

Section A

LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

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LABORATORY QA/QC GUIDELINES

1.0 INTRODUCTION

This chapter specifies essential QA/QC activities to enable laboratories to achieve reproducible results on an ongoing basis. The first part of Section E 'Microbiological Examination' discusses QA/QC as they pertain to microbiological methods.

Guidelines alone cannot guarantee high quality results. Common sense steps to avoid contamination, ongoing programs of staff training, and proactive method improvement procedures are also essential.

All laboratories should regularly participate in cooperative inter-laboratory studies, and standard reference materials should be analyzed frequently, preferably on a blind or semi-blind basis. Large laboratories should have a full time QA Officer.

The procedures for determining method detection limits and for handling blank corrections are controversial. Different procedures and calculation algorithms are being used by various laboratories.

2.0 GENERAL GUIDELINES

2.1 Quality Manual

A Quality Manual shall be set up that documents all resources, policies and procedures making up the Quality System. The Quality Manual is to include detailed descriptions of the topics outlined in this section and clearly define the responsibilities of management, supervisory staff, and laboratory staff with respect to the quality systems. It shall be reviewed and updated regularly.

2.2 Laboratory Record Keeping

The laboratory record system shall be designed to ensure sample, analytical data, and analyst traceability, including dates and analysts' initials or signatures. Dated and signed material shall include forms, instrumental records and printouts, as well as notebooks.

The sample numbering system of the laboratory must be designed to eliminate the possibility of a sample mix-up.

The record storage system should be designed for easy retrieval. A policy on the length of storage and disposal of records should be established.

2.3 Sample History Requirements

Documentation and procedures on sample history shall be maintained, including:

- sample collection
- field sample preparation
- chemical preservation
- sample containers
- holding times
- storage conditions
- condition of samples on receipt at laboratory

Potential deficiencies in sample history requirements shall be monitored and noncompliance must be identified and any affected analytical data flagged.

a. Sample collection

Documentation accompanying all samples should include a test requisition form, or should comply with chain of custody requirements.

b. Sample containers

Sample containers may be purchased pre-cleaned from commercial suppliers. Alternatively, sample containers may be cleaned and prepared by the laboratory using documented procedures. Contaminants or interferences in sample containers and preservatives should be monitored by the analysis of container blanks on a per-batch basis. Results of this monitoring should be documented. Container blanks may be prepared by leaching or rinsing containers with reagent water and performing analyses for the parameters of interest. It is recommended that the monitoring of sample containers for cleanliness be focused on 'low level' studies; i.e., where analytical results are anticipated to be <10 times MDLs (e.g., trace metals, dioxins).

c. Holding times

Refer to individual methods.

d. Storage conditions

Temperatures of refrigerated and frozen storage facilities shall be monitored and recorded daily.

e. Sample condition on receipt

Inspect sample containers for damage; record and report temperature on receipt where appropriate. Where critical, temperature limits should be established and maximum/minimum thermometers should accompany the samples to document compliance with the limits.

2.4 Sample Pre-treatment

Documentation on sample preparation and pre-treatment procedures shall be maintained, including:

- drying or removal of moisture.
- determination of moisture content.
- sub-sampling.
- preparation of geological samples including splitting, sieving, grinding, pulverizing.
- preparation of biological tissue samples.
- homogenization.
- filtration.

Complete records shall be maintained to ensure that potential problems, including cross-contamination, are traceable.

2.5 Test Methods, Existing

An inventory of methods shall be maintained that will include:

- all current methods.
- all previous methods.
- date of transition.

Test method and procedures documentation should include:

- analysis procedure in sufficient detail such that an experienced analyst, unfamiliar with the specific test procedure, should be able to perform the analysis.
- procedures for the preparation of reagent solutions and calibration standard solutions.
- operating instructions for instrumentation, which are supplemental to the manufacturer operating manuals.
- requirement for quality control sample preparation and analysis.
- current quality control criteria (i.e., acceptable limits).

Where data are kept on computer files, changes to methodology should be reflected by changes in related computer codes. A system should be established to review methods and documentation on an annual basis; the system should include periodic re-validation of methods when warranted, such as when personnel or equipment are changed

2.6 **Test Methods, New**

Methods should be periodically reviewed to ensure that the most up-to-date methods are being used. Test methods that are new to the laboratory, methods that have been developed in-house, and changes and modifications to existing methods must be validated. Validation should include determination of method detection limits, linear range, precision, recoveries, interference checks, and performance of equivalency testing where required.

2.7 **Equipment**

Equipment logs shall specify:

- manufacturer, model, serial number
- significant modifications
- repair and maintenance history
- calibration history
- performance history

Routine maintenance should be performed according to manufacturers' instructions and schedules.

Log books or other records shall be kept which record daily operating, calibration, and setup parameters.

