5 PERFORMANCE QUALITY CONTROL and DATA HANDLING

5.1 Introduction

Every element of environmental data acquisition, from sample collection to final data reporting, has associated with it degrees of error. The primary purpose of a total quality assurance program is the optimization of conditions whereby the introduction of error can be either precluded or substantially reduced. The operating procedures and quality control checks practiced in this laboratory and outlined in this manual are implemented to minimize the total error associated with data generation. No number can be affixed to total error; however, analytical performance is measurable and thus definable. Analyses are performed in support of EPA Programs such as RCRA, Superfund, NPDES, Drinking Water, Air Toxics, CERCLA, and other initiatives. The methods used for analysis are based primarily on EPA approved methods, some of which are guidance (e.g., RCRA). Modifications may have been made to increase quality, efficiency, or to support specific requests of the various programs. All performance quality control data (Organic and Inorganic Sections) are transferred from the log books and forms to the appropriate quality control logs, data entry forms, or directly into the Region 4 Laboratory Information Management System (R4LIMS). Quality control logs or forms are maintained for all analyses specifically inorganic parameters, metals, semivolatiles, volatiles, and pesticides/PCBs.

5.2 Terminology

5.2.1 Acceptance Criteria/Limits: specified limits placed on characteristics of a quality control item as defined in required methods. These limits are either statistically defined by historical method performance or by specific method requirements.

5.2.2 Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (NELAC, 1999)

5.2.3 Analyst: the designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality. (NELAC, 1999)

5.2.4 Audit: a systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (NELAC, 1999)

5.2.5 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed

of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC, 1999)

5.2.6 Bias: consistent deviation of measured values from the true value, caused by systematic errors in a procedure. (Standard Methods (SM) for the Examination of Water and Wastewater, 18th edition)

5.2.7 Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value. (Based on NELAC, 1999) See **Method Blank.**

5.2.8 Blind Sample: a sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (NELAC, 1999)

5.2.9 Calibration: to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC, 1999)

5.2.10 Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (NELAC, 1999) See **Initial Calibration Curve.**

5.2.11 Calibration Method: a defined technical procedure for performing a calibration. (NELAC, 1999)

5.2.12 Calibration Standard: a substance or reference material used to calibrate an instrument. (NELAC, 1999)

5.2.13 Certified Reference Material (CRM): a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (NELAC, 1999)

5.2.14 Chain of Custody: an unbroken trail of accountability that ensures the physical security of samples and includes the signatures of all who handle the samples. (NELAC, 1999)

5.2.15 Check Standard: a reference standard obtained from an independent source of the calibration standard used to verify the concentration of the calibration standard.

5.2.16 Confirmation: verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to: Second column confirmation, Alternate wavelength, Derivatization, Mass spectral interpretation, Alternative detectors, or Additional cleanup procedures. (NELAC, 1999)

5.2.17 Conformance: an affirmative indication or judgement that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements.

5.2.18 Continuing Calibration Verification: the analysis of an analytical standard reference used to verify the initial calibration curve.

5.2.19 Corrective Action: the action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (NELAC, 1999)

5.2.20 Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria). (NELAC,1999)

5.2.21 Data Quality Objectives: Data Quality Objectives (DQO's) are statements of data quality required from an investigation as established by the end user during the planning phase of a project requiring laboratory support. The DQO's are qualitative and quantitative statements of the quality of data required to support specific decisions or regulatory actions.

5.2.22 Data Reduction: the process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form. (NELAC, 1999)

5.2.23 Deficiency: an unauthorized deviation from acceptable procedures or practices, or a defect in an item. (NELAC, 1999)

5.2.24 Demonstration of Capability: a procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC, 1999)

5.2.25 Detection Limit: the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence. (NELAC, 1999) See **Method Detection Limit**

5.2.26 Document Control: the act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel,

distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (NELAC, 1999)

5.2.27 Equipment Blank: a sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (NELAC, 1999)

5.2.28 Estimated Detection Limit: (based on 40CFR Part 136 Appendix B) an estimate of the detection limit using one of the following:

5.2.28.1 The concentration value that corresponds to an instrumental signal/noise in the range of 2.5 to 5.

5.2.28.2 The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water (or matrix of interest).

5.2.28.3 That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

5.2.28.4 Instrumental limitations.

5.2.29 Estimated Value: a calculated value based on a reasonable approximation of the true value.

5.2.30 Field Blank: blank prepared in the field by filling a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken. (NELAC, 1999)

5.2.31 Holding Time: the period of time (usually in hours or days) from sample collection until sample preparation or analysis. The initial time is the time a grab sample is collected or the time the last aliquot of a composite is collected. The final time is the time sample preparation or analysis begins.

5.2.32 Holding Times (Maximum Allowable Holding Times): the maximum established times that samples (extracts, digestates or concentrates) should be held prior to sample preparation or analysis. This time requirement can be expressed in various time units (i.e., hours, days, weeks, etc.). Holding times are evaluated in the same units as specified.

5.2.33 Initial Calibration Curve: the calibration curve with concentrations bracketing the range of interest performed at the beginning of the analytical process and again each day prior to sample analysis or at a frequency required by a specific method.

5.2.34 Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method. (NELAC, 1999)

5.2.35 Instrument Blank: a clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (NELAC, 1999)

5.2.36 Laboratory Duplicate: aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (NELAC, 1999)

5.2.37 Laboratory Control Sample (LCS): A Laboratory Control Sample (LCS) is a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. (NELAC, 1999)

5.2.38 Laboratory Control Sample Duplicate (LCS Dup): a second replicate laboratory control sample prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.2.39 Laboratory Replicate Analyses: the measurements of the variable of interest performed identically on two or more sub-samples of the same samples within a short time interval. (NELAC, 1999)

5.2.40 Limit of Detection (LOD): the lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. (NELAC, 1999) See also **Method Detection Limit**

5.2.41 Matrix: the component or substrate that contains the analyte of interest. (NELAC, 1999) For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

5.2.41.1 Aqueous: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts. (NELAC, 1999)

5.2.41.1.1 Drinking Water: any aqueous sample that has been designated a potable or potential potable water source. (NELAC, 1999)

5.2.41.1.2 Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake. (NELAC, 1999)

5.2.41.2 Non-aqueous Liquid/Liquid Waste: any organic liquid with <15% settleable solids. (Based on NELAC, 1999)

5.2.41.3 Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin. (NELAC, 1999)

5.2.41.4 Solids: includes soils, sediments, sludges and other matrices with >15% settleable solids. (NELAC, 1999)

5.2.41.5 Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined. (NELAC, 1999)

5.2.41.6 Air: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (NELAC, 1999)

5.2.42 Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of the target analyte concentration is available. (NELAC, 1999)

5.2.43 Matrix Spike Duplicate (spiked sample or fortified sample duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte. (NELAC, 1999)

5.2.44 May: denotes permitted action, but not required action. (NELAC, 1999)

5.2.45 Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest, which is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. (NELAC , 1999)

5.2.46 Method Detection Limit: the minimum concentration of a substance (an analyte) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (40 CFR Part 136, Appendix B)

5.2.47 Minimum Quantitation Limit (MQL): the concentration level below which the variance of the results for a particular analyte (element or compound) exceeds the acceptable quality control criteria. This value corresponds to the lowest quantitative point on the calibration curve or the lowest demonstrated level of acceptable quantitation.

