Standard Operating Procedure

Documenting Data Quality

SOP #8200.1H

June 2013

Nebraska Health and Human Services
Public Health Environmental Laboratory

Written By: Laurie Wietjes Date: 6/19/13
QA Manager

Approved By: Mary F. Boder Date: 6/19/13
Laboratory Manager

Annual Review

Reviewed By	Date	Approved By	Date
Sandra Ivens	10/1/14	Laurie Wieting Mary Boden	10-1-2014 10-1-14
Laurie Wieting	10-7-2015	Mary Boden	10-7-15
Laurie Wieting	2-13-2017	Mary Boden	2-13-17
Laurie Wieting	2-20-2018	Mary Boden	2-20-18

2-16-16 added instrument to attachments C & D. MB2-16-16

TABLE OF CONTENTS

1. PURPOSE

The purpose of this standard operating procedure (SOP) is to establish uniform procedures and guidance for defining, calculating, documenting and tracking the quality of data (in quantitative terms) generated at the DHHS PHE Laboratory and for implementing a process which will provide for the accumulation of meaningful and beneficial data quality information that will support the data. The resultant data quality information will assist in making decisions, in evaluating analytical results, identifying data quality problems, and in recommending corrective actions relating to data quality. Topics not specifically addressed in this SOP can be found in method specific SOPs. For additional data quality guidance in support of the drinking water program, see *EPA Manual for the Certification of Laboratories Analyzing Drinking Water. EPA815-B-97-001*

2. APPLICATION / GENERAL POLICIES

2.1 The procedures and guidelines contained in this document are applicable to all activities performed by the DHHS PHE Laboratory. Users of this SOP should have some understanding of basic statistics.

2.2 One of the primary goals of the DHHS PHE Laboratory is to provide data of known quality to all customers. The procedures established in this SOP are intended to provide the basis for ensuring that this goal is met. As a minimum, this data must be supported with documented evidence that:

2.2.1 All laboratory and analytical procedures used to collect the data are documented so the work could be reproduced by others skilled in the art.

2.2.2 All methods and equipment were working properly when the data were collected.

2.2.3 There was not a significant amount of contamination.

2.2.4 The methods were capable of producing the values reported (concentrations are above reporting limit and below maximum of calibration curve, for example) and the precision and bias of the data are acceptable for the intended use.

2.3 The documentation of data quality will be accomplished by maintaining the following information:

2.3.1 Standard Operating Procedures for all laboratory functions, from kit preparation through analysis, to data reporting and archiving.

2.3.2 Description of all data review and data reporting procedures (See current version of SOP #8320.1).

2.3.3 Evidence that each of the procedures were in control during the measurement/data generation process. (Internal quality control checks and quality control monitoring).

2.3.4 A measure of the precision and accuracy of the data to satisfy the data quality objectives.

2.4 All quality records will be maintained according to current version of SOP #1500.1.

2.5 Overall quality of the environmental data will be reviewed periodically by the QA Manager.

3. BASIC TERMS AND CONCEPTS

3.1 Definition of Terms

Since some of the terms used in this document may have different meanings or interpretations for different audiences, it is essential that they be clearly defined so that their use is understood by the users of this document. To this end, the following definitions are provided:

3.1.1 **Laboratory Reagent Blank (LRB)** = Laboratory Blank

An aliquot of reagent water that is treated exactly like a sample including exposure to all glassware, equipment, solvents, reagents, etc. This is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.1.2 **Laboratory Fortified Blank (LFB)** = method standard

This is an internal quality control step. An aliquot of known quantities of the method analytes is added to a laboratory reagent blank. This is analyzed exactly like a sample, and the purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.1.3 **Laboratory Control Sample (LCS)** = Quality Control Sample (QCS) = external QC

A solution of method analytes of known concentrations. It is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance.