Instrument operating procedures that supplement instructions given in the manufacturer's operating manuals should be documented.

2.8 **Analyst Qualifications**

Records of qualifications and experience shall include:

- copy of current resume
- records of training in new laboratory operations
- records of attendance at technical meetings and seminars
- records of completion of relevant courses (including in-house courses, night school classes, and courses sponsored by instrument manufacturers)

Initially, proficiency in the performance of an analysis new to the analyst should be demonstrated by the successful analysis of known samples, standards or certified material prior to the analyst being assigned routine analysis.

Continuing proficiency may be monitored through the analysis of routine quality control samples, certified materials, and performance evaluation samples, and also by participation in interlaboratory studies and blind audits.

2.9 **Reagents and Standard Solutions**

All chemicals shall be reagent grade or better, and must meet specifications identified in the test methods. Procedures for the preparation of reagent solutions and calibration standard solutions shall be included as part of the applicable analysis method.

Establish and maintain logs that document the preparation of reagents and standard solutions specifying:

- supplier, grade, batch number.
- if applicable, details on drying, mixing, etc.
- record of all laboratory operations performed and record of weights and volumes.
- all calculations.
- identity of analyst preparing the reagent or standard solution.

A file of certificates of standard solutions that have been obtained from commercial suppliers shall be kept.

Prior to routine use, and periodically throughout its shelf life, performance of a reagent or standard shall be verified. Compare performance of standard solutions by analysis of old and new solutions consecutively. Set criteria for the response of new versus old standard solutions.

All reagent solutions and standard solutions must be properly labelled. Labels shall identify material, concentration, date prepared and expiry date. Expiry dates will vary depending upon the solution and concentration. A general guideline for concentrated stock standard solutions is an expiry date of one year.

2.10 **Reagent Water**

Reagent water shall comply with ASTM D 1193-77, Standard Specification for Reagent Water, Type I, Type II, or Type III, or Standard Methods 18th Edition (1992), Section 1080 Reagent-Grade Water, Type I or Type II.

Reagent water must be free from chemical and microbiological substances that interfere with analytical methods. The presence of contaminants may be monitored for each test by the analysis of blank reagent water with each batch of samples. Microbiological evaluation may be performed by using a Total Plate Count.

The conductivity of reagent water should be recorded daily.

2.11 **Gravimetric Measurement**

Accuracy of gravimetric measurements shall be ensured by referencing calibrations to class S or S-1 weights. Annual balance calibration and daily calibration checks are required and records must be kept. ("S" and "S-1" are terms defined in NIST (formerly NBS) Circular 547).

2.12 **Volumetric Measurement**

The use of class A glassware will ensure accuracy of volumetric measurement.

Delivery volumes of automatic pipettes and diluters shall be checked on a routine basis and records of results maintained.

2.13 **Glassware Cleaning**

Up-to-date documentation shall be kept on all glassware cleaning procedures and requirements.

The effectiveness of cleaning may be monitored by the analysis of blanks using randomly selected glassware.

2.14 Contamination Control

Effective separation between laboratory areas of incompatible activity must be ensured.

Tests in progress and other laboratory operations should not interfere with or lead to contamination of other tests in progress. Scheduling of tests, and scheduling the use of fume hoods and other apparatus and facilities may be required.

The identity of samples and the order in which samples are analyzed on each instrument must be recorded, so that problems such as cross-contamination may be identified.

2.15 Calibration Practices

The accuracy and stability of calibrations is established by setting requirements for the following, as appropriate:

- equivalent standard/sample reagent backgrounds
- sufficient number of standards
- low standards (less than ten times the detection limit)
- reagent blanks used to zero response
- appropriate curve fit
- internal standards
- normalization standards
- control and verification standards to verify accuracy and stability
- associated control limits and specified corrective action

2.16 Quality Control Approaches

Appropriate quality control techniques applied to each batch of samples shall be recorded and documented. QC data must be made available to the client and it is encouraged that batch QC results be included in reports.

The type and number of quality control samples to be analyzed should be stated in the analysis method, or in a section in the overall Quality Manual.

Quality Control samples include:

- method blanks to monitor possible contamination
- duplicates to monitor precision (both inter- and intra-laboratory)
- certified reference samples to monitor accuracy
- internal reference samples to monitor accuracy
- analyte spikes to monitor recoveries
- surrogate spikes to monitor recoveries

Due to the diversity of tests and QC sample requirements, it is not possible to define overall requirements. However, based on an arbitrary sample batch size of ten samples, two examples (not recommendations) are:

a. Analysis of pH of water:

QC approach: run one sample in duplicate per batch

b. Analysis of copper in water:

QC approach: run one method blank per batch
run one sample in duplicate per batch
run one certified reference sample per batch

In general a level of QC in the range of 10-30% is considered appropriate.

