California Environmental Protection Agency

Air Resources Board

LABORATORY QUALITY CONTROL MANUAL

Northern Laboratory Branch
Monitoring and Laboratory Division

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Laboratory Quality Control Manual

1.0 INTRODUCTION

The purpose of this Laboratory Quality Control Manual is to detail the quality system policies and procedures that ensure consistent validation of the data generated by the Northern Laboratory Branch (NLB). It is meant to be used in conjunction with system wide policies and procedures, including Air Resources Board's (ARB) Quality Assurance (QA) Manual, federal and state regulations, and laboratory Standard Operating Procedures (SOP) which contain method specific details to ensure accuracy, precision, and completeness of both the individual results and the supporting quality control (QC) measurements, resulting in a scientifically defensible program.

NLB provides analytical services to support regulatory and non-regulatory programs requiring data quality objectives (DQO) that meet a variety of client requirements. Clients may include ARB's Primary Quality Assurance Organization, other ARB divisions, federal and state agencies, and local air pollution control/air quality management districts.

2.0 ACRONYMS

ACS - American Chemical Society
AQDA – Air Quality Data Action
AQS – Air Quality System
AQSB – Air Quality Surveillance Branch
ARB – California Air Resources Board
ASTM International – American Standards for Testing and Materials International
CAN – Corrective Action Notification
CCV – Continuing Calibration Verification
CFR – Code of Federal Regulations
COC – Chain of Custody
DOC – Demonstration of Capabilities
DQO – Data Quality Objectives
EQL – Estimated Quantitation Limit
IDOC – Initial Demonstration of Capabilities
IDL – Instrument Detection Limit
ILS – Inorganic Laboratory Section
LIMS – Laboratory Information Management System
LOD – Limit of Detection
LOQ – Limit of Quantitation
LSS – Laboratory Support Section

MDL – Method Detection Limit
MLD – Monitoring and Laboratory Division
NIOSH – National Institute of Occupational Safety and Health
NIST – National Institute of Standards and Technology
NLB – Northern Laboratory Branch
OLS – Organics Laboratory Section
PFTE - Polytetrafluoroethylene
QA – Quality Assurance
QC – Quality Control
QMB – Quality Management Branch
RH – Relative Humidity
RPD – Relative Percent Difference
SA – Standard Additions
SAS – Special Analysis Section
SOP – Standard Operating Procedure
SRM – Standard Reference Material
U.S. EPA – United States Environmental Protection Agency

3.0 DEFINITIONS

ACCURACY – the degree of agreement of a measured value with the true or expected value of the quantity of concern.

BATCH – an analytical batch is a set of prepared samples (i.e. extracts) analyzed together as a group in an uninterrupted sequence. A preparation (extraction) batch is a set of samples which is processed all in one group using the same equipment and reagents.

BIAS – a systematic or persistent distortion of a measurement process which causes error in one direction.

BLANK – a sample that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, and/or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value. The different types of blanks used include:

> METHOD BLANK – used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment. The method blank is an analyte-free matrix to which all reagents are added in the same volumes or

proportions as used in sample processing, and which is taken through the entire sample preparation and analysis process.

INSTRUMENT BLANK or SYSTEM BLANK – used to monitor the cleanliness of the instrument used for sample analyses. Instrument blanks consist of the gas, solvent, or acid solution used during sample analyses. System blanks will be specified in Standard Operating Procedures (SOP) as to type and frequency.

FIELD BLANK – used to monitor processes undertaken in the field. In some cases, sampling media will be installed onto monitoring equipment then removed without turning on the equipment then shipped back to the laboratory with other samples. This blank indicates any contamination from shipping and handling in the field.

SOLVENT BLANK – a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

TRIP BLANK – used to assess any contamination attributable to shipping consisting of a sample of analyte-free media in the same type of container that is required for the analytical test, taken from the laboratory (or other point of origination) to the sampling site and returned to the laboratory unopened.

CALIBRATION – the act of evaluating and adjusting the precision and accuracy of measurement equipment using known values (standards).

CHAIN OF CUSTODY – to maintain the identity and integrity of a sample by providing documentation of the control, transfer, analysis, and disposition of the sample.

CHECK STANDARD – a midpoint calibration standard analyzed concurrently with test samples to confirm the stability of the instrument calibration. Also see CONTINUING CALIBRATION VERIFICATION STANDARD.

COEFFICIENT OF DETERMINATION – typically expressed as ‘r^2,’ measures the proportion of the variance (fluctuation) of one variable (y) that is predictable from the other variable (x) such that $0 \leq r^2 \leq 1$, and denotes the strength of the linear association between x and y.

COLLOCATED SAMPLE – a sample used to assess total precision (sampling and analysis) which is located within a specified radius of the primary sampler. The

collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.

CONTINUING CALIBRATION VERIFICATION STANDARD (CCV) – a midpoint calibration standard analyzed concurrently with test samples to confirm the stability of the instrument calibration. Also see CHECK STANDARD.

CONTROL CHART – a graphical plot of test results with respect to time or sequence of measurement that may be used to show that the system monitored is within expected limits, to signal systematic departures, and to identify inconsistencies in precision.

CONTROL LIMIT – the range of values shown on a control chart beyond which it is highly improbable that a point could lie while the system remains in a state of statistical control. Quality control parameters must lie within this range for satisfactory method performance.

CONTROL STANDARD – a material of known composition obtained (when possible) from a source other than that of the primary calibration standards that is analyzed to verify the calibration.

CORRECTIVE ACTION – an action taken to eliminate the causes of an existing non-conformity or other undesirable situation and to prevent a recurrence.

CORRELATION COEFFICIENT – typically expressed as ‘r,’ it measures the linear relationship between two variables, with a value range of -1 to 1. A value close to 1 indicates there is a strong positive linear correlation between two variables; that is, when one variable increases so does the other. A value close to -1 indicates a negative linear correlation; that is, when one variable increases the other decreases. A value close to 0 indicates a non-linear, or random, correlation.

DATA QUALITY OBJECTIVES (DQO) – performance and acceptance criteria that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. This includes completeness, MDL, accuracy and precision.

DUPLICATE – two aliquots taken from and representative of the same sample or product and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis.

ENVIRONMENTAL CHAMBER – an enclosure with controlled temperature and humidity. An environmental conditioning chamber is used to bring samples to a similar state prior to analysis.

ESTIMATED QUANTITATION LIMIT (EQL) - lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. In general, EQLs are approximately 5 to 10 times the MDL.

INSTRUMENT DETECTION LIMIT (IDL) – the smallest signal, or lowest concentration, that can be distinguished from background noise by a particular instrument. The IDL should always be below the method detection limit, and is not used for compliance data reporting, but may be used for statistical data analysis and comparing the attributes of different instruments.

INTERFERENCE – a substance that is present that can cause a systematic error in measurement in the sample being analyzed. Examples: impurities in the purging/carrier gas, elevated baselines from solvents, reagents, glassware, sampling media, and other sample processing hardware that may cause misinterpretation of the data.

INTERNAL STANDARD – internal standards are compounds which analytically behave similarly to the target analytes. Internal standards are compounds not found in the sample that are added to quantitate results, and correct for variability.

LIMIT OF DETECTION (LOD) – see Method Detection Limit (MDL).

LIMIT OF QUANTITATION (LOQ) – the minimum concentration or amount of an analyte that a method can measure with a specified degree of confidence. The LOQ is defined as equal to ten times the standard deviation of the results for the series of replicates used to determine the MDL. LOQ is analyte and instrument specific.

LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS) – a database used to record and store sample information and analytical results as well as perform workflow and data tracking and reporting.

METHOD DETECTION LIMIT (MDL) – the minimum concentration of a substance that can be measured by a single measurement and reported with 99 percent confidence that the analyte concentration is greater than zero and statistically different from a blank. It is determined from replicate analyses of a sample in a given matrix containing the analyte and sampling media as described in Appendix B to Part 136 of Title 40 of the Code of Federal Regulations.

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST) – an agency of the U.S. Department of Commerce. The Material Measurement Laboratory is a metrology laboratory within NIST that serves as the national reference laboratory for measurements in the chemical, biological and material sciences. NIST supplies industry, academia, government, and other users with SRM.

PRECISION – the degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. The scatter of the values is a measure of the precision; the less scatter, the higher the precision.

QUALITY ASSESSMENT – the overall system of activities whose purpose is to provide assurance that the quality control activities are done effectively. It involves a continuing evaluation of performance of the production system and the quality of the products produced.

QUALITY ASSURANCE (QA) – a system of activities whose purpose is to provide a product or service the assurance that it meets defined standards of quality at a stated level of confidence. It consists of two separate but related activities, quality control and quality assessment.

QUALITY CONTROL (QC) – the overall system of activities whose purpose is to control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical.

REPLICATE – an additional analysis of the same sample or sample extract. The sample extract used for replicate analyses must be chosen at random. Percent difference between the sample and its replicate can be calculated and must meet specified QC criteria or be reanalyzed. Replicate analyses results are used to evaluate analytical precision but not the precision of sampling, preservation, or storage internal to the laboratory.

REPORTING LIMIT – a number below which data is not reported. The reporting limit may or may not be statistically determined, and may be established by regulatory requirements or in conjunction with client or program needs. The RL is equivalent to or greater than the LOQ.

SAMPLE CONDITIONING – to hold samples in an environmental chamber or environmentally controlled room at specified temperature and humidity for a specified time prior to analysis.

SAMPLE MEDIA – air sampling is done to capture a sample of the contaminants present within the air. The container or substrate used to capture the air sample is the sample media. Membrane filters made of cellulose, glass fiber, quartz fiber, Teflon (PFTE), etc., sorbent tubes containing charcoal, silica gel, tenax, XAD, etc., and containers such as flasks, canisters (summa polished or silco lined), tedlar bags, etc. are all examples of sample media.

SPIKE – a quality control sample employed to evaluate the accuracy of a measurement. The spike is prepared by adding a known amount of the target analyte(s) to an aliquot of the sample. The recovery of a spike provides an indication of the efficiency of the analytical procedure. Spikes can be added at any point in the sampling and analytical process such as field, laboratory, matrix, trip, etc.

STANDARD (calibration or control standard) – a substance or material with properties believed to be traceable with sufficient accuracy to permit its use to evaluate the same property of another. It is a solution or substance commonly prepared by the analyst to establish a calibration curve or the analytical response function of an instrument.

STANDARD ADDITION – a method in which small increments of an analyte under measurement are added to a sample under test to establish a response function, or to determine by extrapolation the amount of the analyte originally present in the test sample.

STANDARD DEVIATION – the amount of variability or dispersion around the mean. A low standard deviation indicates that the data points tend to be very close to the mean; high standard deviation indicates that the data points are spread out over a large range of values.

