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 (QCM) 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 California Air Resources Board's (CARB) Quality Assurance (QA) Manual, federal and State regulations, and laboratory Standard Operating Procedures (SOP). SOPs 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 CARB's Primary Quality Assurance Organization, other CARB divisions, federal and State agencies, and local air pollution control/air quality management districts.

2.0 ACRONYMS

% RSD – Percent Relative Standard Deviation
AQDA – Air Quality Data Action
AQS – Air Quality System
AQSB – Air Quality Surveillance Branch
ARB / CARB – 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 Objective
EQL – Estimated Quantitation Limit
IDOC – Initial Demonstration of Capabilities
IDL – Instrument Detection Limit
ILS – Inorganic Laboratory Section
LIMS – Laboratory Information Management System

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
PD – Percent Difference
PTFE - Polytetrafluoroethylene
QA – Quality Assurance
QC – Quality Control
QCM – Quality Control Manual
QMB – Quality Management Branch
RH – Relative Humidity
RL – Reporting Limit
RPD – Relative Percent Difference
SA – Standard Addition
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 or LABORATORY BLANK – used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample media, sample manipulations, and the general laboratory environment. This 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.

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 (COC) – 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. See CONTINUING CALIBRATION VERIFICATION (CCV) STANDARD.

COEFFICIENT OF DETERMINATION – typically expressed as ‘r2,’ measures the proportion of the variance (fluctuation) of one variable (y) that is predictable from the other variable (x) such that $0 \leq r2 \leq 1$, 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 – a midpoint calibration standard analyzed concurrently with test samples to confirm the stability of the instrument calibration. 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 not exceed 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 – 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, method detection limit (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 MDL, 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 QUANTITATION (LOQ) – the minimum concentration or amount of an analyte that a method can measure with a specified degree of confidence. The LOQ is equal to five times the standard deviation of the replicate analyses from the MDL determination/verification. 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 – 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 samples containing a known concentration of the analyte in a specified sample matrix, which may include the sampling media

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 Standard Reference Material (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 – 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 – 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. Replicate analyses results are used to evaluate analytical precision but not the precision of sampling, preservation, or storage internal to the laboratory.

REPORTING LIMIT (RL) – a number which data is not typically reported below. The RL 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 or polytetrafluoroethylene (PTFE), 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 (SA) – 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 – 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 – 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 sample handling staff are responsible for:

- 4.1.1 Sample control
- 4.1.2 Shipment and receipt
- 4.1.3 Sample log-in and peer review
- 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 Maintaining and updating the QCM
4.3.2 SOP review and comment
4.3.3 Reviewing and recommending data management policies for QCM, SOPs, and data packages
4.3.4 Document management (e.g., QCM, SOPs, MDL)
4.3.5 Internal method evaluations

4.4 The LIMS administrator(s) is responsible for:

4.4.1 LIMS development and management
4.4.2 Analytical instrument to LIMS communication (i.e., LIMSLink)
4.4.3 Data security

4.5 Management is to ensure the analyst provides complete method development and validation documents (Section 9.0), SOPs (Section 10.0), MDL determinations/verifications (Section 11.0), and analytical data reports (Section 14.6). All documents and data generated must be approved by management. Management is responsible for reviewing logbooks.

4.6 Designated, trained staff submits ambient data to United States Environmental Protection Agency (U.S. EPA) Air Quality System (AQS) database after review/approval. Data reports generated for special projects and by Special Analysis Section (SAS) are submitted directly to clients after review/approval.

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

4.8 The Monitoring and Laboratory Division (MLD) organization chart can be accessed by following this link: https://ww3.arb.ca.gov/html/org/orgmld.htm.

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

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 method's 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 analytical data report. Documentation of the certified material are kept in the laboratory.

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 method’s SOP.

6.3 Control Standards

The control material should be from a source other than the SRM used for calibration purposes, when available. NIST traceability is preferred. Documentation confirms the control material is from a secondary source.

6.4 Calibration Weights

Calibration weights must be American Standards for Testing and Materials International (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 analytical data 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 method’s 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 is either flagged or invalidated based on SOP criteria.