2.17 Control Limits

Control charts for QC samples should be established. Control limits should be statistically based on data generated from QC samples in each laboratory. Initially, control limits can be set using values from external sources including Standard Methods and USEPA. Commonly used limits are: $\pm 2s$ for warning limits and $\pm 3s$ for control limits.

Corrective action must be taken when control limits are exceeded, and records of out-of-control events and actions taken must be maintained.

2.18 Expression of Results in the Final Report

It is good practice to report measurement uncertainty along with measurement results. When measurement uncertainty is reported, it should be as the 95% confidence interval.

Result \pm 95% CI

Many laboratories prefer to report results following the significant figures convention. When that convention is employed, the previous estimates should be based on its 95% confidence interval where practical.

Rounding of results should be deferred until the final calculation for reporting purposes. The ability to store data, to one more significant figure than would normally be the case, is of benefit to those undertaking statistical studies of data and its provision is encouraged.

The reporting convention of the analyte must be stated in unambiguous terms, but "+" and "-" symbols for ions need not be shown unless speciation has been effected. For example:

| | |
|-----------------|------------------|
| Copper | Cu |
| Nitrate | as N |
| Ortho-phosphate | as P |
| Silica | SiO ₂ |
| Sulfate | SO ₄ |

Units must also be expressed in unambiguous terms, for example:

| | | |
|------|------------------------------|----------------|
| mg/L | $\mu\text{g/g}$ (dry weight) | % (w/v) |
| | $\mu\text{g/g}$ (wet weight) | % (w/w)% (v/v) |

2.19 Performance Audits

Where facilities permit, internal audits should be conducted. Performance audits should incorporate blind or other samples in order to check functioning of laboratory QC procedures. This action may be helpful if external audits are imposed. Records of audit results and action taken should be kept.

2.20 Inter-Lab Comparison Studies

Participation in inter-laboratory comparison studies is recommended, as appropriate (e.g., BC EDQA program leading to registration or CAEAL program leading to certification). Records of results and action taken should be kept.

3.0 PROTOCOL FOR SETTING METHOD DETECTION LIMITS

3.1 Introduction

Method Detection Limits (MDLs) are set at the 95% confidence level above zero (or the blank - see section 4.0). For an infinite number of replications this is:

$$\begin{aligned} \text{MDL} &= 2 \times 1.645 \times \text{SD}_{\text{near zero}} \\ &= 3.29 \times \text{SD}_{\text{near zero}} \end{aligned}$$

where SD near zero is standard deviation estimate made within a factor of 10 of the (expected) MDL.

MDL for a smaller number of replicates is

$$\text{MDL} = 2 \times t_{1, 0.05} \times \text{SD}_{\text{near zero}}$$

where $t_{1, 0.05}$ = the one-tailed 't' statistic at $p = 0.05$ (see Table 1).

The standard deviation, SD, of a low level sample may be used to produce this estimate.

The sample used should have the following characteristics:

- i) the sample must be stable
- ii) it must have an analyte concentration that minimizes the overestimation of sigma-zero (σ_0), (the population standard deviation at zero)
- iii) it must have an analyte concentration that is sufficient to produce a measured value that is statistically significant

A concentration in the range of 1 to 3 times the anticipated MDL is recommended.

The standard deviation used to estimate σ_0 may be the within-batch standard deviations provided by duplicate or replicate samples carried through the sample processing steps, or the standard deviations of between-batch replicates.

Calculation of standard deviations should be based on:

- i) blank corrected data, if appropriate, and
- ii) at least 7 observations of the analytical result (sample size $n=7$).

The 't' statistic is used to compensate for the tendency of small sample sizes to underestimate variability.

3.2 Calculation of Standard Deviation

The formulae used to calculate standard deviation, SD, are as follows:

Case 1. duplicate analyses carried out in successive batches

$$\text{SD} = \text{sqrt} [\sum (x_1 - x_2)^2 / 2n]$$

where n = number of pairs of data.

Case 2. replicate analysis carried out in a single batch

$$SD = \sqrt{[\sum (x - x_i)^2 / 2n]}$$

where n = number of pairs of replicates.

Case 3. replicate analysis carried out in successive batches

$$\text{pooled SD} = \sqrt{[\{\sum (v_1 \times s_1^2) + (v_2 \times s_2^2) + \dots (v_i \times s_i^2)\} / (v_1 + v_2 + \dots v_i)]}$$

where v = degrees of freedom for each batch,
and s = standard deviation for each batch.