STANDARD OPERATING PROCEDURE (SOP) – a set of written instructions that document a routine or repetitive activity. The development and use of SOPs are an integral part of a successful quality system as it provides individuals with the information to perform a job properly, and facilitates consistency in the quality and integrity of a product or end-result.

STANDARD REFERENCE MATERIAL (SRM) – certified materials with specific characteristics or component content, used as calibration standards for measuring equipment and procedures, quality control benchmarks for industrial processes, and experimental control standards.

SURROGATE – a substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added for quality control purposes.

TRACEABILITY – the ability to trace the source of uncertainty of a measurement or a measured value through an unbroken chain of comparisons.

VALIDATION – the process by which a sample, measurement method, or a piece of data is deemed useful for a specified purpose.

4.0 PROGRAM ROLES AND RESPONSIBILITIES

This section describes the roles and responsibilities for the review, validation, and approval of all individual sample results and the corresponding QC results, hereafter referred to as "data."

4.1 The laboratory technicians are responsible for:

- 4.1.1 Sample control
- 4.1.2 Shipment and receipt
- 4.1.3 Sample log-in and evaluation
- 4.1.4 Sample media preparation
- 4.1.5 Logbooks
- 4.1.6 Other laboratory support functions

4.2 The analyst generating the data is responsible for:

- 4.2.1 All QC checks as described in the SOPs
- 4.2.2 Initial data validation and raw data review
- 4.2.3 Data transfer to the database (e.g. LIMS)
- 4.2.4 Preparing the data report
- 4.2.5 Logbooks
- 4.2.6 Documenting any corrective actions
- 4.2.7 Peer review of data reports generated by other analysts
- 4.2.8 Documenting laboratory equipment and instrument maintenance
- 4.2.9 Performing duties of the laboratory technicians as needed

4.3 The QA/QC Officer is responsible for:

- 4.3.1 Data management oversight
- 4.3.2 Quality Control Manual (QCM)

4.3.3 QC report oversight
4.3.4 Method modification review
4.3.5 Method evaluations
4.3.6 SOP and logbook document management

4.4 The LIMS administrator is responsible for:

4.4.1 LIMS development and management
4.4.2 Analytical instrument to LIMS communication
4.4.3 Data security

4.5 Management is to ensure the analyst has provided complete and accurate data, and the report generated is correct prior to approval. Data must be reviewed and approved by management before being made available to clients. Management is responsible for reviewing logbooks.

4.6 Management designates staff to prepare QC reports. These reports shall summarize QC activities associated with data for each reporting period (i.e., monthly, quarterly, annually). The following items are required for QC reports:

4.6.1 Summary of QC sample results
4.6.2 QC anomalies and corrective actions
4.6.3 MDL determinations
4.6.4 Calibration range verifications
4.6.5 Audit findings and any actions taken as a result
4.6.6 Deviations from SOP
4.6.7 Method modifications
4.6.8 SOP revisions

4.7 Designated, trained staff submits ambient data to U.S. EPA AQS database after review/approval. Data reports generated by SAS are submitted directly to clients after review/approval.

4.8 The annual QC report for all NLB laboratories is submitted by management to the NLB Chief for review and approval. Once approved, the NLB Chief provides a copy of the annual QC report to the Chief of the Quality Management Branch (QMB).

4.9 DQOs should be reviewed by management to confirm that procedures and criteria continue to meet the needs of the program and the clients.

4.10 The MLD organization chart can be accessed by following this link: http://www.arb.ca.gov/html/org/mld.pdf.

5.0 PERSONNEL TRAINING

This section describes the training and documentation requirements for laboratory staff.

5.1 Management is responsible for the implementation of staff training including training assignments and oversight, training evaluation and verification, and training documentation. Staff is responsible for completing training within the specified timeframe, submitting training documentation, maintaining knowledge of procedures and methods performed, and providing in-house training to staff as directed by management. Staff will not perform any procedure, inspection, or method without supervision until all applicable training has been completed and competency demonstrated; supervisor approval is required. Staff training requirements include:

5.1.1 Familiarization with all work related documents, QCM, SOPs, work instructions, manuals, and regulations
5.1.2 Documentation of educational qualifications and work experience
5.1.3 Observing demonstration of procedure or method by designated trainer
5.1.4 Performance of procedure or method under observation of designated trainer
5.1.5 Evaluation of procedure or method performance documented and submitted to management
5.1.6 Repeat 5.1.3 through 5.1.5 until competency has been demonstrated
5.1.7 Training records maintained by management

5.2 Staff performance for specific procedures or methods is verified by measurement against a defined performance standard. These assessment tools may include:

5.2.1 Written evaluation (e.g. training checklist)
5.2.2 Observation of procedure or method
5.2.3 Testing blind QC samples
5.2.4 Testing known or previously analyzed samples

5.3 Training verification documentation includes any of the following:

5.3.1 Completion of training checklists
5.3.2 Completion of procedure or method with supporting performance evaluation such as results from QC samples (e.g. blind, double-blind), duplicate testing, and/or sample re-analyses
5.3.3 Vendor training certificates
5.3.4 Safety meeting participation
5.3.5 Written evaluations
5.3.6 Acknowledgement of reading QCM, SOPs, or work instructions

5.4 Staff will be retrained and retraining verified whenever significant changes occur in policies, values, goals, procedures, methods, processes, instrumentation, or when staff have not performed the method on a routine basis and as determined by management.

5.5 Example Training Checklist:

Staff:			Section:			
Education:						
Instrument Experience:						
Vendor Training:						
SOP	Analyst	Date	Trainer	Date	Sup	Date
MLD005						
MLD068						
SAS012						
Comments:						

6.0 STANDARDS AND STANDARD SOLUTIONS

National Institute of Standards and Technology (NIST) traceable materials, when available, must be the primary standard material to which all working standards are referenced. NLB works with NIST on the development and procurement of NIST standards. All reagents and chemicals must meet the appropriate reagent grade as detailed in the SOP. Dates of receipt for chemicals must be noted on the container labels. In general, chemicals should not be used or kept past the manufacturer's recommended date of expiration unless otherwise approved by management. If chemical use is approved by management past the expiration date, this information must be included in the QC Report.

6.1 Standard Solutions

Stock, standard, or neat solutions are concentrated solutions that are diluted to make working solutions. They are to be made from chemicals of the highest purity available (commercially prepared NIST certified or NIST traceable standards are preferred).

6.1.1 All solutions prepared from liquid or solid standards in the laboratory should be labeled to identify standard element(s) and/or species, concentration level, preparation date, expiration date, and the preparer's initials.

6.1.2 Stock solutions prepared by the manufacturer should be labeled with the date the solutions were received by the laboratory and first opened. The expiration dates should be noted for each solution. Expiration dates of working standards must not exceed the expiration dates of the stock solutions from which they were prepared.

6.1.3 All stock solutions and working standards must be stored per manufacturer’s instructions (refrigerated, dark glass container, etc.)

6.2 Standard Gas Cylinders

Vendor supplied gas cylinders used for calibration of instruments should be obtained from NIST, NIST traceable or verified within the laboratory against a NIST standard. Where NIST or NIST traceable standards are not available, other reference standards may be used to assign concentrations (for example U.S. EPA protocol gas cylinders). Cylinders must adhere to the purity and pressure requirements of the analysis, as detailed in the SOP.

6.3 Control Standards

The control material should be from a source other than the SRM when available. NIST traceability is preferred. Documentation should confirm the control material is from a secondary source.

6.4 Calibration Weights

Calibration weights must be ASTM International Class 1 or Class S, and certified as traceable to NIST mass standards. Weights must be stored and maintained with absolute attention to following the handling instructions provided by the manufacturer. If the weights are mishandled at any time, or if the weights appear to be deteriorating due to age and normal wear, the

weights must be replaced. Weights must be verified by an outside source annually. Two sets of weights are needed, one set as a working standard and one set as a primary standard. The working standards are used during daily measurements at routine intervals to verify the weighing session is within QC acceptance criteria; the primary standards are used to check the calibration of the analytical microbalance quarterly. Results of all annual verifications and quarterly checks must be documented in the QC reports.

6.5 Reagents and Laboratory Water

All reagents used by laboratory must be the appropriate reagent grade for the specific method. The source and purity of the reagent used must be clearly identified in the SOP.

The purified water (deionized or nanopure) used by NLB must be of Type I, as identified by ASTM International. Specifically, the resistance of the deionized water must be greater than 16 megaohms as indicated by the continuous read output of the purifying system. A resistance log should be maintained for each purification unit that includes resistance readings and dates of cartridge replacement. The analyst is responsible for ensuring proper maintenance, including filter replacements, are performed.

7.0 SAMPLING MEDIA

In general, the analyst must refer to the specific SOP guidelines for treatment, conditioning, inspection, shipping, and overall handling requirements prior to beginning any task concerning sampling media. Individual SOPs will describe acceptance testing procedures for new media, cleanliness criteria for reusable media (i.e. canisters), and indicators of contamination.

If the analyst notices that sampling media have experienced a change or possess a previously unidentified condition, such as an inherent contamination, which could affect the quality or integrity of the results, management must be notified immediately. Management must evaluate the situation to determine if action is necessary when corrective action is not specified in the SOP. If an action is deemed necessary, management must verify that the appropriate action has been taken and documented by the analyst.

Sample media storage times must be identified and documented for each media type. If sample media stored beyond the specified storage times are analyzed, data must be flagged appropriately and documented in the QC report.

8.0 EQUIPMENT, INSTRUMENTATION, AND ENVIRONMENTAL ROOMS

Equipment, instrumentation, apparatus, and materials shall meet or exceed the requirements described in the SOP or as provided below for certain categories to ensure good laboratory practices and minimize contamination.

Equipment and instrument maintenance shall occur as per SOPs, laboratory service contracts, and manufacturer's recommendations, and shall be recorded in a logbook. The analyst is responsible for ensuring that the instruments are maintained and calibrated according to the SOP and manufacturer's recommendations.

8.1 Glassware

All laboratory glassware should be borosilicate Class A, unless an SOP specifies otherwise. Any glassware which is chipped, cracked, becomes permanently etched, or has degraded, shall be disposed in a container marked "GLASS." Treatment and cleaning of glassware must follow individual method requirements or an approved SOP.

8.2 Pipettes and Other Measuring Devices

All electronic pipette units must be calibrated at least annually by an outside vendor.

Automatic dispensing units, such as the Autoblock and other reagent dispensers, should be calibrated according to manufacturer's recommendations.

8.3 Balances

All balances and microbalances must be calibrated at least annually. All calibration and check masses must be the appropriate ASTM International class (e.g., S, 1, etc.) and must be certified by an outside vendor at least annually. Refer to Section 6.4 (Calibration Weights).