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 CARB'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 is notified and corrective action is 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 are recorded in the logbook.

9.0 ANALYTICAL METHODS

An analytical method, either quantitative or qualitative, is a set of processes designed to identify and separate analytes for a particular sample. 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 acceptable methods from credible peer-reviewed sources. ASTM International, U.S. EPA, and NIOSH methods should be used whenever possible. All methods adopted and/or modified by NLB should undergo method development, validation, documentation, and approval.

Method development and method validation share similar components in determining if the analytical method is acceptable for its intended use.

9.1 Method Development

Methods currently not used by NLB must go through method development. A method development plan outlines the steps to take to complete the development process. This plan, produced and collaborated between analyst(s) and management, must be approved prior to implementation. A method development document records this process (i.e., method development plan), analytical results, and decisions made based on findings.

9.1.1 Purpose and Scope: Establish measurement quality objectives, DQO, and the intended use based on program and client requirements.

9.1.2 Method Research: Determine if there is an established method or if one can be modified that will meet the scope and DQO for the intended sample. Assess whether analyte matrix, reagents, safety hazards, and waste production are acceptable with the method. If there are unacceptable factors, or any part of the method is not feasible, then consider subcontracting this method.

9.1.3 Method Set-up: Select analytical technique, and set up required instruments or equipment. If the instrumentation or equipment needed is not already available, determine if purchasing is feasible. Prepare cost proposals for management's review and approval. Order standards (more than one source, if possible), testing materials, reagents, and supplies needed.

9.1.4 Analyses and Optimization: Depending on availability and economic feasibility, types of samples used should be: 1) real-world samples; 2) samples in a given matrix; 3) samples using standards of the highest purity available (NIST traceable preferred). Based on initial analyses, adjust instrument and/or procedure parameters to optimize the method. Establish QC parameters.

9.1.5 Stability Studies: Determine sampling media stability, sampling hold time, extraction hold time, analytical hold time, and archive hold time for samples and extracts. If not possible, a literature review or other reputable sources can be used. Stability and hold time studies should be conducted in accordance with the method development plan and should mimic the environmental conditions expected to be encountered during sample handling (i.e., temperature, light, and humidity).

9.1.6 Ruggedness Testing: Determine the analytical method performs as intended by introducing small, expected, and reasonable variations in operations (e.g., different analysts) and/or environmental

conditions (e.g., pH values, mobile phase composition, temperature, humidity). Use of this information assists in determining suitable analytical parameters and criteria. Examine method performance through precision studies (Section 9.2.7).

9.1.7 Draft an SOP based on method development.

9.2 Method Validation

Method validation is the process of verifying that a method and instrument is fit for its intended purpose. Methods need to undergo the method validation process: 1) before placed in use; 2) when the conditions change for which the method has been validated (i.e., technology, chemical composition, procedural changes, and/or matrix); 3) when a change has been made that deviates from the scope of the method (i.e., addition of analytes). Acceptance criteria for the method validation process are outlined in the QCM and/or SOP. A method validation plan outlines the steps to take to complete the validation process. This plan, produced and collaborated between analyst(s) and management, must be approved prior to implementation. A method validation document records this process (i.e., method validation plan), analytical results, and decisions made based on findings.

Detail all steps in a method validation document:

9.2.1 Purpose and Scope: Determine the use of the data generated by the method or instrument, as described in Section 9.1.1.

9.2.2 Selectivity: The ability of the method to accurately measure the analyte response in the presence of all or potential sample components. Use blanks to evaluate the matrix variations and possible sample media contamination. Blank results must be lower than the RL as determined in Section 11 or compared to acceptance criteria specified in the SOP.

9.2.3 Specificity: The ability to identify the analyte among the matrix. A minimum of seven unique samples (real-world samples preferred) should be used to identify matrix interference. Evaluation of

specificity is dependent on the method and/or instrument, and should be discussed as part of the method validation plan.