5.2.48 Outlier: an observation (or subset of observations) which appears to be inconsistent with the remainder of that set of data. (Barnett, v.; Lewis, T. *Outliers in Statistical Data*, 3rd ed.; John Wiley & Sons; New York, 1994; p.7.)

5.2.49 Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC, 1999)

5.2.50 Preservation: refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample. (NELAC, 1999)

5.2.51 Proficiency Test Sample (PT): a sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (NELAC, 1999)

5.2.52 Pure Reagent Water: shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method. (NELAC, 1999)

5.2.53 Quality Control Sample: an uncontaminated sample matrix spiked with known amounts of analytes from a source independent from the calibration standards. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC, 1999)

5.2.54 Quantitation Limits: the maximum or minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be quantified with the confidence level required by the data user. (NELAC, 1999) See **Minimum Quantitation Limit**

5.2.55 Range: the difference between the minimum and the maximum of a set of values. (NELAC, 1999)

5.2.56 Raw Data: any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, computer printouts, magnetic media, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted. (Based on NELAC, 1999)

5.2.57 Reagent Blank (method reagent 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. (NELAC, 1999)

5.2.58 Reference Material: a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (NELAC, 1999)

5.2.59 Reference Method: a method of known and documented accuracy and precision issued by an organization recognized as competent to do so. (NELAC, 1999)

5.2.60 Reference Standard: a standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived. (NELAC, 1999)

5.2.61 Reporting Limit: also known as the Minimum Quantitation Limit (MQL) in Analytical Support Branch data reporting.

5.2.62 Sample: a particular aliquot of a certain matrix (soil/sediment, water, air, etc.) collected at a specific location, date, and time (grab or composite). This aliquot could be distributed over several different size or type containers depending on the analytical and/or preservation requirements.

5.2.63 Selectivity: (Analytical chemistry) the capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. (NELAC, 1999)

5.2.64 Sensitivity: the capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (NELAC, 1999)

5.2.65 Shall: denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. This does not prohibit the use of alternative approaches or methods for implementing the specification so long as the requirement is fulfilled. (NELAC, 1999)

5.2.66 Should: denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (NELAC, 1999)

5.2.67 Spike: a known mass of target analyte added to a blank sample or sub-sample; used to determine recovery efficiency or for other quality control purposes. (NELAC, 1999)

5.2.68 Standardized Reference Material (SRM): A Standardized Reference Material (SRM) is a certified reference material produced by the National Institute of Standards and Technology or an equivalent organization and characterized for absolute content, independent of analytical method. (NELAC, 1999)

5.2.69 Target Analyte: an individual analyte that is specifically targeted for analysis by using a method designed and validated for the analyte. The technique will include calibration standard and other quality control parameters to calibrate and document the ability of an analytical system to successfully analyze for the target analyte.

5.2.69.1 Non-target Analyte: an analyte that is detected by an analytical system, but the method has not specifically targeted the parameter. In this instance there would <u>not</u> have been a calibration standard used to calibrate the analytical system specifically for this analyte. (This would most often occur with analyses for organic parameters). The identification (qualitative analysis) of the non-target analyte is generally based on a comparison to known or published information (e.g., spectra from published libraries) and is usually considered as tentative or provisional. The amounts reported are calculated relative to known concentrations of other reference materials and as reported would be considered to be estimated. These analytes are also often referred to as tentatively identified compounds (TICs).

5.2.70 Traceability: Traceability is the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (NELAC, 1999)

5.2.71 Verification: confirmation by examination and provision of evidence that specified requirements have been met. (NELAC, 1999)

5.3 <u>QC Study Plans</u>

5.3.1 A QC Study Plan is developed when planning a non-routine MDL/DOC study, method development studies, evaluating a new/modified analytical method, or addressing a non-routine QC issue/problem for corrective action. The most recent form for documenting this QC Study Plan is located in a subdirectory on the EPA Region 4 LAN at K:\ASB\Forms\Branch. It should be noted that for routine studies with a limited focus a QC Study Plan is not required. The decision to develop a QC Study Plan will be made by the Lead Analysts in consultation with the QAO and Section Chief.

5.3.2 For studies requiring a QC Study Plan the appropriate analysts will convene to discuss the issue, define the objective(s), and develop the study procedure. The QAO may be involved in the study planning depending on the nature and complexity of the issue. The final QC Study Plan will be approved by the QAO. A report summarizing the study results will be prepared for the QAOs comments as needed.

5.4 Essential Quality Control Requirements

5.4.1 Demonstration of Capability (DOC): a DOC shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix, or test method where applicable.

5.4.1.1 Specific guidance on frequency of DOC may be specified in methods or as required by programs. New DOC studies will be conducted when the entire work unit staff is displaced or in the judgement of the Section Chief the work unit makeup has changed substantially. If the work unit remains substantially intact, new staff members in the work unit may demonstrate capability by performing at least four consecutive successful LCSs. The DOC certificate can be prepared for the new work unit after four consecutive LCSs with the standard documentation requirements.

5.4.1.2 This demonstration may be specified in the method, but should consist minimally of 4 replicate spikes (matrix spike, LCS, or standard/certified reference materials) prepared and analyzed according to the test method either concurrently or over a period of days. As a general guidance, the analyte concentrations should be approximately 10 times the method-stated or laboratory estimated detection limit. This concentration should fall within the range of the routine calibration curve.

5.4.1.3 The mean recoveries (%R) and standard deviations (S) will be compared to method requirements or laboratory generated acceptance criteria. See specific requirements in the Organic and Inorganic Chapters of this manual.