3.1.4 **Laboratory Fortified Sample Matrix (LFM)** = Matrix Spike (MS)

An aliquot of a sample matrix to which known quantities of the method analytes are added in the laboratory. This is analyzed exactly like a sample, and its purpose is to determine if the sample matrix contributes bias to the analytical results.

3.1.5 **Duplicate Fortified Sample Matrix (LFM/DUP)** = Matrix Spike Duplicate (MSD)

A second replicate of a sample matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision associated with laboratory procedures.

3.1.6 **Reporting Limit**. The reporting limit (RL) for an analyte is the concentration

represented by the lowest level in the initial calibration curve where the analyte is detected. This concentration is typically approximately three times the MDL. The reporting limit is reported and in most cases accompanied with a "<" when the analyte in question is not detected in the sample or is detected at a concentration less than the reporting limit.

3.1.7 **Method Detection Limit (MDL)** This term refers to the quantitative expression for the minimum concentration of a substance that an analytical method is capable of detecting and quantifying with 99% confidence that the concentration of the substance is greater than zero. The MDL is an essential indicator, in conjunction with bias and precision, for determining the capability of an analytical method to reliably detect chemical constituents in the concentration range of interest. The MDL is determined from the analysis of replicate samples in accordance with the procedures outlined in Title 40, Code of Federal Regulations (CFR), Part 136, Appendix B.

3.2 Concepts

3.2.1 **Precision.** This data quality characteristic is the quantitative expression of the amount of scatter among individual measurements replicated under prescribed conditions. Precision (sometimes also referred to as reproducibility) provides an indication of the capability of a measurement system to generate reproducible results from repeated measurements. Precision is usually expressed as a relative percent difference. The calculations are performed using the analytical results from duplicate samples or matrix spike duplicate samples. The analytical results for specific parameters are usually measured at concentrations above the reporting limit. Method Precision is based on the analytical results of laboratory duplicate samples and/or matrix spike duplicate samples.

3.2.2 **Bias.** This data quality characteristic is the quantitative expression of the degree of agreement or closeness of an individual measurement or the average of a number of measurements to a true or known value. Sometimes referred to as the measurement of systematic error, bias provides an indication of how closely a measurement system can estimate the true value of a chemical constituent in the environment. Bias calculated for a single sample is expressed as Percent Recovery (%R).

3.2.3 **Accuracy.** Accuracy is the level of agreement of a measurement with the true of expected concentration. When applied to a set of observed values, accuracy will be a combination of a random component and a systematic (bias) component. Analytical accuracy is expressed as the percent recovery (%R) of an analyte which has been used to fortify an investigative sample or a standard matrix at a known concentration prior to analysis.

4. INITIAL DEMONSTRATION OF CAPABILITY (IDC) AND DETERMINING METHOD DETECTION LIMITS (MDLs)

4.1 Initial Demonstration of Capability (IDC)

4.1.1 The IDC is used primarily to preclude a laboratory from analyzing unknown samples via

a new, unfamiliar method prior to obtaining some experience with it.

4.1.2 Select a representative fortification concentration for each of the analytes of interest. Refer to Attachment A and Attachment B to properly prepare appropriate spiking levels, and meet all of the MDL requirements. Analyze the LFBs according to the method. A LRB must be extracted and analyzed also to demonstrate that all glassware and reagent interferences are under control. Double check your calculations and complete a common sense check on all the data.

4.1.3 Calculate the mean percent recovery and the standard deviation of the recoveries. Each analyte must meet method specific acceptance criteria. For those compounds that fail, this procedure must be repeated using at least 4 fresh samples until satisfactory performance has been demonstrated.

4.2 Determining Method Detection Limits (MDLs)

MDLs will be determined using 40 CFR Part 136, Appendix B – Definition and Procedure for the Determination of the MDL – Revision 1.11. This document can be found as Attachment A.

4.3 Method implementation

4.3.1 The above IDC and MDL studies will be submitted to the Lab manager in report form (including all raw data) for review and then given to the QA manager for approval, and storage in the QA records. The SOP will then be prepared and submitted for review and approval.

