Are Detection Limits & Reporting Levels the Same?

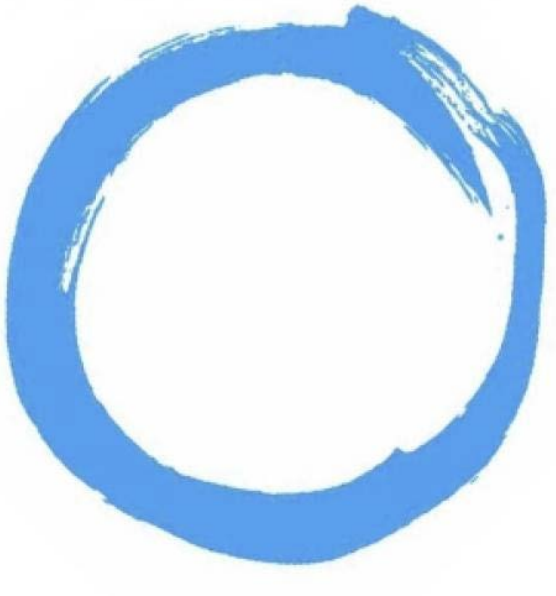
Presented by Marcy Bolek

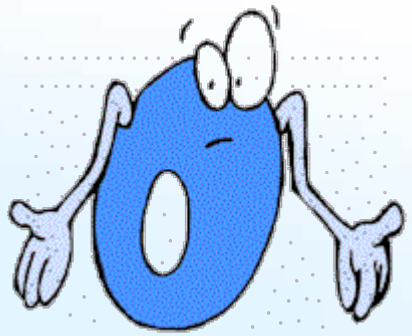
Synonyms of Zero (0)?

- Nothing
- Nil
- Nothing at all
- None
- Zip
- Zilch
- Nada
- Diddly squat
- In terms of dollars and cents
  - Broke

What is Zero (0)

- Zero is both a number and a digit
- It is a placeholder in mathematics
- It is an integer that precedes 1
- It is not positive or negative
- Zero is a number that quantifies a count
- Zero is a number that quantifies an amount of null size





What is Zero divided by Zero?

- Here’s the answer according to Siri (IPhone answer)

Imagine that you have zero cookies and you split them evenly among zero friends.

How many cookies does each person get?

See it doesn’t make sense and cookie monster is sad that there are no cookies and you are sad that you have no friends.

PQL

MRL

RL

LOD

EQL

ML

MDL

LOQ

Agenda

- Detection levels – Background
- Terms and Definitions
- Calculating MDL
- Determining Reporting Level
- Proposed MDL Calculation

Background

- Just as your eye cannot see infinitely smaller details, somewhere between a period and an atom your eye fails to discern detail. All instrumentation has an inherent minimum level below which it no longer functions reliably.

History

- Seminal work on detection and quantitation is by Lloyd Currie (Published in Analytical Chemistry in 1968)
- Introduced terms of
  - “critical level” (LC), “critical value” (CRV); the “detection decision”; with a 50% confidence level
  - “minimum detectable value” (MDV), “detection limit” (LD) with a 99% confidence level
  - “determination limit”, “minimum quantifiable value” (MQV); limit of quantitation” (LOQ); commonly “quantitation limit” (LQ) required precision, accuracy, false negative error rate and qualitative identification criteria for the intended purpose.

History

- On December 3, 1979, EPA proposed the 600-Series organic methods
- GC/MS Methods 624 and 625 contained a “limit of detection” for each compound
  - In Method 624, the LOD was defined as defined as the “minimum level at which entire system must recognizable mass spectra and acceptable calibration points”
  - In Method 625, the LOD was defined as the “minimum level at which the analytical system must give mass spectral confirmation.”
- The LOD in Methods 624 and 625
  - Were estimates of the lowest level that could be measured and the basis for the minimum level of quantitation (ML)

History

- Method detection limit (MDL) was first published in a paper by John Glaser and others at EPA's laboratory in Cincinnati in 1981 in Environmental Science and Technology
  - MDL based on Currie's work
  - Employs low-level spikes rather than backgrounds
  - Uses Student's t-test to allow for varying number of replicates
  - Has remained largely unchanged since publication

History

- The procedure for establishing the MDL for Clean Water Act programs was promulgated in 40 CFR Part 136 Appendix B in 1984. The MDL procedure was adopted by many other EPA programs and written into many state and federal regulations.

Terms and Definitions

CRDL Contract Required Detection Limit	Minimum level of detection acceptable under the contract Statement of Work (SOW). The inorganic SOW for the Contract Laboratory Program gives CRDLs, but laboratory-derived IDLs (adjusted for sample size, dilution and moisture) are used for reporting limits. The CLP CRDLs are based on typical instrument capabilities and should be attained by the laboratory. Inorganic analytes reported at a concentration above the laboratory's IDL but below the CLP CRDL are flagged with a "B".

Terms and Definitions

CRQL Contract Required Quantitation Limit	Minimum level of reliable quantitation acceptable under the contract Statement of Work (SOW). The organic SOW for the Contract Laboratory Program gives CRQLs, and they are used for reporting limits (after adjustment for % moisture and dilution). The CLP CRQLs are arbitrarily set at the concentration of the lowest non-zero standard in the calibration curve. Organic analytes that are positively identified below the CLP CRQL are reported as present, but at an estimated concentration (with a "J" flag).