9.2.4 Method Detection Limit(s): Determine or verify MDLs per Section 11.

9.2.5 Calibration Studies: Prepare standards over a range, extending from a concentration between MDL and RL to expected high concentrations of the target analyte(s). Results must meet the criteria specified in the QCM (Section 11.7) and/or SOP.

9.2.6 Accuracy (Bias / Trueness): Obtain suitable reference material of known concentration. Analyze a minimum of ten replicates for three different concentration levels (3 levels x 10 replicates = 30 measurements). The suggested levels are ≤ 2 x RL (low), check standard or CCV (medium), and the highest calibration concentration (high). Determine accuracy for each concentration level by calculating the PD (Equation 7). The average PD for the low level concentration must be ± 20% between RL and 2 x RL, and ± 40% for concentrations between MDL and RL. The average PD must be ± 20% for the medium and high level concentrations.

9.2.7 Precision (Repeatability): Precision may be determined from measurements obtained in Section 9.2.6. Analyze a minimum of ten replicates for three different concentration levels (3 levels x 10 replicates = 30 measurements). The suggested levels are ≤ 2 x RL (low), check standard or CCV (medium), and the highest calibration concentration (high). Determine precision for each concentration level by calculating the % RSD (Equation 8). The % RSD for low level concentrations must be less than or equal to 15%. For medium and high level concentrations the % RSD must be less than or equal to 10%.

9.3 Method Verification

Changing of similar instrument components, columns, chemical and gas manufacturers, etc. does not constitute a need for method validation. Verify

the method's performance by analyzing QC and comparing to the SOP's QC criteria. These changes must also be documented in the logbook associated with the instrument. If uncertain, then discuss with management.

9.4 Non-routine Analysis

Samples analyzed through a method that has not been fully developed and/or validated are considered non-routine. These are for emergency and temporary situations, and must be approved by management before sample analysis. All supporting documentation and approvals must be included with the affected analytical data report (Section 14.6).

9.5 Method Documentation, Approval, and Archive

A summary must be provided with the method development and/or method validation document. All documents must be peer reviewed and approved by management prior to implementation. All approved method development and/or method validation documents will be permanently archived in the NLB library maintained by the Laboratory Support Section (LSS). At a minimum, the summary will be electronically stored on the NLB shared drive.

10.0 STANDARD OPERATING PROCEDURES

An SOP is a document containing a set of detailed instructions for routine methodologies followed by an organization. The development and use of SOPs provide individuals with the information needed to perform a job properly and facilitate consistency in the quality and integrity of the end product (e.g., data). Utilizing a properly written SOP minimizes variation, promotes quality through consistent implementation of a procedure, and improves comparability, credibility, and defensibility.

The SOP "Preparation of Northern Laboratory Branch's Standard Operating Procedures" (MLD076) documents the procedures to create and modify an SOP.

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 by 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 CARB'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 MLD076 documents all necessary elements for SOPs relating to any physical or chemical analytical method. Some SOPs (e.g., administrative SOPs) may not require all elements and may be waived by management through the SOP review and approval process.

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 shared 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

New and modified methods (Section 9.0) must be approved by management. The approved changes 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.

10.3.1 One-time or temporary procedural modifications for non-routine analysis (Section 9.4) 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 data report.