4.3.2 If the IDC is for a new method not currently certified by EPA, the IDC will be sent to EPA, Region 7 for review and approval. If approved, a blind sample will be completed. If the sample is correct, the Laboratory is given "interim" certification until the next lab on-site evaluation when the auditors will review the method.

4.3.3 If the IDC is to demonstrate that a new instrument is capable of the same quality data or a new analyst is in charge of the method, the above documentation is completed but kept in house and approved by the QA manager.

4.3.4 Complete a Proficiency Documentation form (Appendix C) for each method to document completion of the upfront training process and an IDC form (Appendix D) if this method requires IDC documentation prior to testing compliance samples, if this is a new instrument or method being put into service, or a new analyst completing instrument training.

4.3.5 Be sure to attach all of your raw MDL data with your IDC form in an easily readable format so any auditor can review the data and understand what you did.

4.3.6 When completed give to the Laboratory Manager for review. Once it has been approved it will be given to the QA Manager for approval.

5. DOCUMENTING STATISTICAL CONTROL

5.1 QC Control Charts

Two types of control charts commonly used in environmental laboratories are as follows: **accuracy or means charts** for QC samples (LCS, LFB, LFM); and **precision or range charts** (duplicate analysis). These charts are essential tools for quality control that reveal important information about accuracy and precision. The DHHS PHE laboratory QC charts requires the accuracy (means) chart type.

5.1.1 Definitions for Means Control Chart

Upper Control Limit (UCL): + 3s or + 3σ (+ 3 standard deviations)
Lower Control Limit (LCL): - 3s or - 3σ (- 3 standard deviations)
Upper Warning Limit (UWL): +2s or +2σ (+ 2 standard deviations)
Lower Warning Limit (LWL): -2s or - 2σ (- 2 standard deviations)

The control limits used for DHHS PHE Lab QC Charts will be +/- 3s.
The control chart will also contain the +/- 2s warning limits.

5.1.2 Set up a means control chart by using calculated percent recoveries as discussed in your SOP. Refer to your protocol for specific requirements. Construct a control chart for each measured target analyte. QC charts are updated by the Horizon LIMS as each test batch is completed. NOTE: The method acceptance limits should be the control limits from this historical data or the EPA method, **whichever is stricter**.

5.2 Interpretation of QC Chart Data

5.2.1 If any **one** QC sample measurement exceeds the control limit **(+/- 3s)**, repeat the measurement in the analysis sequence. If the repeat measurement is within the control limits, continue analysis; if it exceeds the control limit, discontinue the analyses and correct the problem.

5.2.2 If any **two** successive QC sample measurements exceed the warning limits **(+/-2 s)**, analyze another sample. If the next point is within the warning limit, continue analyses; if the next exceeds the warning limit, evaluate potential bias and correct the problem.

5.2.3 If four out of five successive points exceed one standard deviation, or are in decreasing or increasing order, analyze another sample. If the next point is less than 1 standard deviation or changes order, continue the analysis; otherwise, discontinue the analysis and correct the problem.

5.2.4 If seven successive QC samples are on the same side of the central line (mean line), discontinue analyses and correct the problem Upward or downward data trends may be a result of deteriorating reference material sample or an instrument related calibration problem. Shifts of data points above or below mean can indicate serious systematic error from analytical bias

(inaccuracy) in calibration reference material. Trends indicate systematic error; random error is revealed when measurements randomly exceed warning or control limits.

5.2.5 Outliers

5.2.5.1 When an outlier is suspected, the first action taken by the analyst is to critically look at all aspects of the measurement process. Outliers may be an indication of arithmetic miscalculation, transcription errors, or malfunctions of the measurement system.

5.2.5.2 If the analyst does not find a process error for rejection of the data point, the analyst can then use a statistical test to confirm the suspicion of outliers. This test gives a statistically supported approach to reject or retain the suspected outlier.

