Environmental Laboratory Detection Limits

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Objectives

- Review definitions used for detection limits and limits for reporting
- Outline methods for calculating, assessing and reporting detection and other limits

This Training

- Presents several definitions for detection limit.
- Identifies the terms based on the regulatory program or client needs.
- Defines several methods used to calculate detection limits.
- Presents terms and methods of determining the limits for results reported to clients.

Procedures – New and Old

- Report of the Federal Advisory Committee on Detection and Quantitation Limits
  - http://www.epa.gov/waterscience/methods/det/

Sensitivity

- Capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest.
- Determine the minimum concentration or attribute that can be measured by a method (detection limit), by an instrument (instrument detection limit), or by a laboratory (quantitation limit).
- Compare the appropriate limit to the action level established during project planning.

EPA QA/G-5 2002

Detection Limit - Current

- Required by Regulation
  - MDL - 40CFR 136 Appendix B
- Calculation?
  - Titration (e.g.; Alkalinity)
  - Gravimetric (e.g.; TDS)
- Instrument?
  - pH
  - Conductivity

The Most Popular

Title 40: Protection of Environment

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

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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.

MDL Calculation

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \qquad S = \left(S^2\right)^{\frac{1}{2}}$$

where:

X_i; i=1 to *n*, are the analytical results in the final method reporting units obtained from the *n* sample aliquots *n* = 7 or more

$\sum$ = sum of the X values from i=1 to *n*

S = Standard deviation

MDL Formula

- Compute the MDL as follows:

$$MDL = t(n-1,1-\alpha=0.99)\ (S)$$

where:

MDL = the method detection limit

t(n-1,1-α=.99)= the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

T Values

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

Number of replicates	Degrees of freedom (n-1)	$t_{cn-1,.99}$)
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

Finishing Steps MDL

- Confidence interval 95%

(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 (χ^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 verify 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_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, 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_{pooled} as calculated in 7b to compute The final MDL according to the following equation:

$MDL=2.681\ (S_{pooled})$

where 2.681 is equal to $t(12,1-\alpha=.99)$.

(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.

MDL Reporting

- All steps of method
- Method used
- Changes to method
- Sample matrix
- Mean analyte value and units
- Iterative procedure used
- Keep data
- Quantitation relationship

MDL – Calculation Based

- Lower limit of measurement based on amount of sample and/or equipment resolution
- Quantitation limit
  - Titration
    - Largest volume of sample, buret resolution
  - Gravimetric
    - Largest volume of sample, balance resolution

MDL – Instrument Based

- pH, Conductivity, etc.
- No standard at the detection limit
- Equipment resolution sometimes stated
- Only quantitation range, not detection limit

Others

- IUPAC/ISO
- EPA Drinking Water
  - Lowest Concentration Minimum Reporting Limit (LCMRL)
  - Long Term Method Detection Limit (LT-MDL)
- NELAC Standard 2003
- Uniform Federal Policy (UFP)
  - Limits Relationship

IUPAC Definition

- **detection limit (in analysis)**
  - The minimum single result which, with a stated probability, can be distinguished from a suitable blank value.
  - The limit defines the point at which the analysis becomes possible and this may be different from the lower limit of the determinable analytical range.