8.4 Mass Flow Controllers

All mass flow controllers must be calibrated or have calibration verified at least annually against NIST traceable standards, where feasible, by an outside vendor or by ARB's Standards Laboratory.

8.5 Refrigerators, Freezers, and Ovens

All laboratory refrigerators, freezers, and ovens shall be of a size and material suitable for their intended purpose. All laboratory refrigerators, freezers, and ovens shall be used for laboratory purposes only (samples, standards, sample media, etc.). No food for personal consumption is allowed in laboratory refrigerators, freezers, and ovens. This equipment must be maintained per manufacturer's recommendations. Temperatures of refrigerators, freezers, and ovens that contain samples or sample extracts should be recorded at a frequency specified in the SOP. If the temperature is out of range, management should be notified and corrective action should be taken.

8.6 Environmentally Controlled Rooms and Chambers

Environmentally-controlled rooms and chambers must be constructed in accordance with applicable regulations, methods, and/or guidance. All such rooms and chambers must be of the appropriate size and materials, and control systems must meet the prescribed standards.

The analyst is responsible for verifying, recording, and ensuring the room or chamber relative humidity (RH) and temperature are in accordance with U.S. EPA or program requirements as specified in SOPs.

Equilibration malfunctions, discrepancies, and maintenance should be recorded in the logbook.

9.0 ANALYTICAL METHODS

In general, the analytical methods used by NLB are: 1) developed within NLB, 2) ASTM International, U.S. EPA, or National Institute of Occupational Safety and Health (NIOSH) methods; or 3) other available methods. Acceptance testing is required for all methods used by NLB as per section 9.3.

ASTM International, U.S. EPA, and NIOSH methods should be used whenever possible. These methods have been validated following a collaborative test process and only require the verification of laboratory performance prior to acceptance, as described in section 9.3. Other analytical methods used by NLB must be validated and accepted prior to laboratory implementation (sections 9.2 and 9.3).

In the event the laboratory performs a non-routine analysis, a complete description of the analytical parameters must be included in the data report.

9.1 Method Development

Before developing a new method, establish the purpose for which the results will be used, define the application, and scope of the method. The acceptance criteria for the performance of the method need to be established and may define or restrict the choice of techniques. Document all decisions and activities related to method development.

9.1.1 Define the performance parameters and acceptance criteria.
9.1.2 Establish data quality objectives (DQO) based on the quality of data required for the program and the client.
9.1.3 Research available methods. Determine if there is an established method that will meet the scope and DQO for the intended matrix or if one can be modified to do so.
9.1.4 Evaluate safety hazards associated with the analyte, matrix, reagents, etc., associated with the method. Determine if the safety hazards pose an acceptable, manageable risk. If not, research if this is a project that can be subcontracted to another experienced laboratory.
9.1.5 Select analytical technique. If the instrumentation or equipment needed is not already available determine if purchasing it is feasible.
9.1.6 Prepare cost proposals for management's review and approval.
9.1.7 Order standards, testing materials, reagents, and supplies needed.
9.1.8 Conduct preliminary analyses and document all results and observations.
9.1.9 Optimize method and document all procedures.
9.1.10 Perform stability studies. Determine sampling media stability, sampling hold time, extraction hold time, analytical hold time, and archive hold time for samples and extracts. Stability and hold time studies should mimic the environmental conditions expected to be encountered (temperature, sunlight, etc.).
9.1.11 Perform method validation as per section 9.2 and method acceptance per section 9.3.

9.2 Method Validation

Method validation is the process of verifying that a method is fit for its intended purpose (i.e., for use for solving a particular analytical problem or identifying a particular analyte).

Analytical methods need to be validated or re-validated: 1) before their introduction into routine use, and 2) whenever the conditions change (e.g., an instrument with different characteristics or samples with a different matrix).

Validation will demonstrate that a laboratory procedure is robust, reliable, and reproducible by personnel performing the test in that laboratory. A robust method is one in which successful results are obtained a high percentage of the time and few, if any, sample analyses need to be repeated. A reliable method is one in which the obtained results are accurate and correctly reflect the sample being tested. A reproducible method is one in which the same or very similar results are obtained each time a sample is tested. All three method qualities are important for techniques performed in laboratories. (Taylor, John K., "Validation of Analytical Methods," *Anal. Chem.*, 1983, Vol. 55, No. 6, pp. 600A-608A.)

Methods developed or modified by NLB must complete the validation criteria given below. Management must approve the method validation findings before method acceptance (9.3).

9.2.1 Obtain suitable reference material of known accuracy.

9.2.2 Prepare standards over the desired concentration range, usually extending from LOQ, EQL, etc. to expected high concentration of the target analyte.

9.2.3 Determine instrument precision and accuracy. Instrument precision is determined by replicate analyses of matrix-free test samples. Instrument accuracy is determined by analysis of laboratory spikes.

9.2.4 Obtain test samples such as spiked media or SRM with known concentrations that are similar in analyte concentration and sample matrix.

9.2.5 Determine method precision by performing replicate analyses of test samples including all sampling media and reagents specified in the method.

9.2.6 Surrogates, additions of known compounds to evaluate analytical efficiency, should be used only when the test matrix is not adversely altered by such additions.

9.2.7 Field, trip, and laboratory blanks should be analyzed to evaluate the matrix variations and the contamination possible due to sample collection, transport, and laboratory preparation based on the method requirements.

9.2.8 Stability must be determined for samples, standards, extracts to determine hold times for extraction and analysis.

9.3 Method Acceptance

Prior to implementing NLB methods, management shall review the following:

9.3.1 All standards, reagents, sampling media, laboratory environmental factors, and instrumental conditions are detailed in the method.
9.3.2 NIST standards, where available, are analyzed at least three times at multiple concentration levels over the linear range, with a correlation coefficient, r, of 0.98 or better. At a minimum, standard concentration levels should be at the low, mid, and high points of the linear range.
9.3.3 The analytical MDLs must be calculated and follow the equations given in Section 11.0. A MDL is acceptable if it meets the data quality objectives established by the client or regulatory program.
9.3.4 Verify laboratory precision and accuracy values were done correctly if method development done in-house.
9.3.5 Confirm media background levels are less than the MDL.

9.4 Method Development Documentation and Approval

9.4.1 Information and data supporting method development, validation, and acceptance shall be summarized in a written report to management.
9.4.2 The method development report shall be provided to QMB for review and comment. The report shall include a final draft SOP.
9.4.3 After considering QMB's comments, the method development report and associated SOP are finalized.

9.5 Method and SOP Modifications

The review and approval process for method modification is provided in the Northern Laboratory Branch Guidelines for Modifications to Methods and Standard Operating Procedures (Appendix A).

10.0 STANDARD OPERATING PROCEDURES (SOP)

Laboratory SOPs describe the steps necessary to conduct a measurement and the critical parameters to be evaluated during the analysis. A SOP is a set of instructions adopted for repetitive use for performing a specific series of tasks. SOPs are developed in order to generate reproducible and scientifically defensible results. Sample analyses

shall follow approved SOPs. Occasionally, deviations may be necessary which shall require documentation and management approval prior to use.

Approved SOPs, and all prior revisions, must be stored and archived in LSS. The effective dates of use must be clear for each SOP revision. Management must verify that the SOPs are maintained and up-to-date.

A current list of ARB's SOPs can be found at the following links:

http://www.arb.ca.gov/aaqm/sop/summary/summary.htm
http://www.arb.ca.gov/testmeth/cptm/sops.htm
http://www.arb.ca.gov/toxics/compwood/outreach/formaldehydesop.pdf

10.1 Components of SOPs

SOPs shall contain the following items (some items may be waived depending on the program with approval from management):

10.1.1 Identification number and procedure title
10.1.2 Author and approving authority
10.1.3 Revision number and date revised
10.1.4 Table of contents
10.1.5 Purpose or summary of method with significance, parameters measured, range, matrix, precision, and accuracy
10.1.6 Personnel requirements
10.1.7 Equipment (apparatus), reagents, materials
10.1.8 Safety requirements
10.1.9 Troubleshooting

10.1.10 Analytical Procedures (step by step)

10.1.10.1 Preparation and/or extraction

Describe media, reagents, equipment, and procedures needed to get the sample into a ready state for analysis.

10.1.10.2 Analysis

Describe instrumentation and analytical procedures used for sample analysis. Include instrument set-up, appropriate computer interface, and appropriate analytical conditions.

10.1.11 QC

Describe the frequency of analysis, acceptance criteria, and corrective actions associated with the following QC checks. Not all of these types are required for each method.

10.1.11.1 Blanks
10.1.11.2 Spikes
10.1.11.3 Calibrations
10.1.11.4 Interferences
10.1.11.5 Continuing calibration verification
10.1.11.6 Replicates
10.1.11.7 Duplicates
10.1.11.8 Collocated
10.1.11.9 Sampling media cleanliness criteria and checks

10.1.12 Calculations, data validation, and documentation
10.1.13 Data handling (transfer to LIMS) and retention
10.1.14 References
10.1.15 Revision history

10.2 SOP Changes

SOPs may be changed or updated as part of periodic SOP review or method modification. All changes are documented in the SOP revision history. All versions of SOPs are stored electronically on the NLB division drive.

10.2.1 SOP Review

SOPs should be reviewed on a periodic basis, but at least every three years to ensure that the policy and procedures remain current and appropriate.

10.2.2 Decimal Revision

Editorial corrections or administrative changes require the approval by management. The approved changes are designated by the "decimal" revision number (for example, Revision 1.0 replaced by Revision 1.1).

10.2.3 Cardinal Revision

Method modifications shall follow the process described in the Northern Laboratory Branch Guidelines for Modifications to Methods and Standard Operating Procedures (Appendix A). The approved modifications are designated by the "cardinal" revision number (for example, Revision 1.0 replaced by Revision 2.0).

10.3 Procedural modifications or deviations to an approved SOP may be necessary. In these cases, the changes to the SOP shall be approved by management and documented. Management is responsible to communicate SOP modifications and deviations to impacted staff.

10.3.1 One-time or temporary procedural modifications may not require a SOP revision. The proposed change must include how the modification will deviate from the SOP and what steps are taken to ensure that data quality objectives, quality control, and quality assurances are met. These modifications shall be documented in the analytical report.

10.3.2 Permanent modifications and deviations to SOPs will require a formal addendum. The addendum will be incorporated in the SOP at the next revision. Addendums and revised SOPs shall be approved by management and retained by LSS.

10.4 All original signed hardcopy versions of SOPs and addendums will be permanently archived in the NLB library maintained by LSS. Electronically secure copies of the original signed SOPs and addendums will be stored on the NLB shared drive.

11.0 ANALYTICAL QUANTITATION

Quantitation is an analytical procedure to accurately and reliably measure the smallest concentration of analytes in a sample by an analytical procedure.