5.4.1.4 Test method DOC requirements may take precedence over the NELAC guidelines, but NELAC requirements must be met.

5.4.1.5 Summary results of initial DOC studies will be transmitted to the QAO by memo. The summary results should include:

5.4.1.5.1 description of the DOC study (including method used, matrix, any method specific criteria, and how the criteria were met)

5.4.1.5.2 DOC certification form is located in a subdirectory on the EPA Region 4 LAN at K:\ASB\Forms\Branch

5.4.1.5.3 Spreadsheet containing analyte list, true value of spikes, % Recovery of each result, Average % Recovery, Population (n-1) Standard Deviation of Recovery, %Relative Standard Deviation of Recovery

5.4.2 Method Detection Limit (MDL): shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, matrix, or test method as per 40 CFR Part136 Appendix B where applicable.

5.4.2.1 Specific guidance on frequency of MDL studies may be specified in methods or as required by programs. New MDL studies will be conducted when the entire work unit staff is displaced or in the judgement of the Section Chief the work unit makeup has changed substantially.

5.4.2.2 MDLs in ASB are accomplished per instructions in 40CFR136 using standard spike mixes into reagent water and then performing an appropriate number of replicate analyses. A minimum of 7 replicate spikes (matrix spike, LCS, or proficiency samples) are carried through the entire analytical process. An MDL study should contain all analytes of interest. Also, as directed by 40CFR136, if the appropriate spiking concentrations are not known, components should be chosen at a concentration approximately 1 to 5 times the expected or "estimated" MDL. This estimated MDL concentration may be determined in several ways as outlined by 40CFR136 such as a positive response 2.5 to 5 times the instrument signal to noise rations. However, even more valuable for determining the spiking level may be historical data or other available information.

5.4.2.3 In any case, as an effort to avoid an unrealistic or 'inflated' MDL as denoted int 40CFR136, the resulting calculated MDL must be greater than or equal to .1 the concentration chosen for spiking. For example, if the chosen spike concentration is 5 ppb, the resulting calculated MDL concentration should be greater than or equal to .5 ppb. If the resulting MDL is less than .1 times the spike concentration, the procedure must be repeated with a lower spike concentration such that the .1 criteria above are met.

5.4.2.4 Some methods, in an effort to avoid an inflated MDL, may suggest actions such as using the % RSD of replicate analyses to determine spike concentration levels. This guidance may be helpful, but the guiding principle to avoid an inflated MDL should be as specified above.

5.4.2.5 The MDL is calculated as the standard deviation times the appropriate T value from the "Tables of Students' T Values at the 99 Percent Confidence Level". For example: for 7 replicates the MDL would be 3.143 times the standard deviation (S) of the seven replicates; for 10 replicates the MDL would be 2.821 times the standard deviation of the ten replicates. See the table in 40 CFR Part 136 Appendix B for more details.

5.4.2.6 Summary results of MDL studies will be transmitted to the QAO by memo. The summary results should include:

5.4.2.6.1 description of the MDL study (including method used, matrix, any method specific criteria, how the criteria were met)

5.4.2.6.2 Spreadsheet containing analyte list, true value of spikes, raw results, Population (n-1) Standard Deviation of Raw Results, %Relative Standard Deviation of Raw Results, Students' T value used, MDL calculated

5.4.3 Standards Traceability: A system of identification of standards allowing for tracking intermediate and working standards back to an original traceable stock will be maintained.

5.4.4 Determination of Outliers

5.4.4.1 Data points may not be disguarded as an outlier without a proper explanation or valid justification. This applies to all data points collected (e.g. LCS, MDL, linear curves, DOC, Dups, etc). Justifiable reasons for removing outliers would include:

5.4.4.1.1 a known and documented laboratory error

5.4.4.1.2 use of an appropriate statistical outlier test.

5.4.4.2 Standard deviation from the mean - typically useful for large data sets

5.4.4.2.1 Calculate the mean and the standard deviation of all the data. Database outliers are established by summarizing all the data in the database, then applying one standard deviation beyond the statistical confidence level required. For example: assuming the statistical confidence level required is 95% (2 standard deviations around the mean), any result greater than 3 standard deviations around the mean would be an outlier.

5.4.4.3 Studentized deviation from the mean - *T* test

5.4.4.3.1 Calculate the sample mean $\left(\overline{X}\right)$ and the standard deviation (s) of the data including the suspect extreme value.

5.4.4.3.2 Calculate the ratio

$$Tcalc = \frac{\left|\text{suspect value} - \overline{\text{X}}\right|}{\text{s}}$$

5.4.4.3.3 Apply the following decision rule:

5.4.4.3.3.1 If the calculated value of T (T_{calc}) is greater than the critical value ($T_{critical}$) at a given level of confidence, then the suspect value is an outlier and should be removed from the data set.

5.4.4.3.3.2 Critical values of *T* as a function of sample size, n, at the 95% level of confidence (level of significance, α =0.05) are given in the following table:

Critical values of the studentized deviation *T* for testing whether a single point should be rejected as an outlier (*a* = 0.05, two-sided test).[1]	
Sample size, n	**Critical value ($T_{critical}$)**
3	1.15
4	1.48
5	1.71
6	1.89
7	2.02
8	2.13
9	2.21
10	2.29
11	2.36
12	2.41
13	2.46
14	2.51
15	2.55
16	2.59
17	2.62
18	2.65
19	2.68
20	2.71
21	2.73
22	2.76
23	2.78
24	2.80
25	2.82

[1] Pearson, E. S.; Hartley, H.O., Eds, *Biometrika Tables for Statisticians*, Vol. I, 3rd ed., Cambridge University Press, London, 1966.

5.4.4.3.4 Example:

MDL	Lead (ug/L)
1	40.3
2	41.0
3	40.1
4	38.0
5	40.7
6	41.3
7	41.1

For the extreme low value, the calculated value of *T* is:

$$T_{calc} = \frac{|suspect - \overline{X}|}{s} = \frac{|38.0 - 40.3667|}{1.1261} = 2.10$$

The critical value of *T* for $\alpha = 0.05$, and for n=7 is 2.02. The calculated value of *T* is greater than the critical value of *T* (e.g. $T_{calc} > T_{critical}$). Thus the suspect value is an outlier and should be removed.

5.4.4.4 Dixon's *Q* test

5.4.4.4.1 Sort the *n* data values in ascending order:

$x_1 < x_2 < \ldots < x_{n-1} < x_n$

Where x_1 is the extreme low value (or x_n is the extreme high value) suspected of being an outlier.

5.4.4.4.2 Calculate the absolute difference between the suspect value and the measurement that is nearest in magnitude (e.g. the next higher or the next lower value).