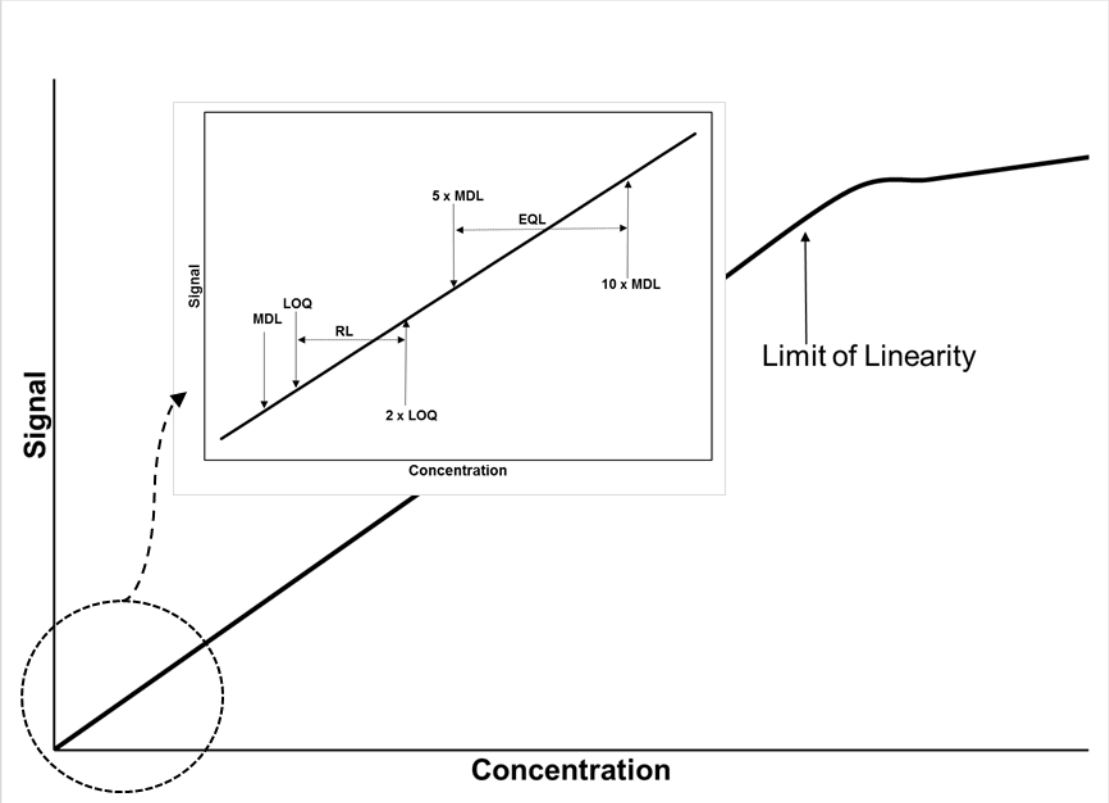
10.3.2 Permanent modifications and deviations to SOPs will require a formal addendum. The addendum will be incorporated in the SOP at the next revision. Addendums and revised SOPs shall be approved by management and retained by LSS.

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 precisely measure the concentration of analytes in a sample. The MDL and LOQ are terms used to describe sensitivity of analytical procedures. The general relationships between these limits, the RL, and the EQL are shown in Figure 11.1.

Figure 11.1. General Analytical Quantitation Relationships



MDL/LOQ determinations and verifications follow the same procedures. MDL/LOQ determinations are conducted when new methods are established, instruments are replaced, or other system changes occur. Subsequently, MDL/LOQ verifications should be performed at least annually. As part of the verification, an LOQ is calculated and compared to the RL.

MDLs and LOQs are analyte and instrument specific. A pooled MDL and LOQ represents a collection of similar instruments for specific analytes.

Management approves MDL, LOQ, EQL, and RL determinations and verifications via MDL data report packages (e.g., MDL calculations, run sequences, QC, etc.).

11.1 MDL Calculation

Unless specified differently in an SOP, the MDL should be calculated using Equations (1), (2), (3), and (4).

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

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

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

Equation (4) $\mu = \frac{1}{n}\sum_{i=1}^{n} x_i$

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
s	=	standard deviation of the replicate analyses
s^2	=	variance of the replicate analyses
μ	=	mean of the replicate analyses
x_i	=	value where i = 1 to n, is the analytical result in the final laboratory instrument reporting units obtained from the n^{th} replicate

Use a minimum of seven replicates. When n = 7, $t_{(6,\ 0.99)} = 3.143$. In this case, the MDL is calculated as follows:

Equation (5) $MDL = 3.143\ (s)$

11.2 LOQ Calculation

The LOQ, the lower level concentration where measurements become quantitatively meaningful, is calculated as:

Equation (6) $LOQ = 5\ (s)$

11.3 MDL Procedure

11.3.1 Calibrate with the same calibration range as for samples.

11.3.2 Estimate the MDL. In conjunction with the program's DQO, an estimated MDL is obtained by one or more of the following methods:

11.3.2.1 Previously determined or verified MDL.
11.3.2.2 Concentration value that corresponds to an instrument signal-to-noise ratio of no less than 2.5:1.
11.3.2.3 Instrument limitations.