11.1 Method Detection Limit (MDL)

The MDL, as found in Title 40 of the Code of Federal Regulations (CFR) Part 136, Appendix B, is defined as the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a

sample in a given matrix (including sampling media) containing the analyte." The MDL can be referred to as Limit of Detection (LOD).

The MDL must be calculated using spike concentrations one to five times the estimated MDL. The MDL should be calculated using Equations (1), (2), (3) and (4).

Equation (1) $MDL = T_{(n-1,1-\alpha=0.99)} \times s$

Equation (2) $m = \frac{1}{n}\sum_{i=1}^{n} x_i$

Equation (3) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - m)^2$

Equation (4) $s = \sqrt{s^2}$

Where :

n = number of replicates

$T_{(n-1,1-\alpha=0.99)}$ = Student t-value at 99% one-tailed confidence level (1-α) for n-1 degrees of freedom

x_i= value where i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots

m = sample mean

s^2 = variance of the sample mean

s = standard deviation of sample mean

It is recommended that a minimum of seven replicate determinations be used (n ≥ 7). At n = 7, T has a value of 3.143. For example:
Equation (5) MDL = 3.143 x s

When multiple instruments are used, MDLs are established for each instrument and each analyte, and the highest result from each MDL determination will be used to represent all of the instruments. This represents a pooled MDL.

11.2 MDL Determination and Verification Procedure

The procedure for determining MDL follows 40 CFR Part 136, Appendix B. MDL determinations are conducted when new methods are established, instruments are replaced, or other system changes occur. At least annually, MDL verifications are performed. For methods with large numbers of analytes, one calibration standard may be chosen to represent a class or group of similar analytes. The following procedure is used to calculate the MDL:

11.2.1 Based on data quality objectives, determine the appropriate calibration range and estimated MDL.

11.2.2 Calibrate using the same calibration range used for samples.

11.2.3 Prepare MDL spikes in the appropriate matrix at the concentration of the lowest calibration point and analyze seven replicates.

11.2.4 Determine the MDL using equation (1) based on the following criteria:

- 11.2.4.1 MDL is valid if both of the following acceptance criteria are met: MDL is less than spike concentration, and Spike concentration is greater than 5 times MDL
- 11.2.4.2 If the MDL acceptance criteria is not met, prepare MDL spikes at a different concentration to re-calculate a new MDL
- 11.2.4.3 Repeat these steps until the MDL acceptance criteria is met

MDL replicate spike recoveries should meet the DQO specified for the method detailed in the SOPs. Standards are sometimes not available at concentrations less than five times the MDL. In these cases, use the lowest available standard concentration to calculate the MDL.

11.3 MDL Determination with Low Level Interferences

Blank subtraction is not permitted for MDL determination or verification. Equation (5) referenced from the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air," (April 1984), Method T01, U.S. EPA Publication No. EPA-600/4-84-04, provides for the

consideration of analyte interferences at low levels and should be used where zero reagent blanks cannot be achieved.

Equation (6) $\mathrm{MDL} = \mathrm{A} + 3.3\,\mathrm{s}$

Where the MDL is in concentration units:

A = absolute value of the least squares intercept in terms of concentration

s = standard deviation, as calculated in section 11.1

11.4 Limit of Quantitation, Estimated Quantitation Limit, and Reporting Limit

The lower level where measurements become quantitatively meaningful is called the limit of quantitation (LOQ) and is defined as:

Equation (7) LOQ = 10 x s

s = standard deviation of the lowest standard

LOQ is analyte and instrument specific. When multiple instruments are used the pooled MDL is used to calculate the LOQ.

Results are not typically reported below the LOQ. Exceptions may be made based on the program and the client needs.

The estimated quantitation limit (EQL) is program specific and is approximately 5 to10 times the MDL. EQL can be used in place of LOQ.

Reporting Limit (RL) is used when the calculated LOQ is not appropriate to meet regulatory requirements or method specific DQOs. Reporting limits will be approved by the laboratory supervisor.

11.5 Calibration

Specific requirements of calibration should be clearly outlined within each SOP. In general, calibrations should be performed at least daily prior to analysis. More frequent calibration may be necessary for some methods, but these are noted in the method SOP.

Daily calibrations may be "single point" or "multipoint" (multipoint is three or more concentration levels as defined in the method SOP) calibrations, depending on the data quality objectives and the needs of the program. The multipoint calibration standards should bracket the expected concentrations of the majority of the samples. Linear multipoint calibrations must have a correlation coefficient, r, of '0.98' or better. Nonlinear multipoint calibrations should use a higher order curve.

11.6 Analytical Range

The minimum analytical range is up to the highest standard of the calibration curve. If the sample concentration exceeds the analytical range by more than 10% of the highest standard, samples should be diluted into the appropriate calibration range. The analytical range may be extended beyond the calibration curve where the linear range has been documented.

12.0 QUALITY CONTROL (QC)

Following is recommended QC for NLB methodology. The SOPs may contain specific criteria for these requirements. When criteria is not met, corrective actions must be taken as described in the sections below or the method specific SOP.

12.1 Analytical Sequence

The sequence of analysis should be detailed in the SOP. The following is an example of an analytical sequence with a maximum of ten samples between control standards and check samples:

12.1.1 System Blank
12.1.2 Calibration
12.1.3 Control Standard
12.1.4 Samples (includes blanks and spikes where applicable)
12.1.5 Replicate/Duplicate
12.1.6 Check Standard (CCV or Control Standard as specified in SOP)

Steps 12.3.3-12.3.6 may be repeated for additional samples in a batch as long as controls remain within specifications.

12.2 Blanks

12.2.1 Laboratory Blanks

Laboratory blanks are used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations and the general laboratory environment. The individual SOPs shall describe the preparation and analytical frequency of laboratory blanks.

System blanks are laboratory blanks used to verify that the analytical system will not produce a result higher than the LOQ or RL due to system contamination from high concentration samples or laboratory sources. The system blank (reagent, gas, etc.) to be used for each method is specified in the method SOP.

12.2.2 Blank Corrective Action Criteria

If the blank result is less than the LOQ or RL, then no action should be taken.

Background subtraction of blanks is allowed where specified in method SOPs.

Where background correction is not specified in the SOP and the blank result is greater than the LOQ or RL, the following apply:

12.2.2.1 When the sample results are at least ten times higher than the blank result, no action is taken.

12.2.2.2 When the sample results are less than ten times higher than the blank result, the analysis result should be invalidated for those samples associated with the blank; the cause shall be investigated and a blank and samples may be re-extracted and analyzed, if sample is available.

12.2.3 Trip and Field Blanks

Trip and field blanks are used to assess contamination during transport and handling of samples. Any trip or field blank result that is greater than the LOQ or RL shall be verified by the analyst. The results of the trip and field blanks shall be reported with the sample results. The data user will determine if associated sample results are impacted.

12.3 Control Standards and Control Charts

Control limits demonstrate statistical evidence that the analytical system is in control and shall be determined for each analytical instrument.

When available, the control standards shall be prepared from a separate source (different manufacturer or different lot) than the primary standard used to prepare the calibration curve. Control standards should be analyzed directly prior to the analysis of samples (see analytical sequence above).

The initial warning and control limits shall be set at ±8 and ±10 Relative Percentage Difference (RPD) respectively from the target value. Once a minimum of 20 control standard results are obtained, the limits for tolerance of the control results around the mean should be set as follows:

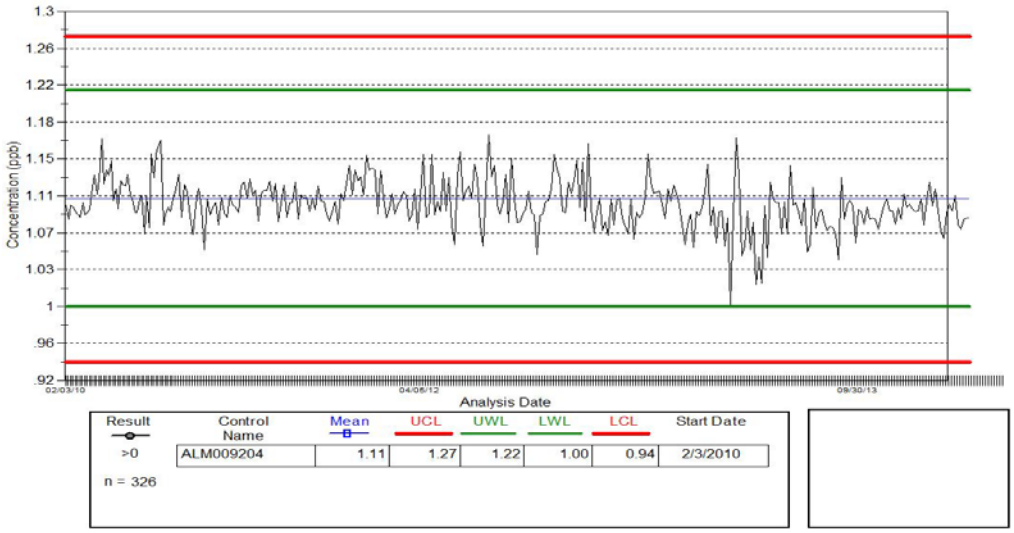
UCL [Upper Control Limit] = +3s of the Mean Value
UWL [Upper Warning Limit] = +2s of the Mean Value

Mean Value

LWL [Lower Warning Limit] = -2s of the Mean Value
LCL [Lower Control Limit] = -3s of the Mean Value

where "s" is the standard deviation of the measurement of the control standard.

Figure 12.1 Example Control Chart



When adjustments to the control limits are needed, the changes must be clearly documented and reviewed by management.

In the event that the instrument method measurement capabilities greatly exceed the sampling method capabilities for precision, the control limits should be set such that the precision of the samples is not falsely represented. Such a case is where the multiple analyses of a standard reference material, which has been modified to closely match the average sample matrix, yields an unrealistically low standard deviation in comparison to anticipated actual sample deviation. The DQOs should be carefully reviewed, and the control limits established to reflect this. However, control limits should not exceed ±10 RPD under these conditions. In such cases, an assigned standard deviation should be back-calculated based on the assigned RPD, and used for establishing the control limits. Any limits set by the analyst should be approved by management and should be documented.

Control standard results shall be reviewed and plotted with each analytical sequence. Should any analysis of a control standard yield a result which falls outside the control limits, the analyst shall restart the analytical sequence. If the control or check standard following a set of samples is outside the control limit, then the sample results are invalid. Take action to bring the system back into control and repeat the sample analyses. Each set of no more than ten samples shall be bracketed by successful control or check standards.