5.4.4.4.3 Calculate the range of the entire data set including the suspect value, which is one of the extreme values.

5.4.4.4.4 Calculate the value of *Q*:

$$Q_{calc} = \frac{\left| \text{suspect value} - \text{nearest neighbor} \right|}{\left(\text{range of entire data set} \right)}$$

$$= \frac{\left| x_1 - x_2 \right|}{\left(x_n - x_1 \right)} \text{ or } \frac{\left| x_n - x_{n-1} \right|}{\left(x_n - x_1 \right)}$$

5.4.4.4.5 Apply the following decision rule:

5.4.4.4.5.1 If the calculated value of Q (Q_{calc}) is greater than the critical value ($Q_{critical}$) at a given level of confidence, then the suspect value is an outlier and should be removed from the data set.

5.4.4.4.5.2 Critical values of *Q* as a function of sample size, n, at the 95% level of confidence (level of significance, α =0.05) are given in the following table:

Critical values of the *Q* in Dixon's *Q*-test for testing whether a single point should be rejected as an outlier (*a* = 0.05, two-sided test).[1]	
Sample size, n	**Critical value ($Q_{critical}$)**
3	0.970
4	0.829
5	0.710
6	0.625
7	0.568
8	0.526
9	0.493
10	0.466
11	0.444
12	0.426
13	0.410
14	0.396
15	0.384
16	0.374
17	0.365
18	0.356
19	0.349
20	0.342
21	0.337
22	0.331
23	0.326
24	0.321
25	0.317

[1] Rorabacher, D. B., "Statistical treatment for rejection of deviant values of Dixon's 'Q' parameter and related subrange ratios at the 95% confidence level,' *Anal. Chem.* **1991**, 63, 139-146

5.4.4.4.6 Example:

MDL	Lead (ug/L)
1	40.3
2	41.0
3	40.1
4	38.0
5	40.7
6	41.3
7	41.1

The data sorted in ascending order are:

MDL	Lead (ug/L)
4	38.0
3	40.1
1	40.3
5	40.7
2	41.0
7	41.1
6	41.3

For the extreme low value, the calculated value of *Q* is:

$$Q_{calc} = \frac{|38.0 - 40.1|}{(41.3 - 38.0)} = \frac{2.1}{3.3} = 0.636$$

The critical value of Q for $\alpha = 0.05$, and for n=7 is 0.568. The calculated value of Q is greater than the critical value of Q (e.g. $Q_{calc} > Q_{critical}$). Thus the suspect value is an outlier and should be removed.

5.5 <u>Instrument Calibration</u>

5.5.1 Initial Calibration Curve: a standard curve with concentrations bracketing the range of interest must be performed prior to sample analysis. See specifics in Inorganic and Organic Chapters of this manual.

5.5.2 Continuing Calibration Verification: an analytical reference standard at a concentration near the mid-point of the initial curve, or as specified by the method, is to be analyzed at the beginning of each analytical batch and on a frequency determined by the analytical method utilized. See specifics in Inorganic and Organic Chapters of this manual.

5.5.3 Calibration Standard Verification: A Check Standard obtained from an independent source of the calibration standard is used to verify the concentration of the calibration standard on a frequency determined by method requirements or by a specified frequency to be established in SOPs or the Inorganic and Organic Chapters of this manual.

5.5.4 Method Blanks: shall be performed at a frequency of at least one per batch of samples per matrix type per sample preparation method. Results of the method blank analysis are used to assess potential contamination of the associated sample batch. See the specific Inorganic and Organic Chapters of this Manual for details on evaluating possible blank contamination.

5.5.5 Bias: Bias refers to the difference between an estimate based on the data and the true value of the parameter being estimated.

5.5.5.1. Bias is expressed as percent recovery (%R) and calculated by the formulas:

Spike Samples Reference Materials

$$\%R = \frac{Z - X}{T}(100) \quad \text{or} \quad \%R = \frac{Y}{T}(100)$$

Where: X = concentration in unspiked sample.
Y = measured concentration.
Z = concentration in spiked sample.
T = True concentration of spike added.

5.5.5.2 Elements of bias are:

5.5.5.2.1 Laboratory Control Sample (LCS): shall be performed at a frequency of one per batch of samples per matrix type per sample preparation method. The LCS is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system (NELAC, 1999). ASB uses the LCS is to serve as a "best case" indicator of the overall performance of the analytical system.

5.5.5.2.1.1 LCS spikes may be prepared using reference materials (including performance evaluation or proficiency testing samples) or internally-prepared spiking mixtures. Clean matrices such as reagent grade water and sand are used to provide consistency for determining system performance.

5.5.5.2.1.2 The components to be spiked shall be as specified by the mandated test method. Any permit specified analytes or client requested analytes shall also be included. If there are no specified components, the laboratory shall spike per the following:

5.5.5.2.1.2.1 For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.

5.5.5.2.1.2.2 For those test methods that have extremely long lists of analytes, a representative number may be chosen. The analytes selected should be representative of all analytes reported. The following criteria shall be used for determining the minimum number of analytes to be spiked.

5.5.5.2.1.2.3 For methods that include 1-10 targets, spike all components

5.5.5.2.1.2.4 For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater

5.5.5.2.1.2.5 For methods with more than 20 targets, spike at least 16 components.

5.5.5.2.1.2.6 Over a period of 2 years, all routine target analytes must have been included in the LCS spike.

5.5.5.2.1.3 All analyte concentrations shall be within the calibration range of the methods.

5.5.5.2.1.4 The LCS is to be carried through the entire analytical process. Control limits should be initially established after at least 20 separate spikes have been performed and shall be matrix and method specific. If the analytical method provides directions for calculating LCS limits, then follow the method specified procedure, otherwise acceptance limits shall be calculated representing 3 standard deviations from the mean recovery for each compound.

5.5.5.2.1.5 Each time a new method is implemented, when significant changes are made to existing methods, or if the spiked components are changed, new LCS limits must be generated.

5.5.5.2.1.6 In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance.

5.5.5.2.2 Matrix Spike (MS): The frequency of the analysis of matrix spike samples shall be determined as part of the systematic planning process (e.g. Data Quality Objectives) or as specified by the required mandated test method. Matrix spike recoveries may be used only to assess the sample matrix which was spiked and are not used to evaluate matrix effects of non-spiked samples in the associated sample batch. ASB does not qualify any batch results based on the matrix spike analysis. Only the sample spiked is flagged if QC results are outside of the matrix spike limits for that sample.

5.5.5.2.2.1 The components to be spiked shall be as specified by the mandated test method. Any permit specified analytes or client requested analytes shall also be included. If there are no specified components, the laboratory shall spike per the following:

5.5.5.2.2.1.1 For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.

5.5.5.2.2.1.2 For those test methods that have extremely long lists of analytes, a representative number may be chosen. The analytes selected should be representative of all analytes reported. The following criteria shall be used for determining the minimum number of analytes to be spiked.

