of samples from various sites, or samples of varying matrix composition within a given site. The MS/MSD results provide information about a specific sample only.

Re-processing a batch based on MS/MSD data, as well as re-preparing and re-running MS/MSD samples could effectively result in providing misleading data. If an MS/MSD sample was rerun repeatedly, until a run, by chance, came within control limits and that data was presented, this would be misleading, as a matrix effect present at a site would effectively be “masked” to the data user. Although this seems to be an unacceptable laboratory practice, there are some methods that actually require the laboratories reanalyze the MS/MSD, indicating that a failed MS/MSD indicate that the laboratory is out of control and the data in that laboratory batch cannot be reported for compliance purposes.

HOW OFTEN ARE MS/MSD SAMPLES ANALYZED?

The frequency that is presently required for MS/MSD samples varies with the regulatory program and with the specific methods within those programs, and there are often conflicts in the use and the frequency of MS/MSD samples. The most common interpretation for the hazardous waste program is that one set of MS/MSD or MS/MD be run per 20 samples. However, as discussed in Attachment 2, this frequency is not a requirement of the RCRA program. Furthermore, MSD sample analyses are not required for either NPDES compliance monitoring

under the Clean Water Act nor drinking water compliance testing under the Safe Drinking Water Act.

To further complicate the issue, and as required by Appendix D, the frequency is often required to be implemented at the laboratory level, based on the samples received by the laboratory, independent of the data need, matrix, site, or customer. While the results from an MS/MSD analysis provides good information about the performance of the method on that sample, it provides only limited information about related samples, and probably little value for other samples from other sites.

The choice of which sample to run for MS/MSD is frequently left to the laboratory, and is often made based on which client has sent in additional volume, or, which sample appears to be the "cleanest." Because most laboratory clients know that the burden is on the laboratory to analyze an MS/MSD per 20 samples, and report those, they do not send in samples designated for MS/MSD analysis, perceiving it as a lab required laboratory QC activity. It can be difficult for a laboratory, particularly with water samples analyzed for organics, to get a sample with enough volume to perform the MS/MSD.

HOW ARE THE MS/MSD REPORTED?

Under the schemes as described above, MS/MSD data is inappropriately considered as "belonging" to a specific laboratory batch and is generally required to be reported with all data generated from that laboratory batch (i.e. MS/MSD information is reported to all parties whose samples were prepared/analyzed in that particular batch). Many laboratory clients and/or regulatory agencies will reject data if not accompanied by this information.

HOW DOES THIS AFFECT ENVIRONMENTAL DATA QUALITY?

It is crucial that the laboratory not report MS/MSD data from a site other than the one from which the native sample was derived. If an MS/MSD is reported with all samples from the laboratory batch, and it shows no matrix effect, the data user may assume there is no bias in the results, even though the MS/MSD is not derived from that data user's site. This assumption would be incorrect, and if there was, for example, a low bias, the decisions made based on these results could result in an underestimation of risk at the site. The EPA Office of Solid Waste recognized this and clarified it in the following statement: "The Agency further recommends that data users should be routinely provided with the MS/MSD results from only those QC samples associated with the field samples from the same site. (Cotsworth)"

WHAT IS THE APPROPRIATE FREQUENCY FOR MS/MSD?

The frequency of MS/MSD in relation to laboratory batches is irrelevant. If ongoing sampling is occurring at a specific site, the frequency should be determined based on that site matrix. The MS/MSD samples should be submitted to the laboratory at a frequency determined to be appropriate by the data user based on data quality objectives and what is known about the complexity of the site matrix. The MS/MSD data should only be associated with and reported to the client who submitted the samples. A default frequency of 5% (MS/MSD per 20 site samples)

may be appropriate. However, for matrices such as drinking water, this may be unnecessary. For waste matrices, it might be advantageous to perform more frequent MS/MSD samples. The frequency of MS/MSD should reflect both the level of matrix effects expected and the data quality objectives applicable to the types of decisions that the data are supporting.

By applying the MS/MSD frequency to laboratory batches, the ability to use the MS/MSD results in the appropriate manner is lost. Laboratory batches comprise samples from various sites. The laboratory does not make decisions based on the MS/MSD results, however the data user should evaluate the effect of the site matrix on the accuracy and precision afforded by the method. The only way to allow the data user to make these decisions is by basing the MS/MSD frequency and application to site specific sample batches.