11.3.3 Prepare an MDL spike in the appropriate matrix. An initial spike concentration of one to five times the estimated MDL is recommended. For methods with large numbers of analytes, one standard may be chosen to represent a class or group of similar analytes.

11.3.4 Analyze a minimum of seven replicates.

11.3.5 Determine the MDL using Equation 1.

11.3.6 MDL acceptance criteria:

11.3.6.1 MDL < spike concentration < 10 x MDL

11.3.7 Additional MDL criteria to consider:

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

11.3.8 If MDL acceptance criteria is not met:

11.3.8.1 Prepare an MDL spike at a different concentration and re-calculate the MDL.
11.3.8.2 Repeat the MDL procedure until the MDL acceptance criteria is met.
11.3.8.3 If the MDL acceptance criteria cannot be met, the MDL obtained from the spike concentration that resulted in the

least deviation from the criteria may be used. This situation must be documented and explained in the MDL data package.

11.4 Pooled MDLs and LOQs

When multiple, similar instruments are used in a method, MDLs and LOQs are established for each instrument and each analyte. The instrument with the highest standard deviation of the replicate analyses (Equation 2) for each analyte will be used to represent all of the instruments for the method. This represents a pooled MDL and pooled LOQ and is calculated using Equation 1 and Equation 6, respectively.

11.5 Reporting Limit

11.5.1 The RL represents a point in which concentrations are typically not reported below.

11.5.2 The RL should meet the following criteria:

11.5.2.1 RL is greater than or equal to the LOQ.

11.5.2.2 RL should be greater than or equal to the lowest calibration standard.

11.5.3 Approaches to determine an RL may include one or more of the following:

11.5.3.1 Background on matrix (i.e., blank study) and instrument limitations.

11.5.3.2 Client and/or program needs.

11.5.3.3 Regulatory requirements.

11.5.3.4 Statistically determined.

11.5.4 Once a method has an established RL, the RL should be verified annually. During the annual MDL/LOQ verification procedure, the LOQ is compared to the RL. The criteria are as follows:

11.5.4.1 If the RL is less than the LOQ, then the RL should be raised to an appropriate limit.

11.5.4.2 If the RL is more than two times the LOQ, then consideration should be given to lower the RL.

11.5.4.3 If neither of the above situations occur, then the RL may remain unchanged.

11.6 Estimated Quantitation Limit

The EQL is used for specific programs in place of the RL and is approximately 5 to10 times the MDL. The specific definition and use of EQLs are defined in the program specific SOP.

11.7 Calibration

Multipoint calibrations should be performed on an annual, weekly, or daily frequency. They must be performed prior to sample analysis. Linear and non-linear calibrations may be used. Multipoint calibrations must have a correlation coefficient, r, of '0.98' or greater.

Depending on DQOs and program needs, daily calibrations may be "single point" or "multipoint" calibrations. Calibration standards should bracket the majority of expected sample concentrations (i.e., analytical range).

Specific calibration requirements (e.g., calibration frequency, concentration levels, linearity type, etc.) should be clearly outlined within each SOP.

11.8 Dilutions

Samples should be diluted when an analyte exceeds the highest calibration standard by more than 10%. Typically, the individual sample is diluted so the analyte in question is within the current method’s calibration curve. When

samples are diluted, the sample results and MDLs/LOQs are adjusted by the dilution factor. RLs/EQLs are typically adjusted by the dilution factor as well but may not be necessary for those programs where the RLs/EQLs are determined by regulation and/or special projects and are orders of magnitude greater than the corresponding LOQ.

The analytical range may extend beyond the current calibration curve. This approach must show the extended calibration curve is linear and be documented and approved by management.