5.5.5.2.2.1.3 For methods that include 1-10 targets, spike all components

5.5.5.2.2.1.4 For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater

5.5.5.2.2.1.5 For methods with more than 20 targets, spike at least 16 components.

5.5.5.2.2.2 All analyte concentrations shall be within the calibration range of the methods.

5.5.5.2.3 Surrogate: Surrogates are added to each sample just prior to sample preparation, i.e., extraction or purging. Surrogate standards are utilized in Organic analysis where appropriate.

5.5.5.2.3.1 The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated by determining whether the measured

concentration falls within an established statistical acceptance limit. Sample results with surrogate limits that fall outside acceptance criteria are qualified appropriately. See specifics in the Organic Chapter of this manual.

5.5.5.2.3.2 Surrogate acceptance limits are calculated yearly based on data generated in samples for the previous two years. Calculate average recovery (%R) and standard deviation (S), in percent recovery, for each surrogate standard using the entire data base.

5.5.5.2.3.2.1 Only results from sample analyses are maintained in the database. (Note: blanks results are not to be used in the calculation of limits).

5.5.5.2.3.2.2 Obvious outliers are not entered into the surrogate database based on the analysts judgement on a case by case basis (i.e. dilutions beyond quantitation range, obvious spiking errors, interference, etc.). Surrogate results from samples exceeding existing limits are only entered into the database when repeat analysis confirm those results.

5.5.5.2.3.2.3 Limits are established as follows:

5.5.5.2.3.2.3.1 Database outliers are established by summarizing all the data in the database then applying one standard deviation beyond that used to determine the limits for the specific analysis.

5.5.5.2.3.2.3.2 Limits are then calculated based on the remainder of the data. For example: assuming the final limits are set using 3 standard deviations. A standard deviation calculation is made of the entire database, then a new calculation is made eliminating all data exceeding 4 times the standard deviation from the entire database.

5.5.5.2.3.3 Each time a new method is implemented, when significant changes are made to existing methods, or if the spiked components are changed, new surrogate limits must be generated.

5.5.5.2.3.4 In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance.

5.5.5.2.4 Proficiency Test (PT): The Branch will participate in independent Proficiency Testing Studies as required for accreditation or more often as deemed necessary by Branch Management or Branch QAO. Performance on these studies further indicates the effectiveness of the laboratory's day-to-day quality control procedure.

5.5.5.2.5 Standardized Reference Material (SRM) & Certified Reference Materials (CRM): These reference materials will be utilized to determine method/analytical performance as deemed appropriate. See specific requirements in Inorganic and Organic Chapters of this manual.

5.5.6 Precision: Precision refers to the level of agreement among repeated measurements of the same characteristic. Elements of Precision are:

5.5.6.1 Laboratory Replicate Analyses: The frequency of the analysis of matrix replicates may be determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method. Replicates analyses are usually part of MDL/DOC studies, recovery studies, or in method development studies.

5.5.6.1.1 Composition: Replicates are performed on replicate aliquots of actual samples, matrix spikes, or laboratory control samples.

5.5.6.1.2 Precision of replicates is expressed as percent relative standard deviation and is calculated by the formula:

$$\%RSD = \frac{S}{X} \times 100$$

Where: S = Standard Deviation
X= Mean

For replicate analysis (any number >2)

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$

Where: X = individual observations and
n = number of observations.

Do not use this formula for n=2.

5.5.6.2 Matrix Duplicate Analyses: The frequency of the analysis of matrix duplicates may be determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method.

5.5.6.2.1 The results from matrix duplicates are primarily designed to assess the precision of analytical results in a given matrix. Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of duplicate precision.

5.5.6.2.2 Precision of duplicates is expressed as relative percent difference (RPD) and is calculated by the formula:

$$RPD = \frac{D}{X} \times 100$$

Where: D = Difference between measurements
X = Mean

5.5.6.3 Laboratory Control Sample Duplicates (LCSD): an LCS shall be performed in duplicate at a frequency of one per batch of samples per matrix type per sample preparation method.

5.5.6.3.1 The results from laboratory control sample duplicates are primarily designed to assess the precision of analytical results for a specific batch Results are compared to established limits for that specific matrix if available.

5.5.6.3.2 Precision of **LCSD** is expressed as relative percent difference (RPD).

5.5.6.3.3 LCSD acceptance limits are calculated based on data generated on a minimum of 20 results from samples of the same matrix.

5.5.6.3.3.1 Limits are established as follows:

5.5.6.3.3.2 Calculate Average RPD and standard deviation of RPDs

5.5.6.3.3.3 The limits for RPD are the average RPD plus 3 times the standard deviation of the RPDs.

5.5.6.4 Matrix Spike Duplicates (MSD): The frequency of the analysis of matrix spike duplicates may be determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method.

5.5.6.4.1 The results from matrix spike duplicates are primarily designed to assess the precision of analytical results in a given matrix. Results are compared to established limits for that specific matrix if available.

5.5.6.4.2 Precision of matrix spike duplicates is expressed as relative percent difference (RPD).

5.5.6.4.3 Matrix Spike Duplicate acceptance limits are calculated based on data generated on a minimum of 20 results from samples of the same matrix.

5.5.6.4.3.1 Limits are established as follows:

5.5.6.4.3.2 Calculate Average RPD and standard deviation of RPDs

5.5.6.4.3.3 The limits for RPD are the average RPD plus 3 times the standard deviation of the RPDs.

5.5.6.4.3.4 Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of matrix spike duplicate precision.

5.5.6.5 Internal Standard: Internal standards are added to each Organic sample extract as appropriate. See specifics in the Organic Chapter of this manual.

5.5.7 Data Handling

5.5.7.1 Acceptance Criteria/Limits: Where acceptance criteria/limits are required new limits must be generated each time a new method is implemented, when significant changes are made to existing methods, or if the spiked components are changed. A minimum of 20 results will be required for developing acceptance limits. After the initial limits are determined, they should be updated again as needed within the first year and then at a minimum of annually thereafter. [Notably, the process of updating limits can produce a statistical anomaly of a continued and impractical decrease in the limits to the point of non-usability. This will occur if the limits included in the calculations are only those that are in the "acceptable" range. To offset this issue there may be a practical limit that occurs after experience with method and several generations of data are used in the limits calculations. These practical limits may be established and used when appropriate, <u>but only after concurrence with the Branch Quality Assurance Officer and Section Supervisor.</u>]

5.5.7.1.1.1 In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance.

5.5.7.1.1.2 All limits shall be provided to the Branch QAO for the initial and each update. These limits will be retained on file by the Branch QAO and will also be maintained by analysts performing the analyses for ready reference.