Terms and Definitions

EDL Estimated Detection Limit	**Minimum concentration required to produce a specified signal-to-noise (S/N) ratio. The SW-846 Method 8290 for dioxins/furans by GCMS requires that EDLs be used for reporting limits. The EDLs are explicitly determined by the laboratory for each analyte in each sample. The noise in the vicinity of the absent analyte is measured then multiplied by a S/N ratio of 2.5. This labor-intensive procedure is used in order to obtain the lowest possible reporting limits for these highly toxic compounds. It could be specially requested for other GCMS analyses as well.**

Terms and Definitions

EQL Estimated Quantitation Limit	Lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. EQLs normally are arbitrarily set rather than explicitly determined. Most organic SW-846 methods give EQLs. The SW-846 EQLs are arbitrarily set at some multiple of typical MDLs for reagent water. Multiplying factors are given for various matrices such as groundwater, wastewater, soil and sludge, etc. Generally, laboratories use the SW-846 EQLs (adjusted for sample size, dilution, and %moisture) for reporting limits, but they may use EQLs that they have generated. SW-846 does not stipulate how to handle organic analytes that are positively identified at a concentration below the SW-846 EQL. Generally, laboratories DO NOT report these as present.

Terms and Definitions

IDL Instrument Detection Limit	Lowest concentration that can be detected by an instrument without correction for the effects of sample matrix or method-specific parameters such as sample preparation. IDLs are explicitly determined and generally defined as three times the standard deviation of the mean noise level. This represents 99% confidence that the signal is not random noise. The inorganic methods in CLP, SW-846, EPA 200 series, and Standard Methods all give typical IDLs, but laboratory-derived IDLs (adjusted for sample size, dilution, and %moisture) are used for reporting limits. The IDL does not include the upward correction necessary to account for the effects of sample matrix or handling/ preparation (minimal for inorganic water analyses). This is important to remember especially for risk assessments and highly contaminated samples.
LLD Lower Limit of Detection	Generally the same as IDL

Terms and Definitions

LLQ Lower Limit of Quantitation	Generally the same as EQL
LOD Limit Of Detection	Generally the same as IDL
LOL Limit Of Linearity	Concentration at or above the upper end of the calibration curve at which the relationship between the quantity present and the instrument response ceases to be linear. In other words, the LOL is set at the concentration of the highest standard analyzed even though it could extend beyond this. Organic analytes that are positively identified at a concentration above the LOL are flagged with an "E".

Terms and Definitions

LOQ Limit Of Quantitation	Generally the same as EQL
MDC Minimum Detectable Concentration	Generally the same as MDL
MDL Method Detection Limit	Lowest concentration that can be detected by an instrument with correction for the effects of sample matrix and method-specific parameters such as sample preparation. MDLs are explicitly determined as set forth in 40 CFR Part 136. They are defined as three times the standard deviation of replicate spiked analyses. This represents 99% confidence that the analyte concentration is greater than zero.

Terms and Definitions

MQL Method Quantitation Limit	Generally the same as EQL
PQL Practical Quantitation Limit	Generally the same as EQL
SDL Sample Detection Limit	The MDL adjusted to reflect sample-specific actions such as dilution or use of smaller aliquot sizes, or to report results on a dry-weight basis.

Terms and Definitions

SQL Sample Quantitation Limit	The EQL adjusted to reflect sample-specific actions such as dilution or use of smaller aliquot sizes, or to report results on a dry-weight basis.
UCL Upper Calibration Limit	Highest concentration that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions. Specifically defined as the concentration of the highest calibration standard in the laboratory's initial calibration curve adjusted for initial sample volume or weight.

Terms and Definitions

Accuracy	The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components, which are due to sampling and analytical operations; a data quality indicator.
Bias	The constant or systematic distortion of a measurement process, different from random error, which manifests itself as a persistent positive or negative deviation from the known or true value. This can result from improper data collection, poorly calibrated analytical or sampling equipment, or limitations or errors in analytical methods and techniques.

Terms and Definitions

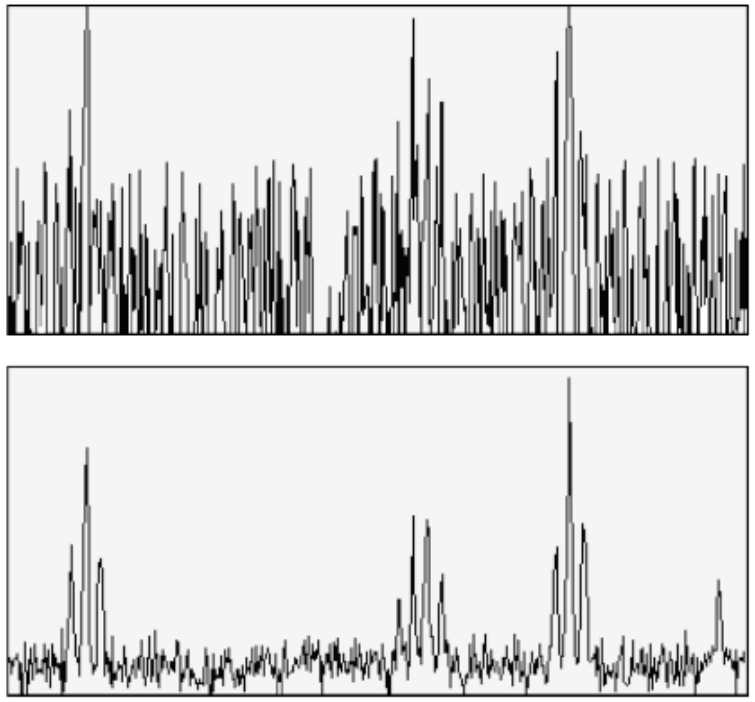
Degrees of Freedom	The total number of items in a sample minus the number of independent relationships existing among them; the divisor used to calculate a variance term; in the simplest cases, it is one less than the number of observations. Degrees of freedom refers to how many variables in a single system are free to vary independently. Degrees of freedom may by none (0) or many. A single variable algebraic equation has no degrees of freedom. This is because there is only 1 right answer for the system described by the equation. For example, for the equation, x + 3 = 4, x is 1. x cannot be anything else. For a 2 variable equation, there is one degree of freedom. One variable is “free” to be anything, but once the value for one variable is selected, the value for the second one is fixed. For example, for the equation, x + y + 3 = 8, x is free to vary. The chosen value of x might be 1 or 7 or 1.25 or -2-. But, as soon as the value for x is chosen, the equation becomes a single variable equation, and the value for y is fixed. If 3 is the value chosen for x, then y must equal 2.