5.2.6 Corrective Actions- Quality control data outside control acceptance limits or exhibiting a trend are evidence of unacceptable error in the analytical procedure. Take corrective action promptly to determine and eliminate the source of error. Do not report data until the cause of the problem is identified and either corrected or qualified (valid data qualifiers). Maintain records on data review document (or run summary) of out-of-control events, determined causes, and corrective actions.

5.3 The stability of the measurement process must be investigated and documented on a daily basis. Quality control samples are analyzed with every batch of samples to provide documentation of the stability and control of the measurement process. The QC samples must be carried through the entire analytical process.

5.4 The analysis of a LCS or LFB with each batch of samples allows for the demonstration and documentation of statistical control of the measurement process on a daily basis.

6. STATISTICAL CALCULATIONS

6.1 Precision

The RPD is calculated by expressing as a percentage the difference between results of analysis of duplicate samples or matrix spike duplicates relative to the average of those results for a given analyte. This lab analyzes a laboratory duplicate or LFMDUP every batch of samples. RPD is used to pass or fail this duplicate. This measurement can be expressed by the following formula:

$$\%RPD = \frac{(C1 - C2)}{(C1 + C2)/2} \times 100$$

Where: RPD = Relative Percent Difference
C1 = Concentration of analyte in sample
C2 = Concentration of analyte in replicate

When calculating %RPD for LFMs, substitute LFM and LFMDUP values for C1 and C2.

6.2 Accuracy

6.2.1 Analytical accuracy is expressed as the percent recovery (%R) of an analyte which has been used to fortify an investigative sample or a standard matrix at a known concentration prior to analysis, and is expressed by the following formula:

$\%R = 100 \times (Xt / T)$ or $\%R = 100 \times (Xs - Xu) / K$

Where: Xt = measured value for reference value
Xs = measured value for spiked sample
Xu = measured value for unspiked sample
K = known value of the spike in the sample
T = true value

6.2.2 Bias is the deviation due to matrix effects of the measured value (Xx - Xu) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$B = Xt - T$ or $B = (Xs - Xu) - K$

6.2.3 From a statistical standpoint, it is recognized that there is an inherent difference between bias and spike recovery. However, for the purposes of establishing the data quality procedures and incorporating them into this SOP, a conscious decision has been made to consider bias and spike recovery to be equal. Bias is not used in the day to day language and quality control at the lab.

7. OTHER QUALITY CONTROL MONITORING / RECORDKEEPING

7.1 Solvents/Chemicals. All solvents and chemicals shall be reagent grade or higher as specified in the analytical method.

7.2 Chemical procurement, distribution and storage. See the DHHS PHE Laboratory Chemical Hygiene Plan for this information.

7.3 Notebooks

7.3.1 Maintenance Notebooks. Analysts will maintain some form of maintenance notebook or electronic data base for each piece of analytical instrumentation.

7.3.1.1 Regular Maintenance. Include all regular maintenance done on the equipment to keep it running properly. All daily, weekly, monthly, quarterly, and yearly scheduled and unscheduled maintenance must be documented.

7.3.1.2 Equipment Failure. Include observations, speculation as to the nature of the problem, conversations with instrument repair technicians, new equipment installed, and corrective action forms.

7.3.1.3 Troubleshooting Steps. Include all steps performed by the analyst and the instrument service technician.

7.3.1.4 Copies of service reports from the manufacturer or repair technician must be retained and inserted in an equipment binder or scanned into a electronic data base. This includes any calibration certificates if given.

7.3.1.5 Notebooks must be stored close to the equipment for easy access.

7.3.2 Standards Notebooks and /or Logs: These notebooks or electronic logs must be maintained and the following facts as a minimum will be entered:

Name of standard, date prepared, manufacturer source, expiration date if not stated in SOP, storage requirements, and analyst initials.

7.3.2.1 Standard and reagent logs must be maintained in the LIMS, when possible.

7.3.2.2 If Standard and reagent logs cannot be maintained in the LIMS, they must be maintained in a notebook or in a similar format.