Examples of methods for estimating SD for MDL calculation:

1. Replicate analysis of a bulk sample of the desired matrix known to be homogenous and stable. Sub-sampling of the bulk sample is performed and each sub-sample is carried through the entire preparative and analytical step. Concentration is not to exceed 10 times the estimated MDL, but is preferred to be 1-3 times the estimated MDL. Estimate SD using formula case 2 for single batch analysis, and formula case 3 for multiple batch analysis.
2. If a bulk sample is not available, prepare a composite sample in the concentration range required. Continue as in 1.
3. If the above two are not possible, use duplicate analyses from several batches, adhering to the described concentration range. Use formula in case 1 for estimation of SD.
4. If the above three are not available, use a spiked blank or clean matrix, to produce a large sample. Take steps to assure the spike is homogeneously distributed (e.g. mixing overnight). Spike to a concentration not greater than 10 times the estimated MDL. Sub-sample this bulk spiked sample and carry each sample through all preparative and analytical steps. Use formula case 2 to estimate SD.
5. If facilities do not allow preparation of a bulk spike sample, spike individual blank or clean matrix samples to a concentration as defined above. Take steps to assure the spike is homogeneously distributed (e.g. mixing overnight). Continue as described above.
6. If no blank or clean matrix is available proceed as in 4 or 5 using pure de-ionized water as the matrix.
7. For methods which employ continuous monitoring of a detector signal, 3 times the noise in the area of the analytical peak can be used if none of the above can be used. This produces an estimate of instrument SD and does not take into account the contribution of preparative and matrix effects.

3.3 **Calculation of Method Detection Limits**

Section 3.2 demonstrates how method standards may be determined for three cases: from pairs of duplicates, from replicates in same batch and for pooled standard deviations from replicates in successive batches.

An example calculation of MDL is presented for each of these three cases:

EXAMPLE 1: MDL ESTIMATION FROM DUPLICATES

EXAMPLE 2: MDL ESTIMATION FROM REPLICATES IN SAME BATCH

EXAMPLE 3: MDL ESTIMATION FROM POOLED STANDARD DEVIATIONS FROM REPLICATES IN SUCCESSIVE BATCHES

These appear as Tables 2, 3 and 4 respectively. For each example the data have been organized in a format convenient for spreadsheet calculation.

3.4 **Recorded Figures**

MDLs should be recorded to one non-zero figure. Data used to estimate SD should be recorded to one or more additional figures, in order to reduce rounding errors in the SD estimate.

3.5 **Modifiers**

The MDL should be modified to describe how the data were obtained.

Instrument Detection Limit (IDL) - the data for determining the MDL are derived using only the instrument steps of the analysis: e.g., a GC analysis of pesticide solutions where no extraction step is used in obtaining the MDL data, and only repeated injection of the analyte in solvent is done, would be an IDL.

Method Detection Limit (MDL) - the data for determination of MDL was obtained by carrying replicate samples individually through all preparative and analytical steps.

MDL should be further defined to indicate the matrix to which it applies and matrix upon which it was determined.

Examples are:

- MDL soil - method MDL intended for use with soil samples and determined on soil matrix.
- MDL soil/water - method MDL intended for use with soil samples BUT determined using water matrix.
- MDL soil/calc - MDL for soil calculated from the dilution factors of a water MDL.

Additional modifiers could be used for plants, animal tissue, water dissolved, water total. It is necessary to accept different types of MDLs because, for example, there may be insufficient sample or no clean matrix to run method MDLs in all situations.

3.6 **Limit of Quantitation**

The limit of quantitation (LOQ) is less rigorously defined as 10 times SD (at MDL). The LOQ is the concentration at which quantitative results are possible (precision approaches $\pm 30\%$). At the MDL, on the other hand, the presence of the analyte is defined with certainty but its concentration cannot be defined (precision approaches $\pm 100\%$).

3.7 **Confidence Interval Convention**

The MDL definition described here (and used by CAEAL) uses a factor of 2 x the one sided 't' factor at $p = 0.05$. For an infinite sample size, this would be $MDL = 3.29 \times SD$. This is the sum of two distributions: one centered on 0 (zero) has a 5% risk of declaring a null quantity as a positive amount, while the other distribution, centered above 0, involves a 5% chance of declaring a measurement as 0, when in fact, it is real (see figure 1).

The MDL definition given at the bottom of Tables 2,3 and 4 is the USEPA convention. This definition uses the one-sided 't' factor for $p = 0.01$. For an infinite sample size, this would set the $MDL = 3 \times SD$. This is derived from a single distribution, centered on 0 (zero) and having a 1% risk of declaring a null quantity as a positive amount.

The two MDLs, while derived from different theory, are in fact very close. The USEPA derived MDLs include lower and upper limits; the CAEAL value always falls within those limits.

3.8 Rules for Reporting Summed Parameters

1. The DL of a Summed Parameter shall be equal to the sum of the DLs of all the component results that comprise the Summed Parameter.
2. The reported numerical result for a Summed Parameter shall be equal to the numerical sum of the component results that comprise the Summed Parameter. Any component result of "<DL" shall be treated as zero.
3. Standard protocols for reporting and interpretation of low level results shall apply.
eg: A summed result of 0.05 with a detection limit of 0.10 shall be reported and interpreted as <0.10. A high degree of variability near the DL is to be expected.
4. It is important that the detection limits for component parameters are reasonable estimates of the method detection limits (determined following the BC Ministry Laboratory Manual protocols).
5. Wherever possible, summations shall be done using raw, un-rounded results.