Another concern is that MS/MSD results, because they are being linked to laboratory batches, are being used solely (and incorrectly) to demonstrate laboratory accuracy and precision. MS/MSD results do not show this. However, since they are being routinely applied, associated and assessed in this manner, it is apparent that they are often used in the manner in which they were not intended. The goal of MS/MSD sample analyses should be to specifically to assess whether or not a bias exists due to a site matrix, and whether or not this should trigger either the use of an additional methodology (i.e. GC/MS instead of GC, Furnace AA instead of ICP), or whether the bias would warrant a concern that positively reported target analytes may be underestimated at a site and might be closer to health and environmental based action levels at a site than the data indicates.

In cases where the MS/MSD samples are site specific and applied at a site specific frequency, laboratories may have multiple MS/MSD samples in a particular batch, and may have some batches without any. Because MS/MSD results do not provide any laboratory control information, this is appropriate. All laboratory batches contain LCS and Method Blanks, which are used to document the control of those batches. MS/MSD samples do not need to be extracted or prepared in the same batch as their associated field samples, because by default they will be prepared in laboratory batches with acceptable levels of accuracy and precision as evidenced by the LCS and Method blank. They may be related to samples from the same site that were run in various laboratory batches.

This is not unprecedented. The Superfund program, as well as most Department of Defense (DoD) programs, requires that MS/MSD be site specific and submitted to the laboratory at a designated frequency (Koran). The Superfund program is set up such that it does not matter what laboratory batch the MS/MSD is run in. In Superfund methods, the laboratory is instructed not to repeat MS/MSD analyses for perceived "outages". Most Sampling and Analysis Plans (SAP) and Quality Assurance Project Plans (QAPP) under DoD include site specific MS/MSD that are presumably assessed for that site only.

Many state programs require the laboratory batch approach to the frequency and reporting of MS/MSD samples, as do the present NELAC requirements in Appendix D.

MS/MSD results are an important measure of the performance of the method relative to the specific sample matrix of interest. The results from these tests are used to help establish the

uncertainty of the measurement. While the MS/MSD results provide extremely useful information, this information is wholly site specific (whether the “site” is an effluent stream under NPDES, a drinking water sample under SDWA, or a waste sample under RCRA). Therefore, the appropriate frequency and the application of that frequency should be based on data quality needs rather than laboratory batches.

HOW ARE CONTROL LIMITS RELATED TO MS/MSD?

Because a laboratory does not control based on MS/MSD samples, the application of “control limits” should be defined as to their significance. This significance has not been adequately defined within the industry, and because of that, is often mis-applied to relate to laboratory control.

The most common approach is to set MS/MSD “control limits” at the limits derived from LCS samples. The limits used for LCS samples reflect the accuracy and precision that the laboratory should be able to achieve in a blank matrix, and would thus tend to represent a best case performance. Comparing the MS/MSD recoveries and RPDs to these limits would demonstrate where a matrix effect exists, i.e. that the laboratory method is accurate and precise within these limits, however, the site matrix shows a marked effect on the method such that the results are biased or imprecise.

Once that is understood, there is a second step in the evaluation process. LCS Control limits simply show how accurately and precisely a laboratory can perform a method with no matrix effects. However, they do not necessarily reflect how accurate and precise the data user needs the data to be in order to make an effective decision based on that data. This can be illustrated using the following example:

If a laboratory is running samples with relatively high salinity by ICP, MS/MSD results may show a high or low bias for selenium and lead, due to interferences associated with the sample matrix. There also may be problems with accuracy and precision seen in the high level analytes like sodium and calcium. LCS ranges for all of these analytes are quite narrow, as ICP analyses are quite accurate and precise, particularly in a blank matrix. Accuracy ranges of 90-110% are common.

Once the data user notes that there are matrix effects based on the results of the MS/MSD, the significance of this should be assessed. A significantly low bias in a lead or selenium result may be of concern at a site due to the health and environmental impact of low levels of those analytes. However, the fact that sodium or calcium are, for example, slightly outside of the “control limits” of 90-100%, should cause little concern on the part of the data user, and no action should be necessary.

WHAT ARE THE RESPONSIBILITIES OF A LABORATORY IN EVALUATING MS/MSD RESULTS?

The requirement to perform MS/MSD sample analyses must arise from the data user and not the laboratory. The laboratory must however have procedures for performing these analyses,

including:

- tracking, managing and reporting MS/MSD analyses,
- spiking appropriate analytes at appropriate concentrations,
- calculating recoveries, and
- evaluating the results for any laboratory performance problems.

These responsibilities would be appropriate items for evaluation under NELAC.

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