5.5.7.2 Significant Figures: The number of digits in a reported result that are known definitely as justified by the accuracy of the analysis with one additional figure that may have some degree of uncertainty. For example for a result reported at “75.6" mg/L the analyst would be certain of the “75" , but may be uncertain as to whether the “.6 “should be “.5" or “.7", because of unavoidable uncertainty in the analytical procedure. Digits beyond this last figure are not significant, therefore in the example analysts reporting to 3 significant figures would report “75.6". Only figures justified by the accuracy of the analysis shall be reported. (Based on Standard Methods (SM) for the Examination of Water and Wastewater, 18th edition)

5.5.7.3 Rounding Rules:

5.5.7.3.1 Round off by dropping digits that are not significant. If the digit 6, 7, 8, or 9 is dropped, increase preceding digit by one unit; if the digit 0, l, 2, 3, or 4 is dropped, do not alter preceding digit. If the digit 5 is dropped, round off preceding digit to the nearest <u>even</u> number: thus 2.25 becomes 2.2 and 2.35 become 2.4. Use only the digit beyond the most significant figure for rounding. Rounding should be performed only after arriving at the final result in the calculation. (Based on Standard Methods (SM) for the Examination of Water and Wastewater, 18th edition)

5.5.7.3.2 For evaluating results with respect to precision and bias acceptance criteria the following rounding rules apply:

5.5.7.3.2.1 For numbers 100 and greater, round to three significant figures.

5.5.7.3.2.2 For numbers less than 100, round to two significant figures.

5.5.7.3.3 For example, if the acceptance window for bias is 90% to 110% and the recovery is 89.6%, this number would round to 90% and would be acceptable. If the acceptance window for bias is 90% to 110% and the recovery is 110.6%, this number would round to 111% and would not be acceptable. If the acceptance criterion for precision is 9.5 and the RPD is 9.55 which rounds to 9.6, this result would not be acceptable.

5.5.7.4 Dry Weight/Wet Weight:

5.5.7.4.1 Sediment/Soil: Percent moisture must be determined on all samples unless otherwise specified by the sample requestor. All soil/sediment samples shall be reported on a dry weight basis.

5.5.7.4.2 Non-aqueous waste: shall be reported on a wet weight basis unless otherwise specified by the sample requestor.

5.5.7.4.3 Tissue samples: shall be reported on a wet weight basis unless otherwise specified by the sample requestor.

5.5.7.5 Holding Times: Results are considered to be within holding times if the preparation and/or analysis is performed within the recommended period of time. Holding times are evaluated in the same units as the Maximum Holding Time Requirements (e.g., Holding times specified in terms of hours will be evaluated based on the hour of collection. Holding times specified in terms of days will be evaluated based on the day of collection.) If analyses are performed outside defined recommended maximum holding times, the results will be "J" flagged and an appropriate remark added to the report.

5.5.7.6 Quantitation Limits: Results are considered to be within acceptable quantitative accuracy if the analyses are performed within the appropriate quantitation range as defined by the calibration curve. Results calculated outside these limits will be qualified with the "J" flag or otherwise as appropriate. A remark describing the reason for the flag will be added to the report.

5.5.7.7 Data Reporting: All analytical data generated in the Branch will be entered into and reported from the Region 4 Laboratory Information Management System (R4LIMS).

5.5.7.8 The analyst generating the results and a secondary analyst are responsible for entering, proofing, and verifying the results in R4LIMS.

5.5.7.9 The Primary or Secondary Analyst is responsible for producing a verified copy of the results for the customer and a copy for the project file. Other copies will be produced as needed. A memo transmitting these results will be generated from R4LIMS and signed at the time of production by the analyst that produced the results. This memo will also explain any anomalies in the results.

5.5.7.10 The Section Chief or an alternate in the Section Chief's absence will review the production copies and memo for completeness and accuracy. The Section Chief signs the transmittal memo, Branch Releases the data in R4LIMS, and forwards the data to the Branch Secretary for appropriate routing.

5.5.7.11 In the event a correction or change needs to be made in data that has been Branch released and transmitted to the customer the Section Chief is responsible for insuring corrected data is produced and transmitted to the customer. A new memo should be created from R4LIMS transmitting the corrected data, describing the changes, and instructing the customer to replace the previously reported data with the corrected data. This is achieved by reversing the above procedure and starting the process over.

5.6 Annual Analytical Performance Summary

5.6.1 During the first quarter of each fiscal year, a summary report of the Branch's analytical performance for the previous year is prepared by the Branch QAO. Each analytical workgroup is responsible for providing the precision data (average percent RSD or RPD), and accuracy data (average percent recovery of laboratory control samples, surrogate recoveries, and spiked samples where possible) for this report. A minimum of 20 results will be required for developing acceptance limits. This summary will contain all parameters for which adequate quality control data have been generated during the year. Acceptance limits generated during this process will be in remain effect until the process is repeated. In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (ie., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance.

5.7 Corrective Action Issues

5.7.1 Corrective action will be taken at any time during the analytical process when deemed necessary based on analyst judgement or when quality control data indicate a need for action. Generally, corrective action will be triggered by such things as: poor analysis replication, poor recovery, instrument calibration problems, blank contamination, etc.

5.7.2 Corrective actions will include, but not necessarily be limited to: reanalysis, calculation checks, instrument recalibration, preparation of new standards/blanks, re-extraction/digestion, dilution, application of another analysis method, additional analysts training, etc. Specific corrective actions are detailed in the Inorganic and Organic Chapters of this manual.

5.7.3 All data corrective actions will be noted on the appropriate log, chromatogram, strip chart or data report.

5.7.4 Most frequently, these corrective actions will be initiated by the analyst at the time of analysis. However, some corrective actions are initiated subsequent to analysis based on evaluations performed by quality assurance or laboratory management personnel. Issues needing QAO involvement would include:

5.7.4.1 When either the Lead Analysts, Section Chiefs, or QAO recognize a QC trend reaching the upper or lower control limits.

5.7.4.2 When consistent and constant blank contamination occurs.

5.7.4.3 When poor performance on any criteria becomes repetitive.

5.7.4.4 Other special performance issues.

5.7.5 The QAO should work with the Section Chiefs to determine a course of action to resolve such performance issues. If necessary a study plan should be developed to determine the source of the problem. This could involve special studies, simple method modifications, or technique changes. All efforts to resolve the issue will be documented.