It should be noted that protocols described above follow a simplistic approach, and can under-estimate the total concentration of any summed parameter by up to 1 x the DL of the summed parameter (i.e. if all <DL component results were actually = DL). This underestimation is deemed acceptable, since variability of up to $\pm 100\%$ at the MDL is normal by definition.

4.0 **BLANKS**

While there are few situations where blank correction is appropriate, monitoring of blanks should be carried out for most samples and blanks should be controlled within defined limits for data to be acceptable.

4.1 Documentation of Blanks

Batch blank values shall be recorded on the analytical result sheet with each batch. In addition, a tabulation of day-to-day blanks shall be maintained and kept current. It will include, at a minimum, analytical date, preparative and analytical operators' initials, individual blank values, a reference to the long term blank and the date range over which it was determined, and any comments explaining unusual occurrences. If possible a control chart of batch blanks will be maintained.

4.2 Determination of Long Term Blank

The long term blank should be estimated, on at least 2 separate occasions, from replicate blank matrices which have been processed through all the preparative and analytical steps applied to a regular sample. It is suggested that 10 replicate blanks be processed on each occasion. The long term blank value should be confirmed at least once each year.

The average and standard deviations of blank readings should be calculated for each occasion. Pooled blank average and standard deviations should be calculated using the following formula (Taylor, 1987):

Pooled Standard Deviation (σ) =

$$\text{sqrt} [\sum \{ (v_1 \times s^2_1) + (v_2 \times s^2_2) + \dots + (v_n \times s^2_n) \} / (v_1 + v_2 + \dots + v_n)] \quad (1)$$

where s_n = standard deviation for n^{th} case,
 v_n = degrees of freedom, usually = $n - 1$.

Test for outliers using the Grubbs test (Taylor, 1987). If outliers are present, remove them and re-calculate the average and standard deviation as above.

4.3 Application

Blank correction should be applied to every sample for which a reliable estimate of long term blank levels has been made (i.e., the blank is in statistical control).

Blank correction should be applied to all samples where the batch method blank(s) exceeds the method detection limit (MDL), and is less than the long term blank control limits.

Samples with concentrations greater than 20x the batch blank, need not be blank corrected (US EPA, 1990).

4.4 Evaluation of batch blanks

If all batch blanks are <MDL, no blank correction is necessary.

4.4.1 Where the long term average batch blank is known.

If all batch blanks are greater than the MDL and less than the control blank limit, all batch samples for that parameter should be corrected by subtracting the average batch blank.

The control blank limits will be set as the long term average method blank plus 1.64 times the standard deviation of the long term average blank.

If the long term average blank is <MDL, the control blank limits will be set as MDL plus 1.64 times the standard deviation of the long term average blank.

This control limit should include approximately 95% of the blank values that will occur.

If the estimate of the long term blank is based on <100 determinations, the appropriate 't 0.05' value from the table of 't' values is substituted for 1.64.

If any batch blank exceeds the long term blank control limit, the batch must be reprocessed.

If this is not possible due, for example, to insufficient sample, or instability of the sample, the parameter results can be blank corrected, but must be flagged in the report as having "High blank, subtraction made, accuracy of results may be compromised".

If multiple parameters are analyzed for the same sample preparation batch, and if more than 5% of the parameters exceed the blank control limits, the batch must be re-processed; e.g., for ICP total metals scans (33 elements), if more than 2 parameters have blank levels greater than blank control limits, the batch must be re-processed. Otherwise the parameters greater than blank control limits can be reported with a flag stating "High blank for parameter XX, subtraction made, accuracy of results may be compromised".

Criteria Concentration

Action to take

Batch blank ≤ MDL

no correction

| | |
|---|-----------------|
| Batch blank > MDL | blank correct |
| Batch blank > long term blank control limit | reprocess batch |
| Sample concentration > 20 x batch blank | no correction |

4.4.2 Incorporation of batch blank into calibration curve

If the batch blank is part of the calibration curve, this effectively corrects for the blank provided the linearity of the calibration curve is not destroyed.

If the batch blank deviates from the linear best fit line, calculated excluding the blank, by greater than 50%, the batch blank is too high, and the batch must be re-processed.

4.4.3 Situation where long term blank is not known:

If all batch blanks are <MDL, no blank subtraction is necessary.

If all batch blanks are greater than the MDL and less than 10X the MDL, all batch samples for that parameter may be corrected by subtracting the average batch blank.