Control charts should be reviewed for trends at least quarterly. Three consecutive control standards falling between the warning and control limits require investigation and corrective action as follows:

12.3.1. Investigate the cause of the warning exceedance
12.3.2. Recommend corrective action
12.3.3. Notify management for approval
12.3.4. Take corrective action and document

12.4 Duplicate/Replicate Analysis

A replicate sample analysis refers to the reanalysis of the same sample extract. A duplicate sample analysis refers to the separate analysis of a distinct extract or aliquot derived from the same sample.

At least one out of every ten samples is randomly designated as the replicate or duplicate sample. In the case of LIMS generated sample list, LIMS defined duplicates are generated for ten percent of total samples within the analytical set.

An evaluation of the duplicate/replicate pairs shall be made with every sample set using one of the equations below.

Equation (8) $$\mathrm{RPD} = \frac{(Y - X)}{(Y + X)/2} \times 100$$

Where:

RPD = Relative Percent Difference

X = the sample result

Y = the duplicate/replicate result

The RPD may be taken as an absolute value.

Equation (9) AD = I(Y – X)I

AD = Absolute Difference

Duplicate/replicate results and the corresponding RPD or AD should be documented. The duplicate/replicate acceptance criteria are specified in the method SOPs. If the duplicate results do not meet specified QC criteria, the samples in the associated batch should be re-analyzed, or invalidated if re-analysis is not possible. Duplicate/replicate concentration values less than five times the LOQ or RL may not be considered when evaluating for the RPD criteria in accordance with regulatory or programmatic requirements.

12.5 Check Standard

Check standards (also referred to as Continuing Calibration Verification standard) are prepared from the reference material used for calibration standards at a point within the calibration curve. Check standards should be analyzed after a maximum of 10 samples, at the end of the analytical run, and whenever the analysis sequence is interrupted. The check standard acceptance criteria shall be within $\pm$ 20 percent of the expected value unless specified within the SOP. In some cases, the analysis of the check standard may be replaced by the analysis of the control standard.

If the control or check standard following a set of samples is outside acceptable limits, the sample results are invalid. Take action to bring the system back into control and repeat the sample analyses. Each set of no more than ten samples shall be bracketed by successful control or check standards.

12.6 Analytical Cleanliness Check for Sample Media (Contamination Check)

Sampling media must be checked for cleanliness prior to being sent to the field for sampling. This includes canisters, filters, sorbent tubes, and any other collection media. Background levels in the sampling media must be below the method's LOQ or RL. SOPs will describe the frequency (e.g. lot, batch, etc.) of cleanliness checks.

12.7 Spikes

The laboratory may analyze various spikes consisting of laboratory, field, trip, or matrix spikes. Spike recoveries provide information about laboratory performance, sample handling, and matrix effects. Spike results are documented and reported with sample results. Spike requirements and recovery criteria are specified in the SOPs.

12.8 Standard Additions (SA) and Internal Standards

SA is a method to determine the amount of analyte in an unknown or in a complex matrix that must behave similar to the target analyte. SA can be applied to most analytical techniques and is used instead of a calibration curve to solve a matrix effect problem. In SA, known quantities of analyte are added to an unknown and the analyte concentration is determined from the increase in instrumental signal.

An internal standard is a known amount of a compound, different from the analyte, added to the unknown sample. Internal standards are used when the detector response varies slightly from run to run because of hard to control parameters. Even if the absolute response varies, as long as the relative response of analyte and standard is the same, the analyte concentration can be determined.

12.9 Collocated Calculations

NLB analyzes collocated samples and only calculates RPD upon request where both sample results are more than five times the LOQ or RL. If RPD is outside acceptable limits for the method, results should be verified. If results are correct, ARB's Air Quality Surveillance Branch (AQSB) or local districts are notified to investigate and perform corrective action as needed on sampling equipment.

12.10 Audits

Performance and technical system audits are important in order to assess the quality of the data generated. The analysis of performance audit materials must follow the same procedures as the analysis of regular samples, where possible. Audit results are documented in LIMS. Audit samples are typically provided by LSS, QMB, and U.S. EPA.

13.0 SAMPLE MANAGEMENT

Sample management is the ability to effectively and efficiently get sample media to and from the laboratory and field, while maintaining all regulatory and hold time requirements, in addition to maintaining sample integrity and providing sample security and tracking capabilities. Sample management includes: sample receipt, chain of custody, sample control, sample tracking, log-in, validation, storage, and archive. Refer to the appropriate SOP for shipping, receiving, and sample handling requirements.

13.1 Sample Receipt

Samples are shipped and received multiple ways between field locations and the laboratory. To ensure the samples are received by the appropriate entity, documentation is required that clearly indicates the dates, times, and individuals that have taken custody of the sample media.

13.1.1. All samples shall be received in the designated sample control area/sample receiving room.

13.1.2. Samples shipped or delivered the following ways will be stamped or notated with the date and time received by staff, then routed to the specified sample receiving room or sample control location:

13.1.2.1. Via regular mail
13.1.2.2. Via stockroom pick-up or delivery by a shipping company
13.1.2.3. Via delivery in person

13.1.3. All samples received shall be stored per the SOP in designated locations in the laboratory (e.g. freezer, refrigerator, or dry storage).

13.2 Chain of Custody (COC)/Sample Control

COC is an accurate written record that tracks the possession, transfer, handling, and location of samples from sample media preparation to sample collection, including sample receipt, to reporting. The COC is an important function of sample control and an integral part of sample receipt.

All samples shall be accompanied by a properly completed COC. If not, laboratory staff may not accept samples depending on the program. If samples are accepted, they will be stored appropriately in the specified sample receiving area but may not be processed until a completed COC is received.

Laboratory staff shall sign and date the COC indicating the laboratory has received the sample and is now responsible for sample control and custody.

All completed, signed, and dated COCs shall be stored and archived appropriately according to program needs or requirements.

13.3 Sample Validation

Once a completed COC has been received and reviewed, the overall sample quality and condition must be compared to the criteria required for validation by regulatory program, SOP, and/or management. Sample validity status may change while under laboratory control.

Laboratory staff shall contact site operators, or other appropriate staff, directly when issues arise that require clarification of information to validate a sample at log-in, when a sample is invalidated, or when a make-up sample is recommended. This notification is performed as soon as possible, and the issue is documented on the COC or sample report form.

13.4 Sample Login

A LIMS generated number or other unique identification number (barcode) must be given to all samples prior to analysis or preparation. Pertinent information from the COC is entered into LIMS during the login process.

The LIMS number and/or barcode assigned to a sample must appear on all associated documentation, such as the COC, sample report form, the sample folder, LIMS, and any laboratory worksheet associated with the sample.

13.5 Sample Storage

Once the samples are logged into LIMS, the samples are stored under SOP-specific conditions (e.g. ambient, refrigerator, freezer) in the appropriate laboratory. Documentation regarding the storage and transfer of samples is maintained in the laboratory and/or sample receiving room.

13.6 Sample Tracking

The sample transfer within the laboratories shall be recorded using sample custody logbooks, COC, and/or LIMS, and shall include the date the samples were transferred, the initials of the person handling the transfer, and the location of the sample.

13.7 Archive, Storage, and Disposal

13.7.1 Samples and sample containers that are not consumed during analysis shall be appropriately stored according to the SOP requirements, returned to the client, or disposed of appropriately.

13.7.2 Sample documentation including COC, logbooks, sample tracking, etc. should be maintained following ARB's records retention policy unless stricter requirements are specified in the SOP or by regulation.

13.7.3 Samples and sample containers exceeding specified holding or retention times may be disposed of properly with the approval of management.

14.0 DATA MANAGEMENT

Data management describes the basic flow of analytical data from generation, review (verification and validation), and reporting. Laboratory staff and management are all integral parts of data management. The laboratory utilizes a laboratory information management system (LIMS) database to perform data management activities.

14.1 LIMS

LIMS facilitates the recording, verification and validation, transmittal, reduction, analysis, management, storage, retrieval, and reporting of analytical data generated by the laboratory. LIMS is maintained by the LIMS administrator.

LIMS administrator creates and/or modifies approved laboratory staff access to LIMS; creates and modifies LIMS methods, data templates and transfers, and data reports; and is able to modify data in LIMS.

All sample and analysis information shall be entered into LIMS or recorded in bound or electronic notebooks. Changes to any data in LIMS must be made by authorized individuals only. Management's approval may be required.

14.2 LIMS Accessibility

All users must be authorized by management and receive a password to logon to LIMS. Different privileges are given to authorized users depending on need.

LIMS users consist of the laboratory staff that has approved access to their programs and data. They are able to log-in, transfer, modify data, and/or run reports in order to validate data generated. Access may include:

14.2.1 Read-only
14.2.2 Addition of analyses
14.2.3 Data entry and modification of preliminary data
14.2.4 Data reporting
14.2.5 Data administration
14.2.6 Data upload

14.3 LIMS Generated Reports

LIMS can be accessed to generate many different report types. They include worklists, data summaries of all varieties, and reformatted reports that can be applied to other applications (e.g. upload to another database such as AQS). Staff use worklists to schedule their sample analyses (e.g. sample hold times, inventory, etc.). Summary reports range from output that displays recently logged-in samples to a complete list of finalized data and results. Staff can also open a LIMS generated file in Excel and perform further calculations and formatting. Reports can be viewed on screen, sent to a printer, or output to PDF, HTML, or Excel.

14.4 Initial Data Assessment

Samples are analyzed and the instrument QC results are reviewed by the analyst to decide if sample analysis is valid prior to transfer into LIMS. Corrective action should be taken as needed when QC criteria are not met, such as re-analysis, dilution, re-integration, etc.

Any sample result that has been invalidated must be reported as "invalid" or “not analyzed,” and its respective reason documented.

All results reported as "not detected" must be associated with a reference value, such as LOQ, estimated quantitation limit (EQL), or minimum reporting value.

Laboratory staff will contact site operators, or other appropriate staff, directly when issues arise that require clarification of information to validate a sample at log-in, when a sample is invalidated, or when a make-up sample is recommended. This notification is performed as soon as possible, and the

issue is documented on the COC or sample report form according to established laboratory procedures. If invalidated samples occur repeatedly and are deemed by management to be indicative of a systemic issue, management will utilize the Corrective Action Notification (CAN) process to initiate a formal corrective action process in order to inform all responsible and impacted parties; document the issue and resolution; and prevent potential future data loss. If a CAN is deemed unnecessary, management will document how the issue has been resolved and what other parties were notified of the issue.

14.5 Data Transfer to LIMS

Data from the analytical system is transferred to LIMS manually or electronically. Instrument to LIMS transfers should be verified by the analyst.

In management-approved special situations where LIMS transfer and storage is not possible the data must be electronically stored in an appropriate file on the NLB shared drive. All raw data should be archived appropriately.