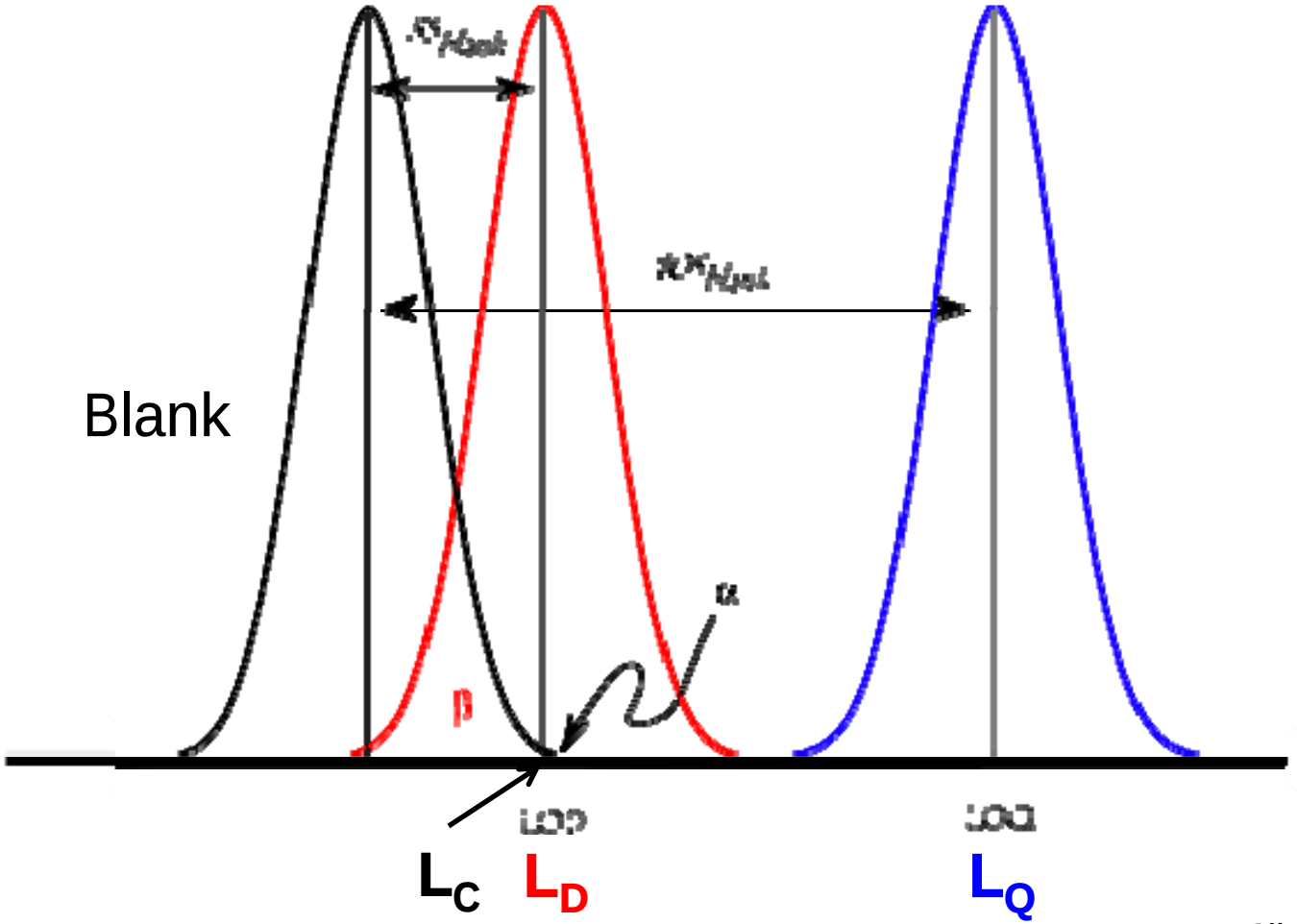
IUPAC/ISO definition

- Detection Decisions (L_c) or Critical Value
  - Minimum significant value of an estimated net signal or concentration, applied as a discriminator against background noise.
- Critical Value (L_C) - The minimum result which can be reliably discriminated from a blank (for example, with a 99% confidence level).
- Critical Value (L_C) – The lowest result that can be distinguished from the blank at a chosen level, α, of statistical confidence.