If any batch blank exceeds 10 times the MDL, the batch must be reprocessed.

If this is not possible, due, for example, to insufficient sample, or instability of the sample, the parameter results can be blank corrected, but must be flagged in the report as having "High blank, subtraction made, accuracy of results may be compromised".

4.4.4 Readable units

Where the batch blank fails the blank control limit test by \leq one readable unit, the batch blank shall be considered acceptable.

4.5 Documentation of Blank QC

Batch blank values are to be recorded on the analytical result sheet with each batch. In addition, a tabulation of day to day blanks shall be maintained and kept current. It will include, at a minimum, analysis date, preparative and analytical operators initials, individual blank values, a reference to the long term blank and the date range over which the long term blank was determined as well as any comments explaining unusual occurrences. If possible a control chart for batch blanks is to be established and maintained.

Analytical reports to clients must indicate whether or not data has been blank corrected. In addition, the reports must indicate batch blank levels for the data, regardless of whether blank correction has been applied.

4.6 Blank Correction Summary

Blank correction is rarely appropriate when these rules are followed, since at high analyte concentrations the correction is insignificant and at low levels (near MDL), the blank, whether subtracted or not, merely increases the uncertainty of the value.

5.0 QC FOR SMALL LABORATORIES

While all laboratories are encouraged to implement a comprehensive QA program, it is recognized that small laboratories with limited resources may find it economically necessary to implement a less comprehensive program.

This section is relevant only to small permittee laboratories that participate in the CAEAL laboratory proficiency-testing program and who have achieved a PE score greater than 70 for each applicable variable in the last four studies and who generally analyze only small batches of samples.

A small batch is defined as less than 11 samples analyzed at one time as a group using a common blank, standards and duplicate data. In cases where a laboratory receives only a few samples per day, and sample stability or treatment permits, it is preferable that samples be stored and run as one small batch on a weekly basis. If stability does not permit, the samples should be analyzed on a daily basis.

5.1 **Small Laboratory Quality Control Level**

a. Group samples (e.g. colorimetric methods)

- one method blank per batch
- one duplicate sample per batch
- one certified reference sample per batch (internal recovery control)

b. Individual sample (e.g. NFR, pH, BOD, AOX)

- one blank daily
- one duplicate per 10 samples (minimum 1 per week)
- one certified reference sample or internally prepared recovery control per 10 samples (minimum 1 per week)

5.2 **Small Laboratory Quality Control Criteria**

a. Calibration control limits of $\pm 2s$ as a warning limit and $\pm 3s$ as a control limit are applicable for quality control standards for most variables.

b. Method blanks

- If the batch blank is \leq MDL, no blank subtraction is necessary.
- If the batch blank exceeds the MDL, refer to sections 4.3 and 4.6 above.

c. Duplicates for water and wastewater must be within the precision limits given in Table 1020:I of Standard Methods, 18th Edition (1992).

d. Internal recovery control must be within the precision limits given in Table 1020:I of Standard Methods 18th Edition (1992).

6.0 **REFERENCES**

6.1 **QA/QC General**

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6.2 **Method Detection Limits**

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6.3 **Blank Correction**

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7.0 **REVISION HISTORY**

February 14, 1994
December 31, 2000

Initial publication

Republication: additional text added to 2.18; item 3.4 clarified; definition of 'significant figures' added to glossary. Revision history added. Several editing changes to clarify items. Rules for reporting summed parameters was added as requested and with wording approved by the BCLQAAC Technical Subcommittee. Reference to the EDQA laboratory proficiency testing was replaced by reference to the CAEAL laboratory proficiency testing program. M. Clark 2000 citation added to References.

TABLE 1: VALUES OF THE ONE-TAILED 't' STATISTIC AT p=0.05, APPLIED TO THE STANDARD DEVIATION, SD, APPEAR IN THE FOLLOWING TABLE:

| <u>Degrees of Freedom</u> | $t_{1, 0.05}$ |
|---------------------------|---------------|
| 7 | 1.90 |
| 8 | 1.86 |
| 9 | 1.83 |
| 10 | 1.81 |
| 15 | 1.75 |
| 20 | 1.73 |
| 25 | 1.71 |
| 30 | 1.70 |
| 40 | 1.68 |
| 60 | 1.67 |
| infinity | 1.64 |

For case 1, duplicates, degrees of freedom = n, the number of pairs of duplicates,

For case 2, replicates in same batch, degrees of freedom = n - 1, where n = the number of replicates,

For case 3, pooled SD from replicates in successive batches, degrees of freedom = sum of $v_1 + v_2 + \dots + v_j$.