5.8 Analytical Data Qualifiers

5.8.1 Data qualifiers are “Flags” added to data in an effort to best describe the quality of the data to the end user. These flags are applied during data reduction by Primary Analyst based on appropriate Quality Control criteria.

5.8.1.1 U - The analyte was not detected at or above the reporting limit.

5.8.1.1.1 The reporting limit for Region 4 laboratory data is the "minimum quantitation limit (MQL)". Every sample has a concentration level below which the variance of the results for a particular analyte (element or compound) exceeds the acceptable quality control criteria. This value corresponds to the lowest quantitative point on the calibration curve or the lowest demonstrated level of acceptable quantitation. This level is the MQL and is reported as the value preceding the "U". The MQL is determined from sample size, dilution required, and instrument sensitivity. The value often varies from analyte to analyte within a sample. Analytes are often detected at levels below the MQL and are reported as estimated values (J).

5.8.1.2 J - The identification of the analyte is acceptable; the reported value is an estimate.

5.8.1.2.1 Estimated Value--Every sample analysis has quality control criteria associated with the quantitative data which have been established based on similar analyses. When these criteria are exceeded, the value for that analyte or similar analytes is reported as an estimated value. Examples are (not intended to be all inclusive):

5.8.1.2.1.1 calculated values are below or above an appropriate linear range as defined by calibration curve;

5.8.1.2.1.2 analytical holding times for analysis are exceeded;

5.8.1.2.1.3 surrogate recovery limits are exceeded;

5.8.1.2.1.4 there are no known quality control criteria for an analyte;

5.8.1.2.1.5 other quality control criteria exceeded.

5.8.1.3 N -There is presumptive evidence that the analyte is present; the analyte is reported as a tentative identification.

5.8.1.3.1 Tentative Identification--There is an indication that the analyte reported is present. The quality control requirements necessary for confirmation were not met. Examples are (not intended to be all inclusive):

5.8.1.3.1.1 A specific list of compounds is analyzed for in every organic analysis by gas chromatography/mass spectrometry (GC/MS). Other compounds are often present and their spectra are compared to published mass spectral data. If a qualitative determination is made, the compound is reported as tentatively identified.

5.8.1.3.1.2 The presence of analytes is often indicated, but there is evidence of possible interferences. There is presumptive evidence that the analyte is present, therefore, it is reported as tentatively identified.

5.8.1.4 C - The analyte is determined to be present. The presence of the analyte was "confirmed by GC/MS".

5.8.1.4.1 Confirmed by GC/MS-Pesticides are routinely analyzed by gas chromatography with an electron capture detector (GC/EC). When identified by GC/EC analysis in sufficient concentrations, pesticides are confirmed on the mass spectrometer by comparing the spectra of the analyte with the spectra of a particular pesticide. If a good spectral match is obtained, the pesticide identification is considered to be confirmed. The concentration is quantitated by GC/EC.

5.8.1.5 A - The analyte was analyzed in replicate. The reported value is an "average value" of the replicates.

5.8.1.5.1 Average Value--Samples are often analyzed in replicate (usually in duplicate). When replicate aliquots of the same sample are analyzed by carrying both aliquots through the entire analytical process the values are reported as an average.

5.8.1.6 K -The identification of the analyte is acceptable; the reported value may be biased high. The actual value is expected to be less than the reported value.

5.8.1.6.1 Less Than Values--The analyte is present, but the amount of the analyte is determined to be below an acceptable level for quantitation. QC measurements indicate a high bias for the sample result reported or an

accurate result can not be calculated, but is determined to be less than the value given.

5.8.1.6.2 Example (not intended to be all inclusive): 10K means that the analyst has determined that the analyte is present at some undetermined amount less than 10.

5.8.1.7 L - The identification of the analyte is acceptable; the reported value may be biased low. The actual value is expected to be greater than the reported value.

5.8.1.7.1 Greater Than Values--The analyte is present, but the amount of the analyte is determined to be above an acceptable level for quantitation. QC measurements indicate a low bias for the sample result reported or an accurate result can not be calculated, but is determined to be greater than the value given.

5.8.1.7.1.1 Example (not intended to be all inclusive): 500L means that the analyte is present at some undetermined amount greater than 500.

5.8.1.8 R -The presence or absence of the analyte can not be determined from the data due to severe quality control problems. The data are rejected and considered unusable.

5.8.1.8.1 Rejected Data-Some or all of the quality control data for the analyte were outside criteria. The presence or absence of the analyte can not be determined from the data. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

5.8.1.9 UJ -The analyte was not detected at or above the reporting limit. The reporting limit is an estimate.

5.8.1.9.1 This is a combination of the "U" and "J" codes.

5.8.1.10 NJ - There is presumptive evidence that the analyte is present; the analyte is reported as a tentative identification. The reported value is an estimate.

5.8.1.10.1 This is a combination of the "N" and "J" codes.

5.8.1.11 RJ - The analysis indicated the presence of the analyte. The data is rejected and the reported value is an estimate. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

5.8.1.11.1 This is a combination of the "R" and "J" codes.

5.8.1.12 RU - The analysis did not indicate the presence of the analyte. The data is rejected and the reported value is the Reporting Limit. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

5.8.1.12.1 This is a combination of the "R" and "U" codes.

5.9 Analytical Data Remarks

5.9.1 Data Remarks are footnotes added to data reports in an effort to best describe the quality of the data to the end user. These remarks are applied during data reduction by Primary Analyst or analyst verifying the data based on appropriate Quality Control criteria.

5.9.2 Up to four remarks can be added to each data report. For purposes of standardization the most common remarks used are easily picked from a list of "Standard Remarks" in R4LIMS (see Figure 5-1). Remarks can be entered in R4LIMS by either the Remark # or picking from a text list. Remarks other than these can be added as necessary by using a Remark # of 00 and entering text up to 80 characters per remark.

5.9.3 Remarks are an integral part of the data results and therefore verified by the same process**.**

5.10 Data Management and Data Security

5.10.1 Data is managed using the Region 4 Laboratory Information Management System (R4LIMS). This is an in-house developed Sybase PowerBuilder® application utilizing an Oracle database residing on an SESD Novell Network Server. Netware-level access to the Oracle Server is limited to the SESD LAN Administrator, the Region 4 LAN Administrator, and the R4LIMS DBA (an SESD computer specialist responsible for R4LIMS application development and database administration).