IUPAC/ISO Terms

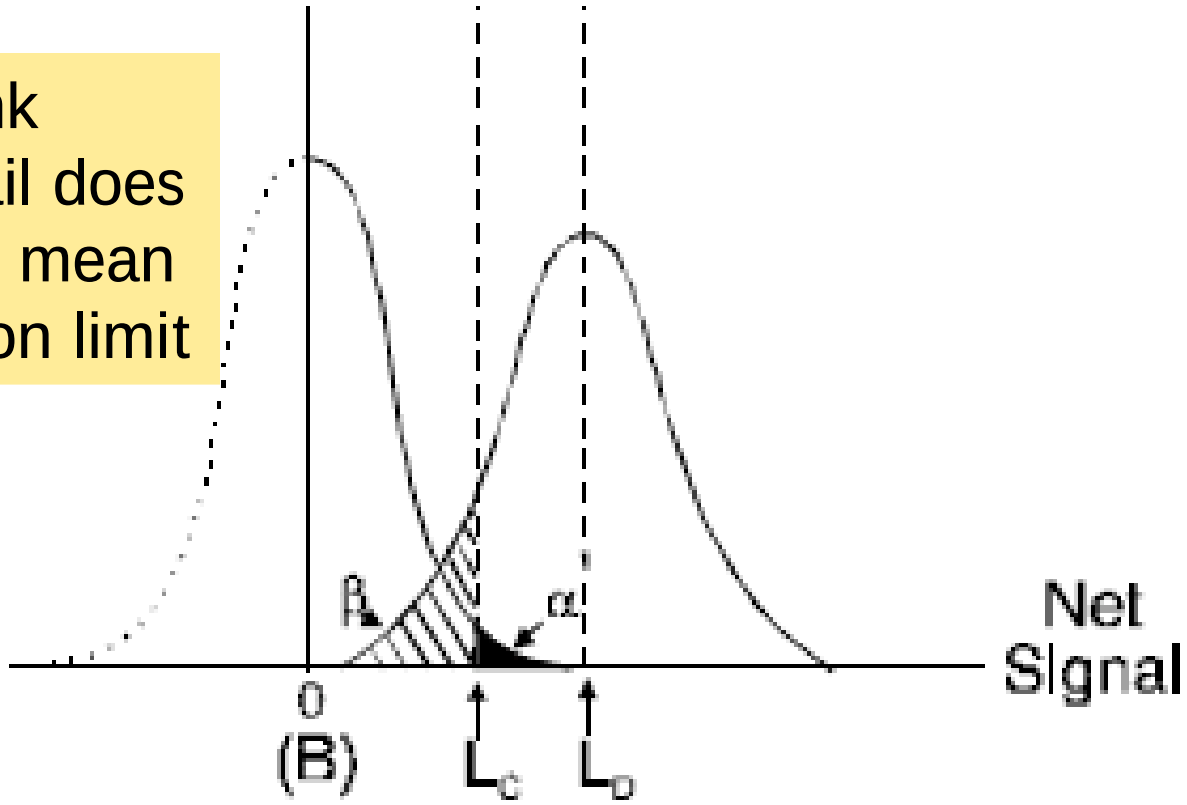
- Detection Capability or *minimum Detectable (true) value (L_D)*
  - *The detection limit*
- Quantification Capability or *minimum quantifiable (true) value (L_Q)*
  - *The quantification limit*
  - The smallest detectable concentration of analyte greater than the detection limit where the required accuracy (precision & bias) is achieved for the intended purpose.

Blank, LOD, LOQ



Blank and Detection Limit

The blank distribution tail does not equal the mean of the detection limit



LCMRL – EPA 2004

- Unregulated Contaminant Monitoring Regulation (UCMR)
- LCMRL > lowest calibration standard
- Analyte peak area
  - At least three times greater than blank sample
- Reliable quantitation concentration

Definition

- Method Reporting Limit - lowest analyte concentration which demonstrates known quantitative quality.
- Lowest Concentration MRL- lowest true concentration for which the future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery.

Calibration Range

- At least 4 calibration levels
  - At least seven replicates
  - Entire procedure
- Alternative;
  - 5 reps at 4 levels or
  - 7 reps at 3 levels

Calculation

- Ordinary Least Squares (OLS)
- Check for constant variance over range
- If not constant
  - Variance Weighted Least Squares (VWLS)
- Calculator Application
  - http://www.epa.gov/safewater/methods/analyticalmethods_ogwdw.html

Demonstration - LCMRL

- Method Development
- Validation of lab performance at or below MRL
  - Initial demonstration capability defined in method
- Daily check at or below MRL
  - 50-150% Recovery for each UCMR analyte

NELAC - Definitions

- Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte-and matrix-specific and may be laboratory-dependent.
- Limits of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

LOD - NELAC

- MDL - 40CFR 136 or Lab Defined
- Verification required if results reported to LOD
  - Initial and Annual
  - All steps of method
  - 2-3 times the reported LOD - must be measured
  - Each instrument

Appendix C NELAC 2003

LOQ - NELAC

- Reporting Limit or Quantitation Limit
  - Lab procedure defines how LOQ determined
  - Reporting results only to LOQ
  - Must have procedure to define relation of LOD with LOQ
  - Confirm validity (Annual if not done for LOD)
    - Spike 1-2 times claimed LOQ
    - Recovery must be within method or client or lab acceptance criteria