14.5.1 Data Analysis Records

14.5.1.1 All raw data, calculations, observations, validation information, and results generated by the analyst must be placed in an appropriate computer file, bound or electronic laboratory notebook, or other approved format. For bound notebooks, all entries must be initialed and dated by the analyst.

14.5.1.2 Modifications to raw data, (e.g. re-integrations of chromatographic peaks) must be documented. Original data and modified data must be maintained for review.

14.5.1.3 All analysis hardcopies must be stored in an appropriate filing system until archiving.

14.5.1.4 Any raw analytical data stored on a computer hard drive should be routinely backed up. A backup copy of all instrument software, including NLB developed parameters, should be made after the initial development.

14.5.1.5 An instrument maintenance logbook must be assigned to each instrument. All calls for service, repair records, reconfigurations, or changes to the instrument operating parameters must be recorded, dated, and signed by the analyst or instrument service representative. The logbook must be kept with the instrument and be available for inspection at any time.

14.6 Analytical Data Reports

Analytical data reports are generated by the analyst and submitted for review/approval after initial data assessment and transfer to LIMS in order to verify and validate the data. At a minimum, the following must be included in the data package:

14.6.1. Method, program, or project name
14.6.2. Signature and date blocks (staff and management).
14.6.3. Timeframe or batch of analyses covered
14.6.4. Data with comments and flags
14.6.5. Copies of appropriate logbook pages (e.g. extraction logs)
14.6.6. Analytical run sequence
14.6.7. Calibrations
14.6.8. QC results
14.6.9. Control charts
14.6.10. Description of unusual occurrences with samples, analysis, and/or data
14.6.11. Corrective actions taken
14.6.12. Any deviations from approved SOP

14.7 LIMS Verification and Validation

LIMS has been programmed to automatically verify and validate data entered into the database. Any data outside QC criteria is highlighted for analyst, peer, and management review and comment. QC parameters programmed into LIMS come from federal regulations, QCM, and SOPs. All programming has been tested and verified by the LIMS administrator.

14.8 Data Review and Approval

The data review and approval process consists of a series of checks to ensure the analytical data generated by the laboratory and transferred to

LIMS meets all the method specific QC criteria. The multistep process includes, at a minimum, analyst and peer review followed by management review and approval prior to submittal to clients. All levels of review and approval are initialed and dated on the cover page of the data package.

14.8.1 Analyst Review

In addition to the Section 14.4, the following items will be documented and verified by the analyst that performed the extractions and sample analyses as required by the method SOP:

14.8.1.1. Extraction solvents and volumes
14.8.1.2. Instrument conditions
14.8.1.3. Analytical run conducted per SOP
14.8.1.4. Expiration dates of standards
14.8.1.5. Retention times
14.8.1.6. Integrations
14.8.1.7. Peak identifications
14.8.1.8. Analytical sequences
14.8.1.9. Environmental conditions
14.8.1.10. QC (such as MDLs, duplicates, standards, blanks, controls)
14.8.1.11. Data reduction and calculations
14.8.1.12. COC data login to LIMS
14.8.1.13. Raw data concentrations transferred to LIMS
14.8.1.14. Holding times
14.8.1.15. Calibrations
14.8.1.16. Parameters of SOP and QC manual are met
14.8.1.17. Anomalies and corrective actions are documented and management notified, as necessary

14.8.2 Peer Review

The following items will be verified by a second analyst:

14.8.2.1. Data package completeness
14.8.2.2. Spot-check calculations
14.8.2.3. Check for documentation of unusual events
14.8.2.4. Corrective action review
14.8.2.5. Check for outliers
14.8.2.6. Analytical run sequence

14.8.2.7. Dilutions performed as necessary
14.8.2.8. QC (such as MDLs, duplicates, standards, blanks, controls)
14.8.2.9. Expiration dates of standards
14.8.2.10. Reasons for invalid samples
14.8.2.11. Flags and comments
14.8.2.12. Parameters of SOP and QC manual are met

If necessary, data package will be returned to the analyst for edits or clarification. After corrections are made the data package will be returned to the peer reviewer for confirmation. Once peer review is complete, the peer reviewer signs and/or initials, and dates the analytical data package.

14.8.3 Management Review and Approval

The following will be reviewed by management prior to data release:

14.8.3.1. Data package completeness
14.8.3.2. Spot-check calculations
14.8.3.3. Check for documentation of unusual events
14.8.3.4. Corrective action review
14.8.3.5. Check for outliers
14.8.3.6. Analytical run sequence
14.8.3.7. QC (such as MDLs, duplicates, standards, blanks, controls)
14.8.3.8. Expiration dates of standards
14.8.3.9. Reasons for invalid samples
14.8.3.10. Flags and comments
14.8.3.11. Check for analyst and peer review
14.8.3.12. Parameters of SOP and QC manual are met

If necessary, data package will be returned to the analyst for edits or clarification. After corrections are made, the data package will be returned to management for confirmation. Once review is complete, management signs and/or initials and dates the analytical data package.

14.9 Data Release and Reporting

Data generated by the laboratory shall go through the defined data review and approval process prior to release and reporting to clients.

During the review and approval process, the data files in LIMS are locked to ensure that data cannot be changed without proper management authorization. Data in LIMS can still be viewed (Read Only) by management and laboratory staff. If changes to finalized data are made, the full review and approval process shall be conducted to amend the data report. The approved data reports are provided to management, who sends the hardcopy and/or electronic data report to the client or the client's representative.

14.10 Amendment to Data

Finalized and approved data may be amended in LIMS per management approval. After the request is approved, laboratory staff and management must follow the data review and approval process. If changes to finalized data are made, the client must be notified and sent a revised report. Data may be amended for reasons such as CANs, AQDAs, requests by clients (i.e. requests to exclude codes), etc.

14.11 Data Archive

All final hardcopy reports with the analyst review, peer review, and management approval signatures shall be filed in a secure manner. Access to hardcopy and LIMS files shall be limited to authorized individuals only. Laboratory retention of hardcopy and electronic LIMS data files shall follow ARB or regulatory retention policies. Final archiving and/or destruction of all data reports shall be approved by management.

14.12 Significant Figures and Rounding Rules

When a measured or calculated quantity is written down, some indication of the precision of the measurement must be given. This is shown by designating the number of significant figures in a result and gives an indication of the confidence with which the number is known. The greater the number of significant figures, the smaller the uncertainty and the greater the precision in its measurement. Data should be rounded to the number of figures consistent with the confidence that can be placed in it.

Unless defined by the client or regulatory program, rounding shall be deferred until all calculations have been made. The final result shall contain no more significant figures than the lowest number of significant figures (least precise) of the values used in the calculations.

Example: 14.80 X 12.10 X 5.05 = 904.*354000* = 904
4 sig figs X 4 sig figs X 3 sig figs = 3 sig figs

14.12.1 All nonzero digits are significant (i.e., 4.006, 12.012, and 10.070).
14.12.2 Zeros placed between nonzero digits are significant (i.e., 4.006, 12.012, and 10.070).
14.12.3 Zeros at the end of a number to the right of the decimal point are significant (i.e., 10.070).
14.12.4 Zeros to the left of the first nonzero digit are not significant. They simply locate the decimal point. (0.0002 has only one significant figure, 0.000020 has two significant figures)
14.12.5 When rounding to correct the significant figures the rule is to increase the final digit by one unit if the digit dropped is greater than five and to leave the final digit unchanged if the digit dropped is less than five. If the digit dropped is five, the final remaining digit is increased by one unit if necessary to make it even otherwise it is left unchanged.

Example: For 3 significant figures:
15.56 rounds off to 15.6
15.54 rounds off to 15.5
15.55 rounds off to 15.6
15.45 rounds off to 15.4

Reference: www.epa.gov/wed/pages/isirf/EP01Final.pdf, EPA Rounding Off/Significant Figure Rules.

15.0 QUALITY CONTROL REPORTS

Quality Control Reports are prepared by each section on an annual basis. The Quality Control Report documents and summarizes the QC activities and measurements associated with each analytical method. QC activities and criteria are outlined in this document and specific method SOP. Quality Control Reports should contain a brief description of each QC parameter as it pertains to the analytical methods and all corrective actions taken during the inclusive time period.

Quality Control Reports should include:

15.1. Introduction
15.2. Blanks
15.3. Calibration and Standards
15.4. Controls
15.5. Replicates/Duplicates
15.6. Spikes
15.7. Limits of Detection and Limits of Quantitation
15.8. Instrument Cross-Checks
15.9. Sample Holding Time Checks
15.10. Confirmations
15.11. Crossover Compounds
15.12. Sample Collection Irregularities and Collocated Results
15.13. Instrument Maintenance and Modification Summary
15.14. Summary of Departures from Current Method and SOP
15.15. Audits and Round-Robins (Check Samples)

16.0 CONFIDENTIAL INFORMATION

NLB has established procedures under California Law for handling information that has been designated as confidential, proprietary, or trade secrets. These procedures are maintained by SAS.

All designated "CONFIDENTIAL INFORMATION" must be maintained in a locked file cabinet in a secure area. Access to this file cabinet is subject to management approval.

17.0 HAZARDOUS MATERIAL AND WASTE MANAGEMENT

All laboratory activities involving the direct or indirect handling of hazardous material or hazardous waste must comply with all federal, State, and local regulations to ensure the safety and quality of the laboratory and the environment. All staff must be familiar with and comply with the MLD Chemical Hygiene Plan and receive required training. The designated hazardous waste coordinator shall oversee all hazardous waste operations.

18.0 REFERENCES

18.1 Anderson, Robert L., Practical Statistics for Analytical Chemists, Van Nostrand Reinhold Company Inc., 1987.

18.2 Taylor, John Keenan, Quality Assurance of Chemical Measurements, Lewis Publishers, 1987

18.3 Wisconsin Department of Natural Resources Laboratory Certification Program, "Analytical Detection Limit Guidance and Laboratory Guide for Determining Method Detection Limits," PUBL-TS-056-96, April 1996.

18.4 California Environmental Protection Agency, Air Resources Board, "Quality Management Plan for Air Quality Monitoring," July 2013.

18.5 California Environmental Protection Agency, Air Resources Board, "Chemical Hygiene Plan," July 2, 2002.

18.6 U.S. EPA Office of Air Quality Planning and Standards, Air Quality Assessment Division, "QA Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program," EPA-454/B-13-003, May 2013.

18.7 U.S. EPA Office of Environmental Information, "Guidance for Preparing Standard Operating Procedures EPA QA/G-6," EPA/600/B-07/001, April 2007.