Terms and Definitions

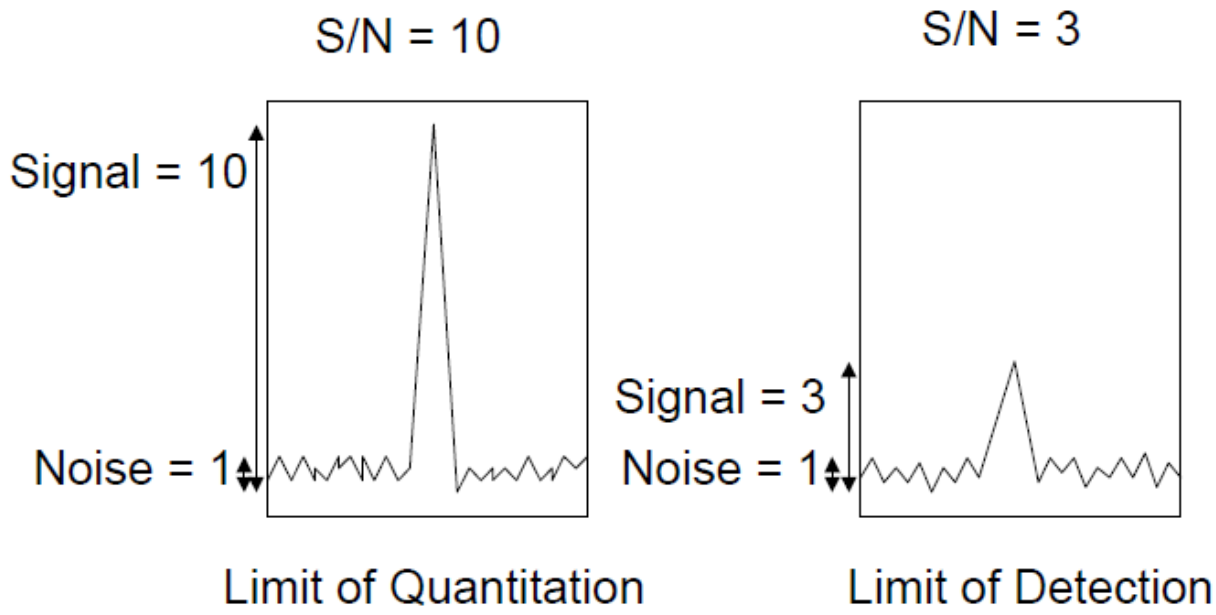
Outlier	An observation that is shown to have a low probability of belonging to a specified data population; any item rejected by the sampler, analyst, or data reviewer, usually accompanied by an attendant explanation.
Precision	The consistency of measurement values quantified by measures of dispersion such as the sample standard deviation. Precision must be defined in context – e.g., for a certain analyte, matrix, method, perhaps concentration, lab or group of labs.
Signal-to-Noise Ratio (S/N)	The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the amplitude of the noise.