7.4 Bottle / Container Quality Control

7.4.1 Bottles and containers that are used to contain samples shall be ensured of cleanliness by one of the following methods:

7.4.1.1 Washed in-house upon their arrival at the lab or after they have been previously used.

7.4.1.2 Purchased pre-cleaned to method specifications.

7.4.1.3 A sample bottle from each box shall be tested for the analytes of interest according to the applicable sample method.

7.5 Chemical, Reagent, Media, Standards, and Solution Documentation

7.5.1 All chemicals, reagents, media, standards and solutions must be labeled with contents name, the date received should be written on the container along with the date opened. Each date should be initialed by the analyst receiving and/or opening the container but it is not required.

7.5.2 All original containers of chemicals, reagents, media, standards, and solutions must

have an expiration date written on the container, if provided by the manufacturer or the analyst. Expired items must not be used and must be labeled as "expired do not use" if they can not be disposed of in a timely manner to prevent accidental use.

7.5.3 Reference standard calibration solutions must include labels that list the date of preparation, the concentration, the name or the initials of the analyst who prepared the standard, and the expiration date.

7.5.4 Stock standard solution logs must list the preparation date, the concentration, the name or initials of the analyst who prepared the solution, the dilution solvent and the expiration date.

7.5.5 All storage containers that contain chemical preparations, chemical wastes, reagents, media, standards, solutions, etc., must be labeled as to the name of the contents, analyst initials who prepared the item or who is responsible for the container's existence, date prepared and expiration date if applicable.

8. REFERENCES

8.1 Statistical Techniques for Data Analysis, 1990, John Taylor

8.2 EPA Region VII SOP No. 2410.15D, August 2000, "Estimating and Documenting Data Quality"

8.3 40 CFR Part 136 Appendix B, Definition and Procedure for the Determination of the Method Detection Limit

8.4 Test Methods for Evaluating Solid Waste Physical / Chemical Methods (SW-846) Volume One, Section A, Chapter One 'Quality Control', Section 4.4.2 'Control Limits', Revision 1 July 1992

8.5 EPA Region VII SOP No. 1610.1C, March 1996, Regional Laboratory Quality Control Policy

8.6 Manual for the Certification of Laboratories Analyzing Drinking Water. Fifth Edition, January 2005

9. ATTACHMENTS

Attachment A - 40 CFR Part 136 Appendix B, Definition and Procedure for the Determination of the Method Detection Limit

Attachment B – MDL Requirements

Attachment C – Proficiency Documentation Form

Attachment D – IDC Certification Documentation Form

ATTACHMENT A

[Code of Federal Regulations]
[Title 40, Volume 22]
[Revised as of July 1, 2009]
From the U.S. Government Printing Office via GPO Access
[CITE: 40CFR136 App B]

[Page 343-346]

TITLE 40--PROTECTION OF ENVIRONMENT

CHAPTER I--ENVIRONMENTAL PROTECTION AGENCY (CONTINUED)

PART 136_GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS--Table of Contents

Sec. Appendix B to Part 136--Definition and Procedure for the Determination of the Method Detection Limit--Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) 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.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method,

including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S\2\) and standard deviation (S) of the replicate measurements, as follows:

[GRAPHIC] [TIFF OMITTED] TC15NO91.208

where:

X[iota]; i=1 to n, are the analytical results in the final method reporting units obtained from

the n sample aliquots and [Sigma] refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

MDL = t<INF>(n-1,1-</INF>[alpha]=0.99) (S)

where:
MDL = the method detection limit
t<INF>(n-1,1-</INF>[alpha]=.99) = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.
S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ([chi]\2\/df).
LCL = 0.64 MDL
UCL = 2.20 MDL
where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verity the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S\2\ from the current MDL calculation and S\2\ from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S\2\ into the numerator S\2\<INF>A</INF> and the other into the denominator S\2\<INF>B</INF>. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if S\2\<INF>A</INF>/S\2\<INF>B</INF><3.05, then compute the pooled standard deviation by the following equation:

[GRAPHIC] [TIFF OMITTED] TC15NO91.209

if S\2\<INF>A</INF>/S\2\<INF>B</INF><ls-thn-eq>3.05, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S<INF>pooled</INF> as calculated in 7b to compute The final MDL according to the following equation:

MDL=2.681 (S<INF>pooled</INF>)

where 2.681 is equal to t<INF>(12,1-</INF>[alpha]=<INF>.99)</INF>.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL
UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Tables of Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	tcn-1,.99)
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

ATTACHMENT B

MDL Requirements

MDL's Considerations:

1. Should be run on instruments that are functioning properly and have been passing all necessary QC
2. Should be run when the instrument is in production condition. Not right after changing a column.
3. Should be run using the same calibration curve used to run typical samples
4. The lowest standard should be approximately equal to the estimated limit of quantitation.
5. A new calibration curve should be generated prior to performing the MDL or at the very least the working calibration curve should be verified at the beginning using appropriate checkstandards.
6. A non-linear calibration curve requires at least 5 standards to characterize the curve
7. For most inorganic analyses, the blank should be included as a point on the calibration curve. It is not acceptable to force any calibration curve through zero.
8. Good GLP would be to establish the linear range for an instrument with at least 3 concentration standards for methods which only require one point calibration. The calibration can then be verified at least once or twice during a shift with a low or midrange standard.
9. If the required MDL is not achieved for a particular instrument, the instrument cannot be used for SDWA analysis. (ex., Cert Manual requires certain VOC MDLs be met)

Choosing Spike Level:

1. The best spiking level is 1-5 times the estimated detection level, as specified in the procedure.
2. Consider the signal response that the spiked level will give on the system that is used
3. Is the signal off scale?
4. Is the signal distinguishable from the background noise? It is recommended to have a S/N ratio of 2.5 to 10.
   $S/N_{est} = X_{ave} / S$ where X_{ave} = avg of either calculated concentrations or analytical signals
   S = sample standard deviation of the replicates
5. Consideration of the signal to noise ratio (S/N) may helpyou choose the appropriate spike level
6. The calculated MDL must be > 1/10 of the spike level.
7. If the calculated MDL exceed the spike level it is not statically possible to differentiate the spiked sample from a blank.
8. WAY TO CHECK YOUR SPIKE LEVEL **Calculated MDL < Spike Level< 10 X Calculated MDL**

Replicate Sample Preparation:

1. Requires a minimum of 7 replicates of a sample at the appropriate concentration
2. Use 8 replicates if you think you may need to toss out one as an outlier
3. Samples must be processed exactly as prescribed in the method. Using unprocessed samples is unacceptable and is not representative of the true MDL.
4. Reagent water MDL's for most environmental samples should be calculated by preparing a single stock solution and splitting it at least into seven replicates. Impractical for many procedures so can also prepare and process each sample individually.
5. It is recommended that you validate each matrix specific (ex. soils) MDL by preparing and analyzing a single matrix spike at the MDL concentration to see if the analytical system can distinguish the sample from the blank.
6. In order to account for day to day variability, analyze the seven or more replicate standards in different sample batches on different analysis dates. Cert. Manual requires that it be made overa period of at least 3 days.

Analyzing Blanks:

1. At least one method blank should be analyzed with each set of MDL samples to measure background contamination.
2. It is not acceptable to subtract blanks for methods that do not allow subtraction for ordinary samples.