12.0 QUALITY CONTROL

This section describes common QC measures and corresponding corrective actions. Any additional and/or more restrictive QC measures and corrective actions are contained in method-specific SOPs.

12.1 Analytical Sequence

An outline of a typical analytical sequence must 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 12.1.1-12.1.6 may be repeated for additional samples in a batch. Each set of samples shall be bracketed by successful control or check standards.

12.2 Blanks

Blanks are used to monitor laboratory cleanliness, sample media, and sample preparation and analysis. Some blanks are used to assess contamination during sampling, transport, and/or handling. Individual SOPs must describe

the blank type, preparation, criteria, frequency, and corrective action. Certain blanks (i.e., trip and field) are reported and the data user will determine if associated sample results are impacted. Background subtraction of blanks is allowed where specified in method SOPs.

A blank result must be less than the LOQ or RL. If the blank result is less than the LOQ or RL, then no action should be taken. If the blank result is equal to or greater than the LOQ or RL, the following apply:

12.2.1 When the sample results are greater than or equal to ten times higher than the blank result, no action is taken.

12.2.2 When the sample results are less than ten times higher than the blank result, the analysis result must 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.

12.3 Controls

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 (Section 12.1).

The initial warning and control limits shall be set at ±8 and ±10 Percent Difference (PD) respectively from the target value.

Equation (7) $$PD = \frac{([actual]-[target])}{[target]} \times 100$$

Where:

[actual] = analyzed concentration of the control standard

[target] = target control value standard concentration

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.

When adjustments to the control limits are needed, the changes must be clearly documented, and reviewed and approved 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 SRM, which closely resembles an 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 Percent Relative Standard Deviation (% RSD) under these conditions. In such cases, an assigned standard deviation should be back-calculated based on the assigned % RSD, and used for establishing the control limits. Any limits set by the analyst will be documented, and approved by management.

Equation (8) $\%\ RSD = \frac{s}{|\bar{x}|} \times 100$

Where:

s	=	standard deviation
$\lvert\bar{x}\rvert$	=	absolute value of the mean

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 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 Replicates/Duplicates

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.

Unless specified differently in regulation, an evaluation of the duplicate/replicate pairs shall be made with every sample set using the equation below.

Equation (9) $RPD = \frac{(Y-X)}{((Y+X)/2)} \times 100$

Where:

RPD = Relative Percent Difference

X = the sample result

Y = the duplicate/replicate result

The RPD may be taken as an absolute value.

Duplicate/replicate results and the corresponding RPD must be documented. The duplicate/replicate acceptance criteria are specified in the method SOPs. If the duplicate results do not meet specified QC criteria, the affected samples in the associated batch are to 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 Standards

Check standards (also referred to as CCV 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 sequence, and whenever the analysis sequence is interrupted. The check standard acceptance criteria shall be within ± 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 samples shall be bracketed by successful control or check standards.

12.6 Analytical Cleanliness Check for Sample Media (Contamination Checks)

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 Collocated Samples

NLB analyzes collocated samples and only calculates RPD where both sample results are greater than or equal to five times the LOQ or RL. If RPD is outside acceptable limits (e.g., 25 RPD) for the method, results should be verified. If results are correct, CARB's Air Quality Surveillance Branch (AQSB) or local districts are notified to investigate and perform corrective action as needed on sampling equipment.

12.9 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 samples are typically provided by LSS, QMB, and U.S. EPA. Audit results are documented in LIMS. Audit findings and any actions taken as a result must be documented.

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, COC, sample control, sample tracking, log-in, sample validation, storage, and archive. All viable samples, whether valid or invalid, will be analyzed.

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/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 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.

13.4 Sample Validation

Once a completed COC has been received and processed (i.e., logged into LIMS), 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 sample information. This notification is performed as soon as possible, and the issue is documented on the COC or sample report form.

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 CARB's records retention policy unless stricter requirements are specified in the SOP or by regulation.

13.7.3 COCs, 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, approval, and reporting. Laboratory staff and management are all integral parts of data management. The laboratory utilizes a LIMS database to perform data management activities.