19.0 REVISION HISTORY

Version	Effective Date	Primary Changes
1.0	1993	N/A
2.4	June 2001	Unknown
3.0	September 2015	Updates to improve data quality and define corrective actions; address US EPA Technical System Audit findings

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Appendix: Northern Laboratory Method Modification Procedures

MAILED
12/30/13 DP

Air Resources Board

Mary D. Nichols, Chairman
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Sacramento, California 95812 • www.arb.ca.gov

Matthew Rodriquez
Secretary for Environmental Protection

Edmund G. Brown Jr.
Governor

TO: Michael Miguel, Chief
Quality Management Branch

Cindy Castronovo, Chief
Northern Laboratory Branch

FROM: Michael Benjamin, Chief
Monitoring and Laboratory Division

DATE: December 20, 2013

SUBJECT: NORTHERN LABORATORY METHOD MODIFICATION PROCEDURES

Thank you for the opportunity to discuss the proposed Northern Laboratory Branch (NLB) method modification procedures and guidelines. I approve the proposed guidelines and procedures as recommended by the chiefs of the Quality Management Branch (QMB) and NLB to replace the Memorandum of Understanding referenced in the November 27, 1996 memo (Attachment A of the proposed guidelines).

cc: Jeff Wright
Donald Hammond
Michael Werst
Kathy Gill
Russell Grace

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: http://www.arb.ca.gov.

California Environmental Protection Agency

MAILED
12/16/13 DP

Air Resources Board

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Matthew Rodriquez
Secretary for
Environmental Protection

Edmund G. Brown Jr.
Governor

TO: Michael Benjamin, Chief
Monitoring and Laboratory Division

FROM: Michael Miguel, Chief
Quality Management Branch

Cindy Castronovo, Chief
Northern Laboratory Branch

DATE: December 13, 2013

SUBJECT: NORTHERN LABORATORY METHOD MODIFICATION PROCEDURES

Please find attached Monitoring and Laboratory Division (MLD) guidelines and procedures defining a new process to review and approve changes to laboratory methods and standard operating procedures (SOP). These guidelines and procedures are recommended for approval by the chiefs of the Quality Management Branch (QMB) and the Northern Laboratory Branch (NLB) to replace the Memorandum of Understanding referenced in the November 27, 1996 memo (Attachment A of the proposed guidelines).

The proposed MLD guidelines and procedures were developed jointly by NLB and QMB staff to reflect changes in MLD roles and responsibilities, as well as advances in laboratory standard practices over the last 16 years. The guidelines draw substantially from established organizations such as the U.S. Environmental Protection Agency and The NELAC Institute.

We request your review and approval of the proposed guidelines and procedures.

Attachments

cc: Jeff Wright
Donald Hammond
Michael Werst
Kathy Gill
Russell Grace

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: http://www.arb.ca.gov.

California Environmental Protection Agency

NORTHERN LABORATORY BRANCH GUIDELINES

FOR MODIFICATIONS TO METHODS AND STANDARD OPERATING PROCEDURES

1. Introduction

These guidelines describe the process for proposing, reviewing, and approving modifications to the Northern Laboratory Branch's (NLB) analytical methods and associated revisions to standard operating procedures (SOP). This document supersedes the requirements described in the November 27, 1996, memorandum to Bill Loscutoff entitled "Laboratory Method Modification Procedures" (Attachment A) but still maintains the three original goals of the process: 1) to identify and quantify any significant bias caused by changing a method, 2) inform the Division Chief of this bias while seeking approval to change methods prior to its implementation, and 3) provide data users with information regarding the method change impacts on the trend.

U.S. Environmental Protection Agency (U.S. EPA) has allowed flexibility in alternatives to reference test methods as long as specified performance criteria are achieved. This is commonly known as the "performance-based" methods approach. U.S. EPA has used this method approach for wastewater treatment (revised 40 CFR 136.6, "Method modifications and analytical requirements," May 18, 2012). Section 9 of the May 2013 revision of the Quality Assurance Handbook for Air Pollution Measurement Systems states that "The PAMS, NATTS and CSN networks follow the performance based measurement process paradigm."

In the federal rule, "equivalent performance" means that the modified method produces results that meet or exceed the quality control (QC) acceptance criteria of the approved method. These guidelines provide several QC elements that should be incorporated in all SOPs where applicable (Attachment B).

However, meeting quality control and assessment elements does not mean that a method change will not produce a shift or bias in the data. Ambient air trends are an important assessment tool in the evaluation of emission control programs. The documentation of any method change that results in a significant bias of any target analyte may be important for clients that are examining air quality trends, assessing regulatory impacts, and/or assessing health risks.

These guidelines describe an approval and notification process for proposed modifications to existing laboratory methods.

2. Method Modification Requests

A written request describing the proposed method modification evaluation will be routed through the section manager and approved by NLB Chief in advance of conducting the evaluation of the proposed method modification. Any proposed change in equipment and materials or analytical process of a method is considered a method modification. Acceptable reasons to propose a method modification include analytical practices that lower detection limits, improve precision and/or accuracy, reduce interferences, lower laboratory costs, or reduce generation of laboratory waste. If approved by NLB Chief, the statistical test for bias is initiated.

3. Process for Bias Statistical Tests

Upon approval of NLB Chief, the laboratory will conduct a comparison test between the existing method and the proposed method to generate paired data for the bias statistical analysis. NLB will strive to obtain as many paired samples as practically possible (30 or more is ideal), but will obtain a minimum of 20 paired results to be used in the assessment of bias and apply the student t-test as described in Attachment C. The significance level (alpha) will be 0.05. The laboratory will attempt to identify real samples that contain target analytes that are of sufficient concentration to be measured at or above the Limit of Quantitation (LOQ). If a sufficient number of samples can't be found during the testing period that meet this criteria, then the laboratory will prepare appropriate spikes to elevate target analytes to meet or exceed the LOQ.

Insignificant Bias

If the analysis indicates no statistically significant bias between the existing and the proposed methods, then the laboratory may incorporate the method changes in an SOP revision. The QC criteria listed in Attachment B should be applied where applicable to the new SOP; and all new performance tests with respect to the method's accuracy, precision, and sensitivity will be reported in the quality control report. The revised SOP will be approved and signed by NLB Chief prior to use on samples that will be reported as data for record. Since the analysis has demonstrated no statistically significant bias, there is no requirement to notify QMB or the Division Chief of the change other than documenting the change in the quality control report.

Significant Bias

If the results of the comparison test show that a statistically significant bias exists between the existing method and the proposed method, and NLB wishes to continue with the method change proposal, then the bias will be documented in a formal report

and presented to the Division Chief for approval prior to initiating a method change. Before finalizing the report, NLB will share the draft report, which will include all comparison tests, with QMB. QMB will review the draft report and provide any comments, including any recommendations for additional tests, within 20 business days.

Based on the QMB comments, the laboratory section manager will decide whether further studies are needed, contact the client(s) for their input on data quality objectives, submit the proposed method for approval, or discontinue the method change.

If the laboratory section manager decides to proceed with the method modification, a draft report, which includes responses to QMB comments, and proposed SOP are provided to NLB Chief for review and approval.

Upon approval, NLB Chief will prepare a memorandum to present the proposed method change to the Division Chief for approval and/or direction. The memorandum will present the following:

1. the proposed method's accuracy, precision, sensitivity (limit of detection), and bias.
2. reason for the change.
3. consequences if the method change is not implemented.

Upon approval to the method change by the MLD Chief, a memorandum from the laboratory manager will be sent to the client(s) of the SOP modification, the effective date of the revised SOP, and estimated bias from changing to the new method.

4. Expedited Method Modifications

The MLD Chief may authorize use of modified SOPs in the event that unforeseen and compelling circumstances do not allow the process described above to be completed. The MLD Chief may also authorize modifications to the method concurrent with the comparison studies. NLB's justification for requesting such action will be documented.

Attachment A

November 27, 1996, memo to Bill Loscutoff entitled

"Laboratory Method Modification Procedures"

Attachment B

Recommended Quality Control Elements

1. Method detection limit (MDL) and linearity check (if one-point daily calibrations are used)
2. Laboratory reagent blank (aka method blank)
3. Control run (aka spiked blank) with control charts
4. Matrix spike (if applicable)
5. Calibration verification (using NIST traceable standard if available)
6. Continuing calibration verification (periodic checks on a daily run)
7. Replicate sample runs (precision check)
8. Predetermined corrective action
9. Instrument cross-checks (if more than one instrument is used)
10. Periodic confirmations (use of an alternative methodology or check samples analyzed by an outside laboratory)
11. QC acceptance criteria for all quality assessments
12. Minimum frequency of conducting QC elements

Attachment C

Statistical Test for Bias Determination

The paired student t-test is applied to the data set of at least 20 samples performed by the same analyst using the existing method and the proposed method. The null hypothesis is that there is no significant difference between the data sets, so the test is to see if the mean of the differences between the data deviates significantly from zero. The two-sided test is used as it is not known in advance whether the proposed method will give higher or lower results, if a bias is present.

The equations presented below are taken from Section 5.2.4 of "Practical Statistics for Analytical Chemists" by Robert L. Anderson (1987).

$$t = \frac{\bar{d}}{s_d}\sqrt{n} \ ; \text{df} = n - 1$$

Where:

$$s_d = \sqrt{\frac{\sum d^2 - \frac{(\sum d)^2}{n}}{n-1}}$$

d = the difference in each pair of values

$\bar{d}$ = the absolute value of the average difference in the pairs of values.

n = the number of pairs of values

df = degrees of freedom associated with t

s_d = standard deviation of the differences between the pairs of observations

In the following example, the manual method of weighing PM2.5 filters is compared to an automated filter weighing system. Twenty-two filters were weighed by both methods, giving 21 degrees of freedom. The critical value of t for 95% confidence (α = 0.5) is 2.08. As can be seen, the calculated t value is less than the critical value (1.05 < 2.08), so the null hypothesis holds and there is no significant bias between the existing and the proposed methods.