Calculations:

1. Always use the sample standard deviation
2. Always use the correct Student t-value at the 99% level. For 7 replicates this is 3.14
3. Always use all significant figures through the calculation and round the final MDL to the number of digits used when reporting results for the method. It is acceptable to round the calculated value up to the nearest decimal place. It should never be rounded down unless you can routinely achieve the rounded value.
4. MDL=(t-value)(standard deviation of the samples)

Frequency of MDL Determinations:

1. Perform at least as often as required in the method.
2. Perform prior to each analyst generating and reporting sample results
3. Performed whenever changes are made to the method (ex. different extraction solvent) or instrument (ex. different column type).
4. Performed at least yearly per the DHHS PHE QAP.
5. Performed on each instrument used for each method.
6. The MDL's should be within 50% of each other when there are multiple analysts/instruments. Always report the highest calculated MDL. Can modify the F-Ratio test in 40 CFR Part 136 to test reasonableness of considering two MDL determinations equivalent.

Common Sense Check:

1. Is the MDL reasonable? Perform a five point check:
   a. Does the spike level exceed 10 times the MDL? If so, the spike level is too high. (Required)
   b. Is the MDL higher than the spike level? If so, the spike level is too low. (Required)
   c. Does the calculated MDL meet regulatory requirements for necessary programs? (Required)
   d. Is the signal/noise (S/N) in the appropriate range? (Typical range is 2.5-5)
      1. A S/N less than 2.5 indicates that random error in the series of measurements is too high and the determined MDL is probably too high. In that instance the samples should be spiked at a higher level to increase the signal.
      2. A S/N greater than 10, usually indicates the spike concentration is too high and the calculated MDL is not necessarily representative of the LOD. It that instance, the samples should be spiked at a lower level to decrease the signal.
   e. Are the replicate recoveries reasonable?

Percent Recoveries:

1. In order for the MDL to be realistic, the average %Rec for samples should be reasonable.
   Average % Rec = (X_{ave}/spike level)x 100% X_{ave} = the average concentration of the samples

2. **Use the limits of the LFB if not specified in the method.**

Attachment C

PROFICIENCY DOCUMENTATION

FOR _____

Instrument _____

Type of Training: INITIAL

I verify that _____ has been trained and has met the requirements specified
(Trainee-analyst's name)

below for the following:

1. _____ Appropriate SOP's read and understood _____.
(SOP'S)

2. _____ Trainee has acquired _____ formal in-house training.
(hours)

3. _____ Trainee was observed while performing the procedure in conformance with SOP(s) delineated above.

4. _____ Trainee has successfully completed tasks with minimal supervision.

5. _____ Trainee has successfully completed an MDL Study if method requires a MDL study.

6. _____ Trainee has passed a blind or PT sample and results are attached.

7. _____ Other Specify):_____

Analyst: _____ Date: _____
(Trainee)

Approved by: _____ Date: _____
(Qualified Trainer)

Approved by: _____ Date: _____
(QA Manager)

Attachment D

INITIAL DEMONSTRATION OF CAPABILITY CERTIFICATION STATEMENT

Date_____

Analyst:_____ Instrument:_____

Matrix_____

Method #_____ SOP#_____

Parameter(s) or class of analytes:_____

We the undersigned, CERTIFY that:

1. The analyst identified above, using the cited test method, which is in use at this facility for the analyses of samples under the United States Environmental Protection Agency (EPA) or National Environmental Laboratory Accreditation Program (NELAP), has met the ***Initial Demonstration of Capability.***

2. The test method was performed by the analyst identified on this certification.

3. A copy of the test method and the Laboratory specific SOP's are available for all personnel on site.

4. The data associated with the demonstration capability are true, accurate, complete and self explanatory.

5. The following must be performed and documented prior to analysis of "real world environmental samples and the completion of this IDC:
   A. Reagent Blank must contain analyte of interest at a concentration no greater than half the RL
   B. Accuracy (mean recovery of a minimum of 4 LFB samples), must be within method limits,
   C. Precision (%RSD relative standard deviation), must be within method limits,
   D. MDL study must meet MDL study requirements (See the back of this form for MDL requirements),
   E. Pass an unknown PT or blind sample,
   F. SOP must be reviewed and/updated if changes are needed.

6. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized assessors.

7. The certification form will be kept in the analyst's training file in the QA office. The IDC data will be kept on file in the QA office. All raw data will be stored with the analyst's records.