5.10.2 Direct access to the Oracle database table space is restricted to a Contract Programmer (for R4LIMS application development), the ASB R4LIMS coordinator, the SESD LAN Administrator, and the R4LIMS DBA. Access by the Contract Programmer and the ASB R4LIMS coordinator is limited and on an as-needed basis. The Contract Programmer only has rights to a development database and not the active R4LIMS database. The ASB R4LIMS coordinator has rights to certain tables in the active R4LIMS database for generation of custom reports. The SESD LAN Administrator and R4LIMS DBA have unrestricted rights to the database.

5.10.2.1 End-user access to the database is controlled through the compiled R4LIMS Powerbuilder application and the Allaire Coldfusion® web server (currently limited to read-only access of "public"data).

5.10.2.1.1 All R4LIMS application users are required to login to the system using an R4LIMS application USERID and PASSWORD. An R4LIMS PUBLIC account and the Coldfusion web server, both with limited access as described later are the only exceptions to this requirement. Otherwise, access is controlled by USERID, with varying rights assigned to each User.

5.10.2.1.2 Access to the EPA network and an account in R4LIMS is required for access to data for entry or reporting purposes.

5.10.2.1.3 Rights are assigned to each R4LIMS User upon request by their supervisor. Telephone requests will not be accepted. Rights are assigned by the ASB R4LIMS coordinator, the SESD LAN Administrator, or the R4LIMS DBA.

5.10.2.1.4 Users are restricted to certain functions within R4LIMS based on their need and job function. Immediate supervisors generally have rights equivalent to or greater than their subordinates as deemed appropriate. The R4LIMS DBA has the overall responsibility of security and functionality of the database. The ASB R4LIMS coordinator has the responsibility of security, accuracy, and integrity of the data in the database.

5.10.2.1.4.1 Project log entry is restricted to sample custodians, Region 4 Waste Division technical liaison, project leaders and their supervisor, and ASB QAO, and other project custodians as deemed necessary.

5.10.2.1.4.2 Modifications to project log entries are restricted to sample custodians and ASB QAO after the project has been entered.

5.10.2.1.4.3 Sample log entry is restricted to sample custodians and ASB QAO.

5.10.2.1.4.4 Data entry is restricted by Analysis Groups. Analysis Groups are groups of analysts responsible for producing segments of analytical data. Current Analysis Groups are:

5.10.2.1.4.4.1 Algal Assays: designated EAB staff

5.10.2.1.4.4.2 Toxicity Tests: designated EAB staff

5.10.2.1.4.4.3 Classical/Nutrients: designated Inorganic Chemistry staff

5.10.2.1.4.4.4 Metals: designated Inorganic chemistry staff

5.10.2.1.4.4.5 Extractables: designated Organic Chemistry staff

5.10.2.1.4.4.6 Volatiles: designated Organic Chemistry staff

5.10.2.1.4.4.7 Pesticides/PCBs: designated Organic Chemistry staff

5.10.2.1.4.4.8 Sediment Lab: designated EAB staff

5.10.2.1.4.4.9 Biological: designated EAB staff

5.10.2.1.4.4.10 FASP - Organic: designated Organic Chemistry staff

5.10.2.1.4.4.11 FASP - Inorganic: designated Inorganic Chemistry staff.

5.10.2.1.4.5 Final data verification and production rights are limited similarly to data entry but not necessarily to the same designated staff.

5.10.2.1.5 After a final production copy of the data is generated, the Inorganic and Organic Sections Chiefs, their assigned alternates, or the ASB QAO, Branch release their respective data.

5.10.2.1.6 After the data for a project has been Branch released the project leader gains read-only access to the analytical results for that project. This access is restricted to results for their own projects until the results have been released to the Public.

5.10.2.1.7 After the project leaders review the data, build data tables, and write their reports they have the option to release the data to the Public, facilitating any requests for data distribution by other interested parties.

5.10.2.2 The R4LIMS USERID (recorded from the login process) of the staff member performing the data verification, data production, Branch Release, or Public Release along with a date/time stamp is automatically recorded in R4LIMS.

5.10.2.3 Users without R4LIMS accounts can gain access to R4LIMS Data through a generic Public account in R4LIMS. This PUBLIC account requires no entry of USERID or PASSWORD. Public rights only allow for viewing and extracting information from the database that has been released to the public by a Project Leader.

5.10.3 After data has been released it can not be modified without being unreleased. For example; Corrections are required to an analytical result for a Volatiles analysis of a sample that has been Branch Released. That sample for Volatiles analysis must be

un-Branch Released by the Section Chief, un-produced and un-verified by the analyst in that order before the correction can be made. The sample must subsequently go back through the process of verification, production, and Branch Release.

5.10.4 The name of the analyst producing the data and the date/time stamp of production are printed on all production copies. Corrected copies are identified as amended copies displaying the date amended.

Figure 5-1
Analytical Data Standard Remarks

REMARK NUMBER	REMARK
101	Data Reported as Identified by CLP Lab - IDs Not Verified
102	Cyanide Analysis Not Requested
103	Data Is Provisional-Limited Precision & Accuracy Data
104	This Data Has Not Been Subjected to a QC Review--use for "Screening" Only!
105	CLP ICP-MS method does not include: Al, Ca, Fe, Mg, K, & Na
106	No Sample Container Received
107	Improper Sample Container Used
108	Sample Container Broken When Received
109	Sample Lost During Preparation or Analysis
110	Sample Improperly Preserved
111	Sample at Improper pH
112	Sample Received unPreserved; Holding Time & all other Criteria Met!
113	Canister Received at 760mm Pressure-Not Analyzed
114	Cannot Exceed TCLP Regulatory Levels based on Total Scan Analyses
115	Insufficient Sample for TCLP Extraction
116	Insufficient Sample Received for Analysis
117	Recommended Holding Time Exceeded:
118	Results Estimated-QC Limits Exceeded
119	Ar1242 Indistinguishable from 1248-calculated as Ar1242
120	Ar1248 Indistinguishable from 1242-calculated as Ar1248
121	Ar1248 Indistinguishable from 1254-calculated as Ar1248
122	Ar1254 Indistinguishable from 1248-calculated as Ar1254
123	Mixture of Aroclors in sample; predominant Aroclors Reported
124	Analysis Artifact - Dechlorination of Water Not Performed
125	BOD Result Estimated-Sample Exhibited Evidence of Toxicity
126	DOC Result higher than TOC result
127	Results Represent Analysis of Filtrate Only
128	Sample Distillation not required for Ammonia
129	Matrix Spike Recovery outside Method Acceptance Criteria for:
130	Matrix Precision outside Method Acceptance Criteria for:
131	Matrix Spike Precision outside Guidance Levels for:
132	Data Reported by Memo