Signal-to-Noise

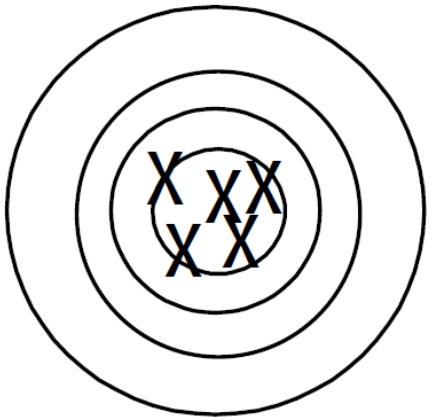
“Signal-to-Noise” (S/N) Ratio



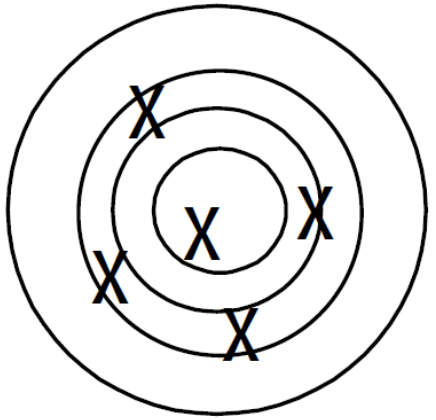
“Signal-to-Noise” (S/N) Ratio



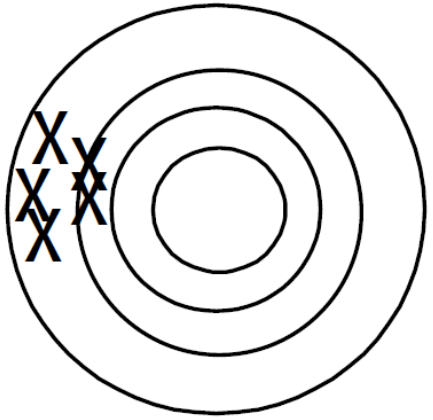
Accuracy and Precision



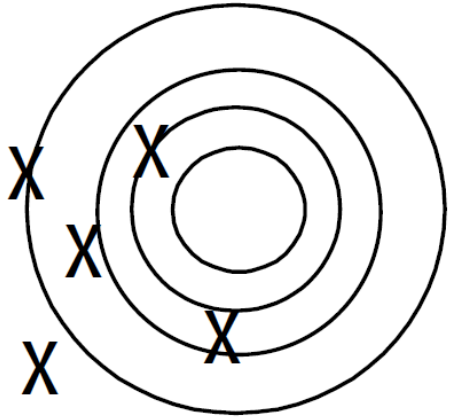
High precision
High accuracy



Low precision
High accuracy



High precision
Low accuracy



Low precision
Low accuracy

Grubb’s Test for Outlier

- Data points cannot be arbitrarily dropped or omitted from a data set unless the data point has been statistically proven to be an outlier **or** if there is a **clear and documented** reason to omit the data point (for example, analyst documented on data sheet the wrong pipet was used). Analysts will follow the Grubb’s Test in determining statistical outliers.

- If an analyst knows to have used an incorrect pipet or knowingly used the wrong standard and documents this at the time the data point was generated the data point can be omitted from the data set. If no external cause can be found then a statistical test can be performed on the data set.

Grubb’s Summary

- If a data point appears to be an outlier (value is far away from rest of the data set), then the data reviewer must use a scientific method of determining whether or not the data point can be omitted from the data set prior to using the data set to evaluate performance.

- A common statistical test used to determine whether or not a data point is a statistical outlier is the Grubb’s test. The Grubb’s test is used for two tailed P values using critical values (Tn) or (Z) at 5% for the number of data points in the data set (N).

Grubb’s Procedure

To determine a statistical outlier, perform the following steps:

- Identify the suspected outlier
- Calculate the mean of the data set (include the suspected outlier)
- Calculate the standard deviation of the data set (include the suspected outlier)
- If the suspected outlier is larger in value than the mean use the following equation to calculate the critical value (Z) from the data set:

Grubb's Equation for Larger Value

$$Z = \frac{X_L - \bar{X}}{s}$$

X_L = suspected outlier that is larger in value than the mean

$\bar{X}$= average of mean of data set *X*

s = standard deviation

Grubb's Equation for Smaller Value

If the suspected outlier is smaller in value than the mean use the following equation to calculate the critical value (Z) from the data set:

$$Z = \frac{(\bar{X} - Xs)}{s}$$

X_S = suspected outlier that is smaller in value than the mean

$\bar{X}$= average of mean of data set *X*

s = standard deviation

Grubb’s Evaluation

- From the following table find the critical value (Z) corresponding to the number of data points in the data set.

- If the calculated Z (critical value) is larger than the critical value from the table the suspected data point has been confirmed statistically to be an outlier and can be discarded from the data set.

- If the calculated Z (critical value) is smaller than the critical value from the table, the suspected data point **IS NOT** an outlier and must remain as part of the data set.

Critical Value Table

N (Points in Data Set)	Critical Z 5%
3	1.15
4	1.48
5	1.71
6	1.89
7	2.02
8	2.13
9	2.21
10	2.29
11	2.34
12	2.41
13	2.46
14	2.51
15	2.55
16	2.59

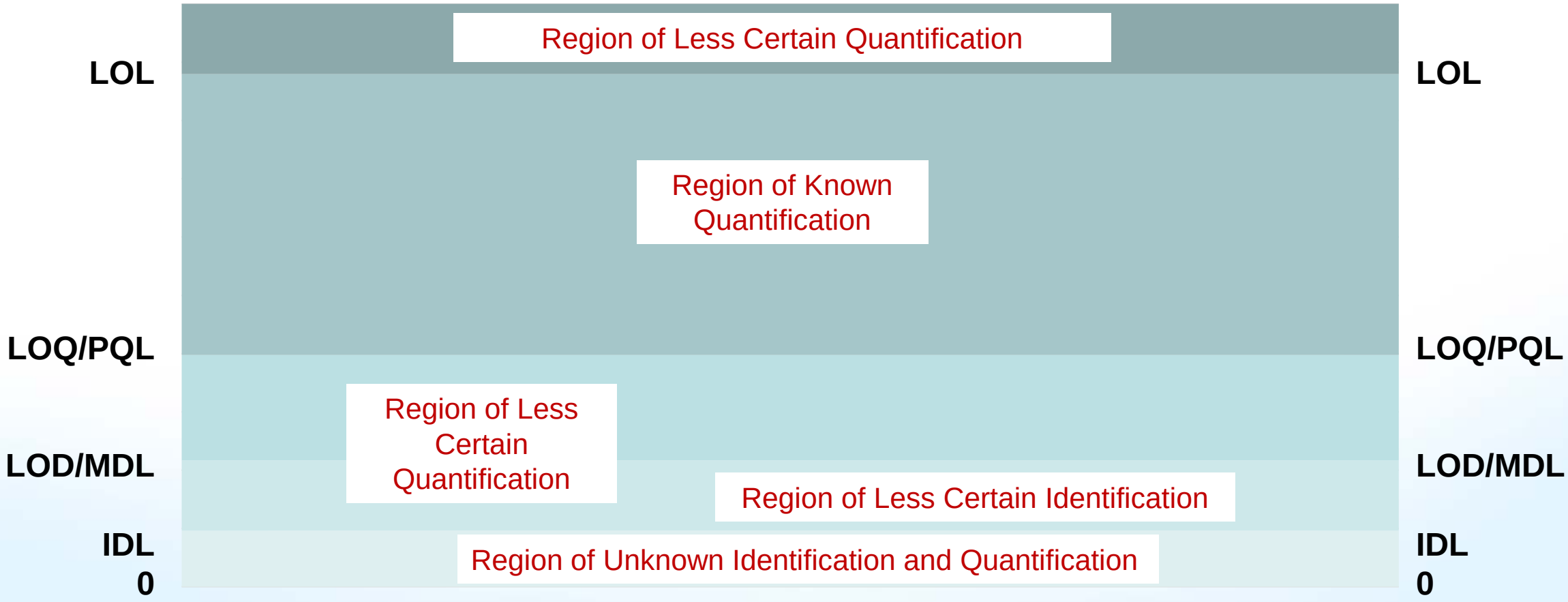
Detection limits and **Quantitation limits**