14.1 Laboratory Information Management System and Data Transfer Software

LIMS and data transfer software (e.g., LIMSLink) facilitate the recording, verification and validation, transmittal, reduction, analysis, management, storage, retrieval, and reporting of analytical data generated by the laboratory. These are maintained by the LIMS administrator(s).

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 analyses that produce data-for-record must be entered into LIMS. Changes to any data in LIMS must be made by authorized individuals only. Management's approval may be required.

14.2 LIMS Access

All users must be authorized by management to receive program access to LIMS. Different privileges are given to authorized users depending on need.

Access may include:

- 14.2.1 Read-only
- 14.2.2 Data entry
- 14.2.3 Addition of test methods
- 14.2.4 Modification of preliminary data
- 14.2.5 Data transfer
- 14.2.6 Data reporting
- 14.2.7 Data upload
- 14.2.8 Data system administration

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 QC 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 is taken 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" along with its respective reason documented.

All results reported as "not detected" must be associated with a reference value, such as LOQ, EQL, or RL.

Laboratory staff will contact site operators, or other appropriate staff, directly when issues arise that require clarification of sample information. 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 are to 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 records must be archived.

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 data package must include the following information:

14.6.1 Description of samples (i.e., method, program, audit, and/or project name)
14.6.2 Signature and date blocks (i.e., analyst, peer, and management)
14.6.3 Sample timeframe or batch of analyses covered
14.6.4 Description of standards used (i.e., expiration dates, lot numbers)
14.6.5 Description of unusual occurrences with samples, analysis, and/or data
14.6.6 Corrective actions taken
14.6.7 Additional supporting documentation (if applicable)
14.6.8 Any approved SOP deviations or non-routine analysis (i.e., management approval documentation)
14.6.9 Data results with invalid and flag comments
14.6.10 Analytical sequence
14.6.11 Calibrations
14.6.12 QC results including control charts (if applicable)

14.7 Verification of LIMS Changes

LIMS is programmed by the LIMS administrator(s) to automatically verify and validate data. Data outside QC criteria are highlighted for analyst, peer, and management review, comment, and corrective action.

Requested changes to LIMS (e.g., QC criteria, calculations, etc.) must be approved by management in writing. QC parameters may come from federal and/or State regulations, program guidance documents, QCM, and/or SOPs.

LIMS programmed QC parameters are tested and reviewed by the LIMS administrator(s) before placement into LIMS production. LIMS also utilizes an audit trail function. Management is notified when updates have been completed 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

The following items, when applicable, will be documented and verified by the analyst that performed the analyses:

- 14.8.1.1 Extraction solvents and volumes
- 14.8.1.2 Instrument conditions
- 14.8.1.3 Analytical sequence conducted per SOP
- 14.8.1.4 Expiration dates of standards
- 14.8.1.5 Retention times, integrations, peak identifications, and dilutions performed as necessary
- 14.8.1.6 Calibrations
- 14.8.1.7 Environmental conditions
- 14.8.1.8 QC (such as RLs, duplicates, standards, blanks, controls, holding times)
- 14.8.1.9 Data reduction and calculations
- 14.8.1.10 Raw data concentrations transferred to LIMS
- 14.8.1.11 Check for outliers
- 14.8.1.12 Reasons for invalid samples
- 14.8.1.13 Flags and comments
- 14.8.1.14 Parameters of SOP and QCM are met
- 14.8.1.15 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 (documented and management notified, as necessary)
14.8.2.5 Check for outliers
14.8.2.6 Calibrations and analytical sequence
14.8.2.7 QC (such as RLs, duplicates, standards, blanks, controls)
14.8.2.8 Expiration dates of standards
14.8.2.9 Reasons for invalid samples
14.8.2.10 Flags and comments
14.8.2.11 Parameters of SOP and QCM 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 (documented and management notified, as necessary)
14.8.3.5 Check for outliers
14.8.3.6 Calibrations and analytical sequence
14.8.3.7 QC (such as RLs, 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 QCM 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

After the review and approval process, sample results and related information in LIMS are locked to ensure no changes are made without management authorization. Data in LIMS can still be viewed (Read Only) by management and staff.