TABLE 2: EXAMPLE 1: MDL ESTIMATION FROM DUPLICATES

MDL determination for Carbon in Soil Samples

Parameter: Total Carbon, Leco Matrix: Soil, sediment
 Sparcode: C--T Units: $\mu\text{g/g}$

Procedure Results for duplicates analyses of soil samples on different days were recorded.
 All data are less than 10x the MDL.

| Sample # | result 1 | result 2 | difference | difference ² |
|----------|----------|----------|------------|-------------------------|
| 4486 | 4100 | 4600 | 500 | 250000 |
| 262 | 5200 | 5300 | 100 | 10000 |
| 25074 | 2600 | 2200 | 400 | 160000 |
| 25080 | 3500 | 3700 | 200 | 40000 |
| 25090 | 1600 | 1500 | 100 | 10000 |
| 25099 | 2000 | 2300 | 300 | 90000 |
| 26011 | 2100 | 2100 | 0 | 0 |

SD dup = $\sqrt{\text{difference}^2 / (2 \times \# \text{ of duplicates})}$ 200

MDL = SD dup x 2 x t 0.05, t (df = 7)
 = SD dup x 2 x 1.895
 = 758

TABLE 3: EXAMPLE 2: MDL ESTIMATION FROM REPLICATES IN SAME BATCH

MDL determination for BTEX in soil samples

Sparcode: BTEXF092 Matrix: Soil units: µg/g
 Instrument: HP5890A/FID GC#5 Operator: *** MDL listed = 1
 Prep. Extract 5 g with Freon Date: 7-Jul-93

5 g of sea sand was spiked to 10 µg/g with BTEX standard, mixed, sealed in a purge & trap vial, and retained for 2 days in freezer. The samples were then individually processed. m,p-Xylene was spiked at 20 ug/g.

| | Benzene | Toluene | m- & p-Xylene | o-Xylene |
|-----------------------------------|---------|---------|---------------|----------|
| | 8.978 | 8.936 | 18.182 | 9.130 |
| | 8.280 | 8.340 | 16.980 | 8.560 |
| | 7.578 | 7.654 | 16.282 | 8.250 |
| | 5.732 | 6.184 | 14.076 | 7.230 |
| | 5.428 | 5.662 | 12.960 | 6.682 |
| | 8.924 | 8.864 | 18.074 | 9.088 |
| | 6.434 | 6.602 | 14.308 | 7.276 |
| | 8.668 | 8.494 | 17.244 | 8.642 |
| | 6.624 | 6.896 | 15.318 | 7.804 |
| average | 7.405 | 7.515 | 15.936 | 8.074 |
| std dev | 1.389 | 1.221 | 1.867 | 0.873 |
| count | 9 | 9 | 9 | 9 |
| MDL | 5.1668 | 4.5407 | 6.9451 | 3.2464 |
| MDL (1 sig fig) | 5 | 5 | 7 | 3 |
| MDL (USEPA) =2.896 x SD | 4 | 4 | 5 | 3 |
| LCL (USEPA) =0.72 x MDL | 2.9 | 2.5 | 3.9 | 1.8 |
| UCL (USEPA) =1.65 x MDL | 6.6 | 5.8 | 8.9 | 4.2 |

TABLE 4: EXAMPLE 3: MDL ESTIMATION FROM POOLED STANDARD DEVIATIONS FROM REPLICATES IN SUCCESSIVE BATCHES

Parameter: Cd-D **Units:** mg/L **Instrument:** Varian GFAA in ppb mode.

Cd MDL for GFAA - attempt to achieve 0.1 ppb

| Date | Between day data. | | | | |
|----------|-------------------|----------|----------|----------|----------|
| | conc 1 | conc 2 | conc 3 | conc 4 | conc 5 |
| design | 0.00000 | 0.00050 | 0.00240 | 0.00060 | 0.00120 |
| 10-Sep | 0.00002 | 0.00048 | 0.00238 | 0.00065 | 0.00116 |
| 14-Sep | -0.00001 | 0.00055 | 0.00256 | 0.00066 | 0.00126 |
| 15-Sep | 0.00000 | 0.00049 | 0.00242 | 0.00065 | 0.00124 |
| 15-Sep | -0.00002 | 0.00047 | 0.00242 | 0.00069 | 0.00138 |
| 16-Sep | -0.00001 | 0.00054 | 0.00252 | 0.00067 | 0.00136 |
| 17-Sep | 0.00000 | 0.00052 | 0.00234 | 0.00070 | 0.00124 |
| 19-Sep | 0.00000 | 0.00049 | 0.00249 | 0.00068 | 0.00119 |
| 21-Sep | -0.00001 | 0.00052 | 0.00247 | 0.00065 | 0.00120 |
| 23-Sep | -0.00001 | 0.00053 | 0.00247 | 0.00067 | 0.00122 |
| 23-Sep | 0.00001 | 0.00050 | 0.00235 | 0.00064 | 0.00121 |
| 24-Sep | -0.00002 | 0.00054 | 0.00246 | 0.00068 | 0.00128 |
| 25-Sep | -0.00001 | 0.00046 | 0.00255 | 0.00065 | 0.00127 |
| 28-Sep | 0.00000 | 0.00047 | 0.00242 | 0.00057 | |
| 30-Sep | | 0.00046 | 0.00238 | 0.00065 | |
| 1-Oct | | 0.00040 | 0.00233 | 0.00068 | |
| average | -0.000005 | 0.000495 | 0.002437 | 0.000659 | 0.001251 |
| std dev | 0.000011 | 0.000040 | 0.000074 | 0.000030 | 0.000066 |
| count | 13 | 15 | 15 | 15 | 12 |
| MDL mg/L | 0.000040 | 0.000141 | 0.000260 | 0.000107 | 0.000236 |
| MDL µg/L | 0.040 | 0.141 | 0.260 | 0.107 | 0.236 |