- **Detection limits** refer to a minimum concentration of an analyte that can be measured above the instrument background noise. Thus, when detection limits are used as reporting limits, the laboratory is saying that the analyte is not present at or above the value given. It may be present at a lower concentration, but cannot be "seen" by the instrument.

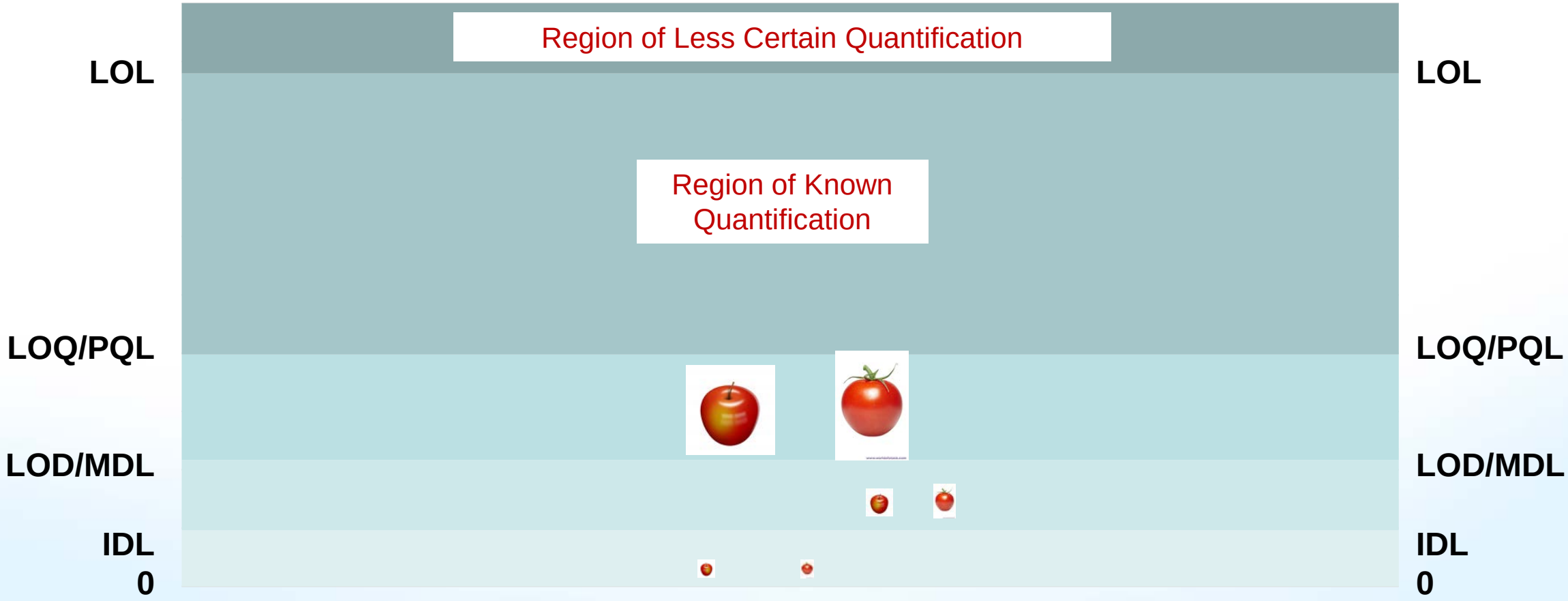
Detection limits and **Quantitation limits**

- **Quantitation limits** refer to a minimum concentration of an analyte that can be measured within specified limits of precision and accuracy. They are generally 5-10 times the detection limit. Thus, when quantitation limits are used as reporting limits, the laboratory is saying that the analyte is not present in a sufficient amount to be reliably quantified (i.e., at a concentration above the quantitation limit). It may be present and even positively identified or "seen" at a lower concentration.