Data are released in electronic and/or hardcopy form, depending on the client's request. Management-approved data reports may be sent to the client (or the client representative) by management or assigned staff.

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 may be notified and sent a revised report. Data may be amended for reasons such as CANs, Air Quality Data Actions (AQDA), 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

five years plus current, or regulatory retention policies, whichever is stricter. 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. (e.g., 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

15.0 CONFIDENTIAL INFORMATION

NLB policy and procedures follow Title 17, California Code of Regulations, sections 91000-91022 for data designated as confidential, proprietary, or trade secrets. NLB consults with CARB's Office of Legal Affairs regarding confidential information.

All information (e.g., electronic and hardcopy data, etc.) designated as "Confidential" must be maintained and archived in a secure location (i.e., locked storage cabinet, storage unit, object cannot be freely removed). Management must approve access to all "confidential" materials. Any confidential information provided must be documented with 1) person(s) who requested, removed, and returned the material; 2) date when action occurred; and 3) reason for confidential information. Only authorized individuals are allowed to handle and discuss confidential information. Disposal of confidential information involves destroying the material (i.e., shredding paper).

16.0 REFERENCES

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

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

16.3 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.

16.4 California Air Resources Board, "Quality Assurance Manual, Volume 1 Quality Management Plan for Ambient Air Monitoring," Revision 1.0, March 6, 2019. https://ww3.arb.ca.gov/aaqm/qa/drupal/QMP.pdf

16.5 California Air Resources Board, “Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street,” November 2021 or current.

16.6 U.S. EPA Office of Air Quality Planning and Standards, Air Quality Assessment Division, “Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program,” EPA-454/B-17-001, January 2017. https://www.epa.gov/sites/default/files/2020-10/documents/final_handbook_document_1_17.pdf

16.7 U.S. EPA Office of Environmental Information, “Guidance for Preparing Standard Operating Procedures EPA QA/G-6,” EPA/600/B-07/001, April 2007. https://www.epa.gov/sites/default/files/2015-06/documents/g6-final.pdf

16.8 California Air Resources Board, Northern Laboratory Branch, “Standard Operating Procedure for Preparation of Northern Laboratory Branch’s Standard Operating Procedures, MLD076, Revision 0.0,” July 18, 2017, or current.

16.9 “Validation and Peer Review of U.S. Environment Protection Agency Chemical Methods of Analysis”, FEM Document Number 2005-01, Revision February 3, 2016. https://www.epa.gov/sites/production/files/2016-02/documents/chemical_method_guide_revised_020316.pdf

16.10 “A Guide to Analytical Method Validation” (poster); https://www.waters.com/webassets/cms/library/docs/720001826en.pdf

16.11 “Key aspects of analytical method validation and linearity evaluation”, Pedro Araujo. Journal of Chromatography B. 877 (2009) 2224-2234. September 29, 2008.

16.12 Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program, February 2018, https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf

17.0 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
3.0, Addendum A14	August 18, 2016	Analytical Quantitation (Section 11.0) to align with 40 Code of Federal Regulations (CFR) Appendix B to Part 136, Revision 1.11: clarified initial spike concentration to be one to five times the estimated MDL; and MDL criteria is "MDL < analyte level < 10xMDL"
3.0, Addendum A-24	July 2, 2018	Analytical Quantitation (Section 11.0): organized for clarity; define LOQ to equal five times the standard deviation of the replicate analyses from the MDL determination/verification; and additional MDL verification criteria.

Version	Effective Date	Primary Changes
4.0	September 17, 2018	Update Standard Operating Procedures (Section 9.0), and Control Standards and Control Charts (Section 12.3).
Addendum A36	December 18, 2020	Corrective action update per U.S. EPA's 2018 Technical System Audit Finding PM3 reflecting all viable samples be analyzed.
5.0	December 7, 2021	Updated Section 9 (Analytical Methods) procedures. Administrative edits throughout QCM.