Based on a single concentration.

Design >10x MDL >10x MDL
Note: conc'ns. 3 & 5 are too high & not used to calculate MDL.

Pooled sd 0.00003 with 40 df for blank, 0.0005, and QCB.
 The pooled standard deviation for other 3 concentrations is

$$\text{Pooled sd} = \sqrt{((n1-1) \times sd1^2 + (n2-1) \times sd2^2 + (n4-1) \times sd4^2) / ((n1-1) + (n2-1) + (n4-1))}$$

 MDL from pooled sd: 0.00010242

MDL (CAEAL), µg/L (1 sig. fig.): 0.1

USEPA MDL, µg/L 0.07 lower control limit 0.05; upper control limit 0.12

Note: Pooling of standard deviations is appropriate over concentrations up to 10 x the MDL, and over several days of data acquisition.

GLOSSARY OF STATISTICAL TERMS USED IN QUALITY ASSURANCE

Accuracy - indicates the closeness of a measured value to a true value; combines bias and precision.

Bias - consistent tendency of measured value to deviate, either positively or negatively, from a true value.

Calibration check standard - standard, usually mid analytical range, used to monitor the validity of instrument calibration between periodic full recalibration.

Confidence coefficient - the probability, expressed as a percentage, that a measurement result will reside in the confidence interval (between the confidence limits).

Confidence interval - the set of possible values within which the true value will reside with a stated probability level.

Confidence limit - upper or lower boundary values delineating the confidence interval.

Detection limits - various limits are defined; in increasing order these are:

Instrument detection limit (IDL) - the analyte concentration that produces a response five times greater than the signal/noise ratio of the instrument. This is similar to the "criterion of detection" which is defined as 1.645 times the standard deviation, s , of blank analyses.

Lower limit of detection (LLD) - also called "detection limit" (DL) and "limit of detection" (LOD)- the analyte concentration in reagent water that produces an instrument response $2(1.645)s$ above the mean of blank analyses. This criterion sets the (maximum?) probability of both Type I and Type II errors at 5%.

Method detection limit (MDL) - the analyte concentration that, when processed through the complete method, produces an instrument response with a 99% probability that it is non-blank.

Limit of Quantitation (LOQ) - the analyte concentration that produces an instrument response sufficiently greater than the response by the blank that it can be measured within specified accuracy limits by competent laboratories in routine operation. Typically it is regarded as the analyte concentration that produces a response ten times greater than the standard deviation, s , of the reagent water blank signal.

Duplicate - least case of replicates (two); in general, while any portion of the analytical protocol can be duplicated, the term duplicate is usually applied to duplicate samples, i.e. two samples taken at the same time from the same location.

Internal standard - a pure compound different from, but similar enough to, the analyte, that, when added at a known concentration to the sample extract immediately prior to instrumental analysis, allows corrections due to instrument inefficiencies or vagaries.

Laboratory control standard - a standard, optimally certified by an outside authority, used to measure method bias.

Precision - gauge of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation.

Quality assessment - procedure for determining the quality of laboratory data using internal and external quality control measures.

Quality assurance - a system of laboratory operation that specifies the measures used to produce data of documented accuracy.

Quality control - a set of procedures applied to an analytical methodology to demonstrate that the analysis is in control.

Random error - the deviation experienced in any step of an analytical procedure that can be estimated by standard statistical techniques.

Replicate - repeated operation of part of an analytical procedure. Two or more (instrumental) analyses for the same analyte in a processed sample are termed replicate extract analyses.

Significant figures - A convention of reporting numeric results where all digits in result are known without doubt, except for the right-most figure.

Surrogate (or surrogate standard) - a pure compound different from, but similar enough to, the analyte that, when added at a known concentration to the sample prior to processing, provides a measure of the overall efficiency of the method (recovery).

Type I error - also called alpha error, is the probability of deciding an analyte is present when it actually is absent.

Type II error - also called beta error, is the probability of deciding an analyte is absent when it actually is present.