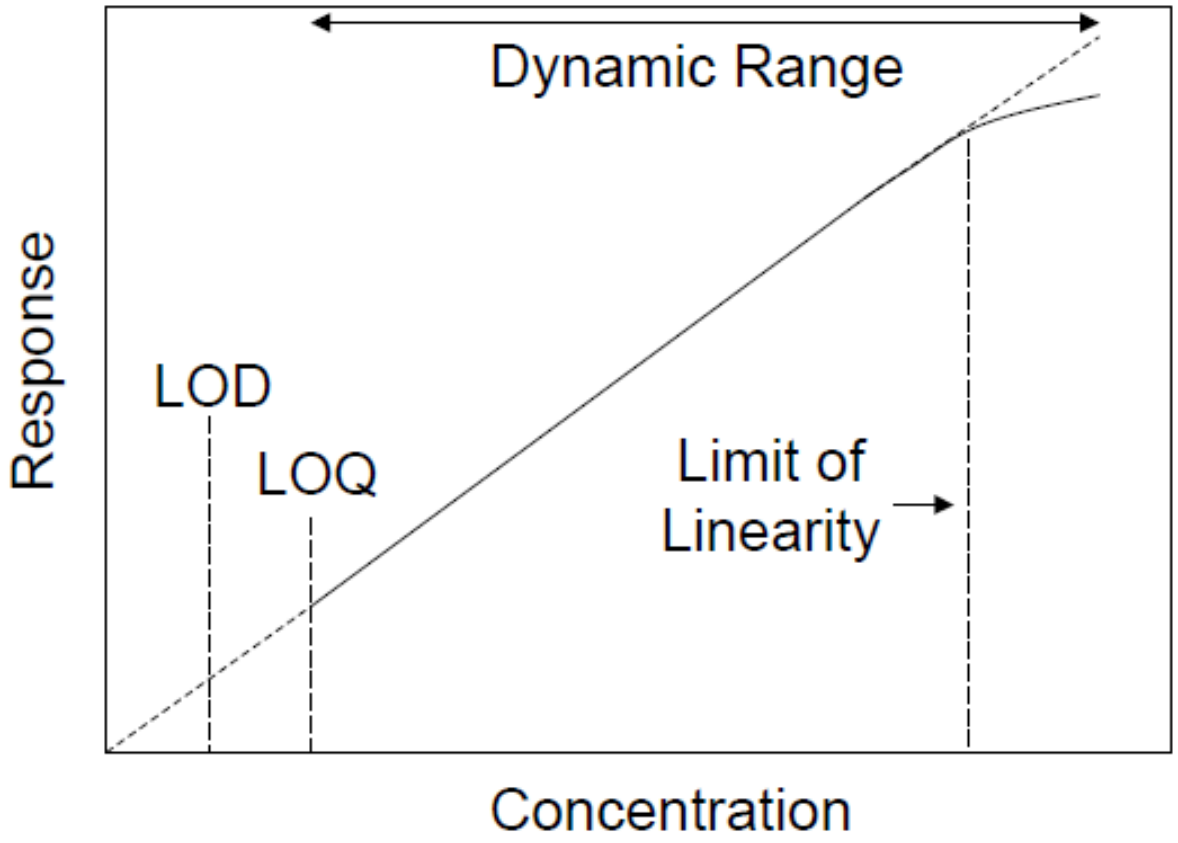
Detection limits and **Quantitation limits**



Detection limits and **Quantitation limits**



Detection limits and **Quantitation limits**



NELAC Definitions

- Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. A 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

2011 NELAC Standards

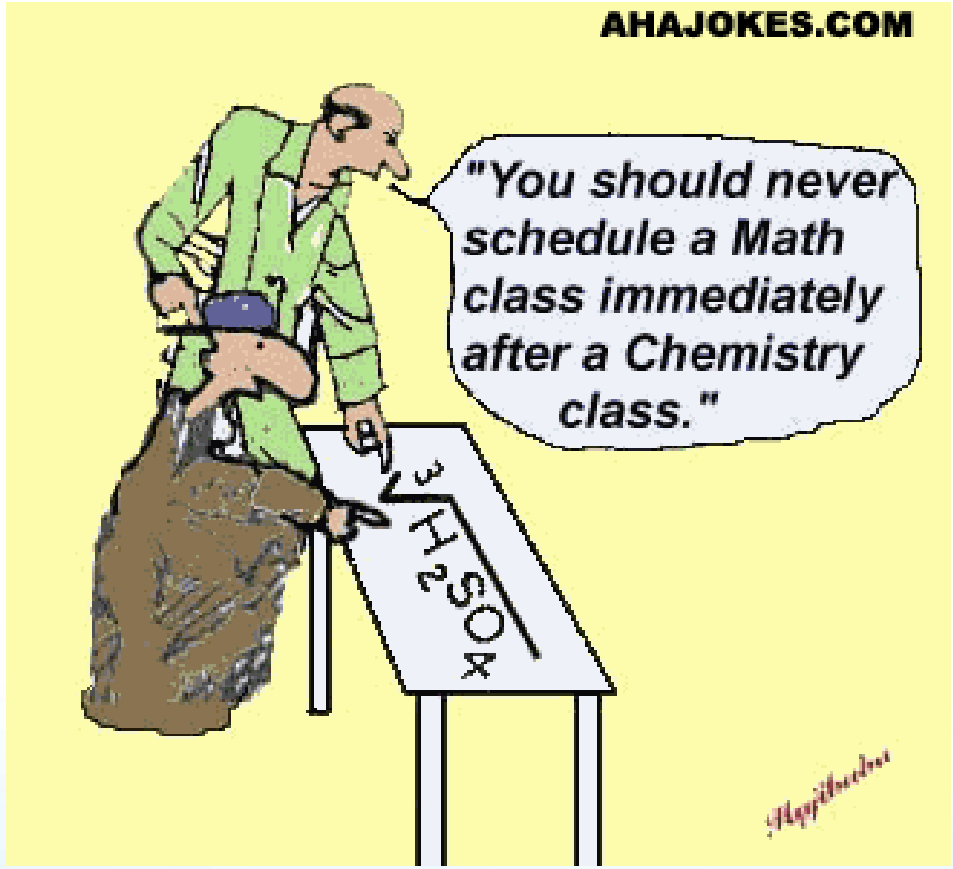
- LOD however named:
  - Not required if lab is not reporting below the LOQ
- LOD study
  - Must be relevant and appropriate for intended use of data
  - Lab must follow mandated method or regulation LOD procedure if part of procedure
  - Standards must be introduced to all sample preparation and analysis steps
  - Lab must determine LOD for each target analyte in each quality system matrix
  - When required verify the LOD on each instrument
    - Single analyte – use standard no more than 3 times the LOD concentration
    - Multiple analyte – use standard no more than 4 times the LOD concentration
  - Not required when spiking solutions or QC solutions are not available

2011 NELAC Standards

- LOQ however named:
- All sample-processing and analysis steps of the analytical method shall be included in the determination of the LOQ.
- The LOQ study is not required for any component or property for which spiking solutions or quality control samples are not available or otherwise inappropriate .
- The validity of the LOQ shall be verified by successful analysis of a QC sample containing the analytes of concern in each quality system matrix at 1 to 2 times the claimed LOQ. A successful analysis is one where the recovery of each analyte is within the laboratory established method acceptance criteria or client data quality objectives for accuracy.