Table 1
Comparison Results between Manual XP6 and Robot F-A747
Whatman PM2.5 Pre-Weight Filters
22 Comparison Pairs

Barcode	Manual XP6 (mg)	Robot F-A747 (mg)	d	d^2
TF000171	140.421	140.4200	0.001	0.000001
TF000172	138.799	138.7980	0.001	0.000001
TF000173	140.074	140.0730	0.001	0.000001
TF000174	139.584	139.5860	-0.002	0.000004
TF000175	139.226	139.2260	0.000	0.000000
TF000176	142.704	142.7040	0.000	0.000000
TF000177	140.889	140.8900	-0.001	0.000001
TF000178	141.170	141.1660	0.004	0.000016
TF000179	139.054	139.0570	-0.003	0.000009
TF000180	138.327	138.3270	0.000	0.000000
TF000179D	139.056	139.0580	-0.002	0.000004
TF000191	149.057	149.0560	0.001	0.000001
TF000192	148.579	148.5790	0.000	0.000000
TF000193	148.648	148.6460	0.002	0.000004
TF000194	147.462	147.4630	-0.001	0.000001
TF000195	147.042	147.0430	-0.001	0.000001
TF000196	145.569	145.5710	-0.002	0.000004
TF000197	147.136	147.1380	-0.002	0.000004
TF000198	146.588	146.5900	-0.002	0.000004
TF000199	145.838	145.8390	-0.001	0.000001
TF000200	146.768	146.7690	-0.001	0.000001
TF000199D	145.840	145.8400	0.000	0.000000
		Total	**-0.008**	**0.000058**
		Avg(d)	**0.0003636**	
		n	**22**	
		df	**21**	
		s_d	**0.0016197**	
		t	**1.0530484**	
		$t_{0.05/2,21}$	**2.08**	

Table 2

Critical Values for Student T-Test

Significance level = α

Degrees of Freedom	.005 (1-tail) .01 (2-tails)	.01 (1-tail) .02 (2-tails)	.025 (1-tail) .05 (2-tails)	.05 (1-tail) .10 (2-tails)	.10 (1-tail) .20 (2-tails)	.25 (1-tail) .50 (2-tails)
1	63.657	31.821	12.706	6.314	3.078	1.000
2	9.925	6.965	4.303	2.920	1.886	.816
3	5.841	4.541	3.182	2.353	1.638	.765
4	4.604	3.747	2.776	2.132	1.533	.741
5	4.032	3.365	2.571	2.015	1.476	.727
6	3.707	3.143	2.447	1.943	1.440	.718
7	3.500	2.998	2.365	1.895	1.415	.711
8	3.355	2.896	2.306	1.860	1.397	.706
9	3.250	2.821	2.262	1.833	1.383	.703
10	3.169	2.764	2.228	1.812	1.372	.700
11	3.106	2.718	2.201	1.796	1.363	.697
12	3.054	2.681	2.179	1.782	1.356	.696
13	3.012	2.650	2.160	1.771	1.350	.694
14	2.977	2.625	2.145	1.761	1.345	.692
15	2.947	2.602	2.132	1.753	1.341	.691
16	2.921	2.584	2.120	1.746	1.337	.690
17	2.898	2.567	2.110	1.740	1.333	.689
18	2.878	2.552	2.101	1.734	1.330	.688
19	2.861	2.540	2.093	1.729	1.328	.688
20	2.845	2.528	2.086	1.725	1.325	.687
21	2.831	2.518	2.080	1.721	1.323	.686
22	2.819	2.508	2.074	1.717	1.321	.686
23	2.807	2.500	2.069	1.714	1.320	.685
24	2.797	2.492	2.064	1.711	1.318	.685
25	2.878	2.485	2.060	1.708	1.316	.684
26	2.779	2.479	2.056	1.706	1.315	.684
27	2.771	2.473	2.052	1.703	1.314	.684
28	2.763	2.467	2.048	1.701	1.313	.683
29	2.756	2.462	2.045	1.699	1.311	.683
Large	2.575	2.327	1.960	1.645	1.282	.675

Air Resources Board

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Matthew Rodriquez
Secretary for
Environmental Protection

Edmund G. Brown Jr.
Governor

MAILED
8/22/16

TO: Jeff Wright, Manager
Laboratory Support Section

FROM: Patrick Rainey, Manager
Quality Management Section

DATE: August 18, 2016

SUBJECT: ADDENDUM TO THE LABORATORY QUALITY CONTROL MANUAL

Thank you for your submission of the addendum to the Northern Laboratory Branch Laboratory Quality Control Manual, Revision 3. The addendum contains all of the required elements and is approved by the Quality Management Branch (QMB). The addendum is to be used in conjunction with the Laboratory Quality Control Manual, Revision 3. Attached is a signed copy of the addendum. The addendum has been given a tracking number, A14, and a copy will be kept on file with QMB.

Please direct comments or questions to Darsi Goto at 916-324-9656 or by email at darsi.goto@arb.ca.gov.

Attachment

cc: Mike Miguel, Chief
Quality Management Branch

Darsi Goto
Quality Management Section

State of California
California Environmental Protection Agency
Air Resources Board
MLD/QMS-066 (NEW 4/14)

QUALITY MANAGEMENT DOCUMENT ADDENDUM

Section 1. ARB Document
☐ Quality Management Plan (QMP)
☐ Quality Assurance Project Plan (QAPP)
☐ Standard Operating Procedure (SOP)
☒ Laboratory Quality Control Manual (QCM)

Section 2. District Information		
Submitter Name:	Jeff Wright	
Submitter Signature/Date	Jeff Wright	8/12/16

Section 3. Document Title *(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)*	Date
Laboratory Quality Control Manual, Northern Laboratory Branch, Monitoring and Laboratory Division. Revision number 3.0.	September 17, 2015.

Section 4. Proposed Deviation(s)
(specify exact section(s), page number(s) and language in existing ARB document that your District proposes to modify and then specify proposed modification (including any spreadsheets or forms).

Propose replacing Section 11.1 and 11.2 of the QCM:

Current 11.1 and 11.2
11.1 Method Detection Limit (MDL)

The MDL, as found in Title 40 of the Code of Federal Regulations (CFR) Part 136, Appendix B, is defined as the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sampling media) containing the analyte." The MDL can be referred to as Limit of Detection (LOD).

The MDL must be calculated using spike concentrations one to five times the

estimated MDL. The MDL should be calculated using Equations (1), (2), (3) and (4).

Equation (1) $MDL = T_{(n-1,1-\alpha=0.99)} \times s$

Equation (2) $m = \frac{1}{n}\sum_{i=1}^{n} x_i$

Equation (3) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - m)^2$

Equation (4) $s = \sqrt{s^2}$

Where :

n = number of replicates

$T_{(n-1,1-\alpha=0.99)}$ = Student t-value at 99% one-tailed confidence level (1-α) for n-1 degrees of freedom

x_i = value where i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots

m = sample mean

s^2 = variance of the sample mean

s = standard deviation of sample mean

It is recommended that a minimum of seven replicate determinations be used ($n \geq 7$). At n = 7, T has a value of 3.143. For example:
Equation (5) MDL = 3.143 x s

When multiple instruments are used, MDLs are established for each instrument and each analyte, and the highest result from each MDL determination will be used to represent all of the instruments. This represents a pooled MDL.

11.2 MDL Determination and Verification Procedure

The procedure for determining MDL follows 40 CFR Part 136, Appendix B. MDL determinations are conducted when new methods are established, instruments are replaced, or other system changes occur. At least annually, MDL verifications are performed. For methods with large numbers of analytes, one calibration standard may be chosen to represent a class or group of similar analytes. The following procedure is used to calculate the MDL:

11.2.1 Based on data quality objectives, determine the appropriate calibration range and estimated MDL.

11.2.2 Calibrate using the same calibration range used for samples.

11.2.3 Prepare MDL spikes in the appropriate matrix at the concentration of the lowest calibration point and analyze seven replicates.

11.2.4 Determine the MDL using equation (1) based on the following criteria:

- 11.2.4.1 MDL is valid if both of the following acceptance criteria are met: MDL is less than spike concentration, and Spike concentration is greater than 5 times MDL
- 11.2.4.2 If the MDL acceptance criteria is not met, prepare MDL spikes at a different concentration to re-calculate a new MDL
- 11.2.4.3 Repeat these steps until the MDL acceptance criteria is met

MDL replicate spike recoveries should meet the DQO specified for the method detailed in the SOPs. Standards are sometimes not available at concentrations less than five times the MDL. In these cases, use the lowest available standard concentration to calculate the MDL.

<u>Proposed new 11.1 and 11.2</u>

11.1 Method Detection Limit (MDL)

The MDL, as found in Title 40 of the Code of Federal Regulations (CFR) Part 136, Appendix B, is defined as the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sampling media) containing the analyte." The MDL can be referred to as Limit of Detection (LOD).

It is recommended that the MDL be calculated using a spike concentration of one to five times the estimated MDL. The MDL should be calculated using Equations (1), (2), (3), and (4).

Equation (1) $MDL = T_{(n-1,1-\alpha=0.99)} \times s$

Equation (2) $m = \frac{1}{n}\sum_{i=1}^{n} x_i$

Equation (3) $s^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - m)^2$

Equation (4) $s = \sqrt{s^2}$

Where :

n = number of replicates

$T_{(n-1,1-\alpha=0.99)}$ = Student t-value at 99% one-tailed confidence level (1-α) for n-1 degrees of freedom

x_i= value where i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots

m = mean of n replicates

s^2 = variance of the replicate analyses

s = standard deviation of the replicate analyses

It is recommended that a minimum of seven replicate determinations be used (n ≥ 7). At n = 7, T has a value of 3.143. For example:
Equation (5) MDL = 3.143 x s

When multiple instruments are used, MDLs are established for each instrument and each analyte, and the highest result from each MDL determination will be used to represent all of the instruments. This represents a pooled MDL.

11.2 MDL Determination and Verification Procedure

The procedure for determining MDL follows 40 CFR Part 136, Appendix B. MDL determinations are conducted when new methods are established, instruments are replaced, or other system changes occur. At least annually, MDL verifications are performed. For methods with large numbers of analytes, one calibration standard may be chosen to represent a class or group of similar analytes. The following procedure is used to calculate the MDL:

11.2.1 Based on data quality objectives, determine the appropriate calibration range and estimated MDL.

11.2.2 Calibrate using the same calibration range used for samples.

11.2.3 Prepare an MDL spike in the appropriate matrix. An initial spike

concentration of one to five times the estimated MDL is recommended. Analyze a minimum of seven replicates.

11.2.4 Determine the MDL using equation (1) based on the following criteria:

11.2.4.1 MDL is valid if: calculated MDL < spike level < 10 x calculated MDL

11.2.4.2 If the MDL acceptance criteria is not met, prepare an MDL spike at a different concentration to re-calculate a new MDL

11.2.4.3 Repeat these steps until the MDL acceptance criteria is met

MDL replicate spike recoveries should meet the DQO specified for the method detailed in the SOPs.

Section 5. Justification for Deviation(s) *(provide explanation of why modification(s) to existing ARB document is necessary)*
Amend QCM to more closely align with 40 CFR Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11. Specifically, the initial spike concentration to be used was clarified (i.e. recommendation of one to five times the estimated MDL) and the acceptable MDL criteria was amended (MDL < analyte level < 10 x MDL) to reflect what is in 40 CFR Appendix B to Part 136.

Section 6. Attachment(s) ☐ *(specify attachment titles and number of pages, include modified spreadsheets or forms)*	**# of Pages**

Section 7. ARB Approval *(completed by ARB)*		
Name/Phone Number:	PATRICK RAINEY	8/18/2016
Title:	MANAGER QMS	
Signature/Date:		8/18/2016
Addendum Number	A14	

Completed form must be scanned/emailed or mailed to:

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