Analyst Name and Title	Signature	Date
QA Managers Name	Signature	Date

MDL Requirements

MDL's Considerations:

10. The lowest standard should be approximately equal to the estimated limit of quantitation.
11. For most inorganic analyses, the blank should be included as a point on the calibration curve. It is not acceptable to force any calibration curve through zero.

Choosing Spike Level:

9. The best spiking level is 1-5 times the estimated detection level, as specified in the procedure.
10. Consider the signal response that the spiked level will give on the system that is used
11. Is the signal off scale?
12. Is the signal distinguishable from the background noise? It is recommended to have a S/N ratio of 2.5 to 10. $S/N_{est} = X_{ave} / S$ where X_{ave} = avg of either calculated concentrations or analytical signals
    S = sample standard deviation of the replicates
13. Consideration of the signal to noise ratio (S/N) may help you choose the appropriate spike level
14. The calculated MDL must be > 1/10 of the spike level.
15. If the calculated MDL exceed the spike level it is not statically possible to differentiate the spiked sample from a blank.
16. WAY TO CHECK YOUR SPIKE LEVEL **Calculated MDL < Spike Level< 10 X Calculated MDL**

Replicate Sample Preparation:

7. Requires a minimum of 7 replicates of a sample at the appropriate concentration. Use 8 replicates if you think you may need to toss out one as an outlier
8. Samples must be processed exactly as prescribed in the method. Using unprocessed samples is unacceptable and is not representative of the true MDL.
9. Reagent water MDL's for most environmental samples should be calculated by preparing a single stock solution and splitting it at least into seven replicates. Impractical for many procedures so can also prepare and process each sample individually.
10. It is recommended that you validate each matrix specific (ex. soils) MDL by preparing and analyzing a single matrix spike at the MDL concentration to see if the analytical system can distinguish the sample from the blank.
11. In order to account for day to day variability, analyze the seven or more replicate standards in different sample batches on different analysis dates. Cert. Manual requires that it be made over a period of at least 3 days.

Analyzing Blanks:

3. At least one method blank should be analyzed with each set of MDL samples to measure background contamination.
4. It is not acceptable to subtract blanks for methods that do not allow subtraction for ordinary samples.

Calculations:

5. Always use the sample standard deviation
6. Always use the correct Student t-value at the 99% level. For 7 replicates this is 3.14
7. Always use all significant figures through the calculation and round the final MDL to the number of digits used when reporting results for the method. It is acceptable to round the calculated value up to the nearest decimal place. It should never be rounded down unless you can routinely achieve the rounded value.
8. MDL=(t-value)(standard deviation of the samples)
9. The MDL's should be within 50% of each other when there are multiple analysts/instruments. Always report the highest calculated MDL. Can modify the F-Ratio test in 40 CFR Part 136 to test reasonableness of considering two MDL determinations equivalent.

Common Sense Check:

2. Is the MDL reasonable? Perform a five point check:
   f. Does the spike level exceed 10 times the MDL? If so, the spike level is too high. (Required)
   g. Is the MDL higher than the spike level? If so, the spike level is too low. (Required)
   h. Does the calculated MDL meet regulatory requirements for necessary programs? (Required)
   i. Is the signal/noise (S/N) in the appropriate range? (Typical range is 2.5-5)
      3. A S/N less than 2.5 indicates that random error in the series of measurements is too high and the determined MDL is probably too high. In that instance the samples should be spiked at a higher level to increase the signal.
      4. A S/N greater than 10, usually indicates the spike concentration is too high and the calculated MDL is not necessarily representative of the LOD. It that instance, the samples should be spiked at a lower level to decrease the signal.
   j. Are the replicate recoveries reasonable?

Percent Recoveries:

3. In order for the MDL to be realistic, the average %Rec for samples should be reasonable.
   Average % Rec = (X_{ave}/spike level)x 100% X_{ave} = the average concentration of the samples
4. **Use the limits of the LFB if not specified in the method**