Appendix C NELAC 2003

UFP QAPP Manual, V1 March 2005

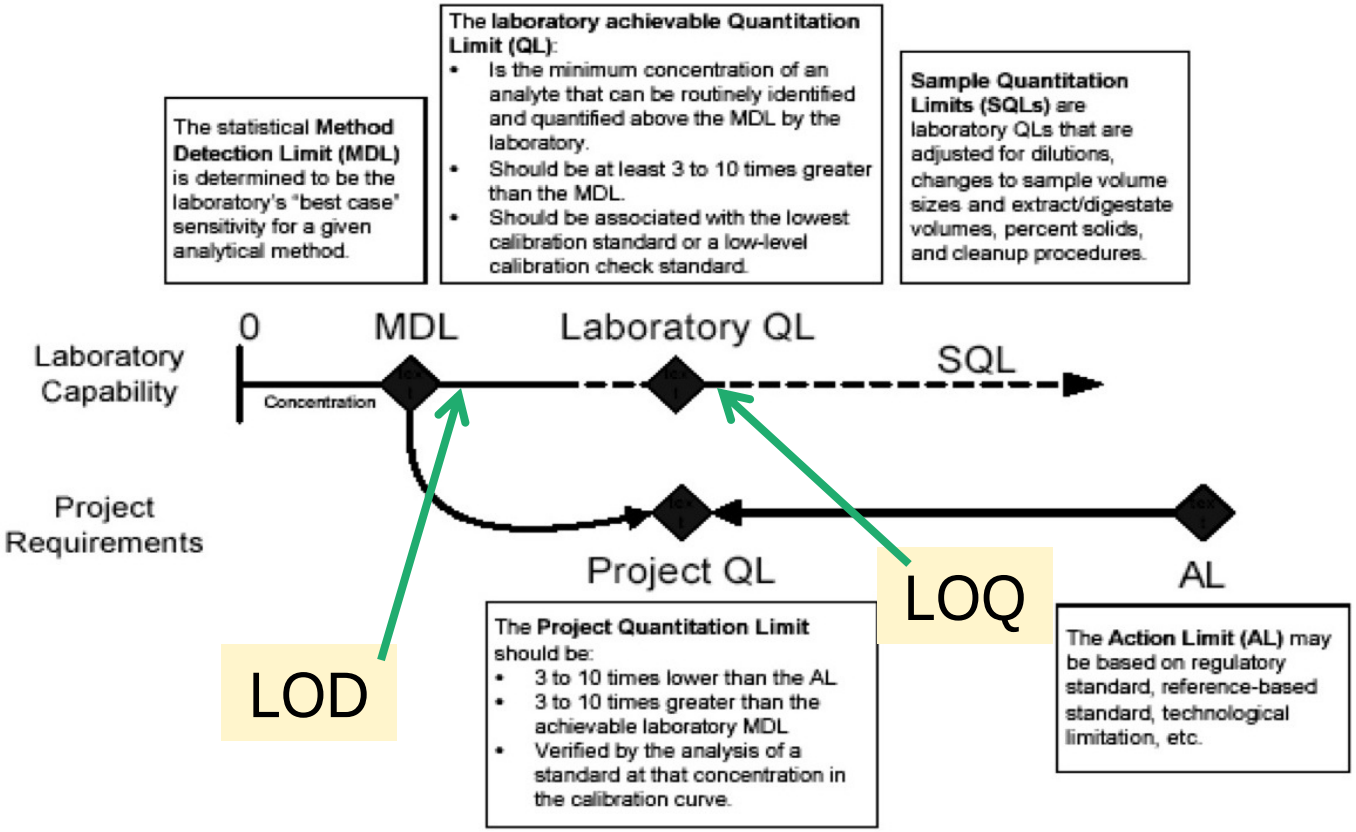


Figure 15. Relationships to Project Quantitation Limits

Summary

- Define the Limits
- Develop Detailed Procedures for:
  - Calculating
  - Assessing
  - Reporting
- Review Detection Limit Data

Any Questions?

How do we know which limits are right?

Question !

End Teleconference

Thank you !!