2011 NELAC Standards

- When an LOD is determined or verified by the laboratory, the LOQ shall be above the LOD.
- The LOQ shall be verified annually for each quality system matrix, technology, and analyte.
- However, the annual LOQ verification is not required if the LOD was determined or verified annually on that instrument.


AHAJOKES.COM
"You should never schedule a Math class immediately after a Chemistry class."
$3H_2SO_4$

Method Detection Limits (MDL)

- Definition
  - The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration is greater than zero
  - The MDL differs from the Instrument Detection Limit (IDL). The IDL is the observed signal due to the sample and not the blank

Method Detection Limits (MDL)

- Influences on MDL
  - Matrix
  - Sample preparation
  - Instrumentation

Method Detection Limits (MDL)

- Determining MDL
  - Estimate MDL from:
    - 2 to 5 times instrument noise
    - 3 times standard deviation of duplicate measurements
    - Instrument limitations
    - Point of discontinuity in standard curve

Method Detection Limits (MDL)

- Determining MDL
  - Prepare standard sample containing the analyte at a concentration of 2 to 5 times the estimated MDL
  - Perform the entire analytical method on at least 7 aliquots of the standard sample

Method Detection Limit Calculations

- The MDL equation is:

  MDL = t x s

  where:

  t = value for *t*-test determined for n – 1 degrees of freedom and 99% confidence level

  s = standard deviation (sample)

Method Detection Limit Calculations

- We first must learn to calculate the standard deviation (s)

$$s = \sqrt{\frac{(1)\left(\sum\left(x_1 - \bar{x}\right)^2 + \left(x_2 - \bar{x}\right)^2 .... + \left(x_7 - \bar{x}\right)^2\right)}{n-1}}$$

Where:

s = standard deviation

n = number of data points

$x_1 \ldots x_7$ *= individual data points*

$\bar{x}$ ***= average of data set***

Method Detection Limit Calculations

- Let's assume an MDL study was performed for NH_3 using a standard of 0.2 mg/L
- The following results were obtained
  - 0.19 mg/L (x_1)
  - 0.21 mg/L (x_2)
  - 0.22 mg/L (x_3)
  - 0.18 mg/L (x_4)
  - 0.20 mg/L (x_5)
  - 0.23 mg/L (x_6)
  - 0.17 mg/L (x_7)

- Step 1 – calculate mean

$$mean = \frac{(0.19 + 0.21 + 0.22 + 0.18 + 0.20 + 0.23 + 0.17)}{7}$$

$$mean\ (\bar{x}) = 0.2$$

Method Detection Limit Calculations

- Step 2
  - Calculate the numerator of the standard deviation equation

$$\left(\sum \left(x_1 - \bar{x}\right)^2 + \left(x_2 - \bar{x}\right)^2 .... + \left(x_7 - \bar{x}\right)^2\right)$$

x_i	$\bar{x}$	$x_i - \bar{x}$	$\left(x_1 - \bar{x}\right)^2$
0.19	0.20	-0.01	0.0001
0.21	0.20	0.01	0.0001
0.22	0.20	0.02	0.0004
0.18	0.20	-0.02	0.0004
0.20	0.20	0.00	0.0000
0.23	0.20	0.03	0.0009
0.17	0.20	-0.03	0.0009

$$\textit{sum of } \left(x_1 - \bar{x}\right)^2 = 0.0028$$

Method Detection Limit Calculations

- Step 3
  - Calculate the standard deviation

$$s = \sqrt{\frac{(1)\left(\sum\left(x_1 - \bar{x}\right)^2 + \left(x_2 - \bar{x}\right)^2 .... + \left(x_7 - \bar{x}\right)^2\right)}{n-1}}$$

$$s = \sqrt{\frac{(1)\ (0.0028)}{(7-1)}}$$

$$s = \sqrt{\frac{0.0028}{6}}$$

$$s = \sqrt{0.0004666667}$$

$$s = 0.0216$$

Method Detection Limit Calculations

- Step 4
  - Calculate the MDL
  - MDL = t x s
  - t = *t*-test for n – 1 degrees of freedom at 99% confidence
  - MDL = 3.143 x 0.0216
  - MDL = 0.068

Data Points	Degrees of Freedom	t Value
7	6	3.143
8	7	2.998
9	8	2.836
10	9	2.821
16	15	2.802
21	20	2.526
31	30	2.457

Method Detection Limit Calculations

- Requirements for Valid MDL Study
  - Average of data points is 50-150% R
  - Calculated MDL meets 10 times rule
    - The calculated MDL must be within 10 times the true value of the MDL standard concentration
  - All obtained values of MDL standards analyzed must be greater than the calculated MDL result

Method Detection Limit Calculations

- Does the previous MDL example met all 3 criteria?
  - Is the average of data points between 50-150%R?
    - $$\%R = \frac{0.20}{0.20} \times 100$$
    - Yes – the average %R = 100%
  - Are all data points above the calculated MDL?
    - Yes, the lowest value obtained = 0.17 and it is > 0.068
  - Is the 10 times rule met?
    - Yes, 0.068 ≥ 0.02

$$\text{MDL} \geq \frac{(\text{concentration of MDL standard})}{10}$$

Method Detection Limit Calculations

- The MDL Study is:
  - Performed during method validation prior to analyzing samples
  - Performed at a minimum of once per year
  - Performed on each instrument
    - If lab performs metals determinations using two separate ICP's, the MDL study must be performed on each ICP
  - Performed on each matrix type
    - Waste water
    - Solid waste

Method Detection Limit Calculations

- Practical Quantitation Level (PQL)
  - Lowest level achievable within specified limits
  - Determined for routine analyses
  - Stays consistent from year to year
  - It is approximately 5 times the calculated MDL
  - Represents a practical level routinely achievable
  - The PQL must be part of the calibration curve
    - Must prove the PQL can be seen on daily basis

Method Detection Limit Calculations

- If a laboratory calculated the MDL for phosphorus analysis to be 0.01 mg/L
  - What would the PQL be for phosphorus?

$$\mathbf{PQL = 0.01\ mg/L\ x\ 5}$$

$$\mathbf{PQL = 0.05\ mg/L}$$

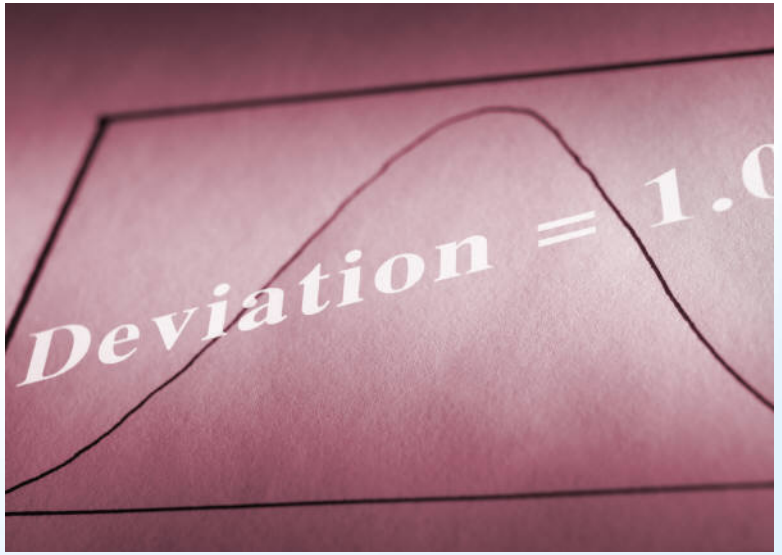
Method Detection Limit Calculations

- A laboratory who reports a PQL for phosphorus at 0.05 mg/L prepares a phosphorus calibration curve containing the following standards:
  - 0.10 mg/L
  - 0.25 mg/L
  - 0.40 mg/L
  - 0.50 mg/L
  - 1.00 mg/L
    - The ICV and CCV standards are prepared using 0.40 mg/L and 0.50 mg/L respectively.
- Do the above procedures meet method requirements?
- NO – The PQL needs to be part of the calibration curve or a reporting level check standards at 0.05 mg/L would need to be prepared and analyzed daily.

Statistics – Words of Wisdom

- Why don't statisticians like to model new clothes?
  - Lack of fit.

- Did you hear about the statistician who was thrown in jail?
  - He now has zero degrees of freedom.



Analyses Not Requiring Method Detection Limit, Precision, or Accuracy

- pH
- Demands (BOD, SOD)
- Salinity
- Color
- Temperature
- Microbiology
- Transparency
- Ignitability
- Titrimetric tests
- Organoleptic tests (odor, taste)

Analyses Not Requiring Method Detection Limit, Precision, or Accuracy

- Turbidimetric tests
- Residuals or solids (TSS, TDS, Volatile Solids, Settleable Solids)
- Specific Conductance
- Dissolved Oxygen
- Macrobenthic Invertebrates
- Oxygen Reduction Potential
- Paint Filter Liquids
- Residual Chlorine by electrode *requires an MDL* but not Accuracy
- Parameters calculated from the results of several different tests (Organic Nitrogen,
- Corrosivity, Unionized Ammonia)

Main problems with the current definition of the MDL

- The current procedure for calculating the MDL (3.14 times the standard deviation of seven low level spiked blanks) assumes that the spiked blank results are centered around zero. If the spiked blank results aren’t centered around zero, then the MDL will be too low and false positives will result. Realistically, results of spiked blank are not centered around zero.

Main problems with the current definition of the MDL

- The current MDL procedure assumes that short term and long term variance are the same. In other words, the procedure assumes that the variability in instrument response over one batch of analyses is the same as the variability in instrument response over a longer time period. The current procedure also assumes that the response is the same for all instruments used to analyze a particular parameter.

Main problems with the current definition of the MDL

- The current MDL procedure has no verification that the results obtained are reasonable.

Proposed MDL Revision 2015 MUR

- How to obtain a copy of the proposed MDL revision?
- http://water.epa.gov/scitech/methods/cwa/mur2015.cfm
- Under proposed changes click on the following link:
  - Federal Register Notice (PDF)
- Go to page 120 of the PDF document

Main changes to the MDL proposed by EPA in the February 19, 2015 Federal Register

- The revised MDL procedure accounts for background contamination. In the revised MDL procedure, two MDLs are calculated — one from seven low level spiked sample as in the current procedure and one from seven method blanks. The MDL is then set as the **higher** of the two.

Main changes to the MDL proposed by EPA in the February 19, 2015 Federal Register

- The proposed revision to the MDL procedure requires that MDL samples be run in at least three separate preparation and analysis batches. In addition, if a laboratory uses multiple instruments, then it will be required to calculate the MDL using spiked samples and blank samples from all the instruments. This modification will make the MDL more representative of a laboratory’s actual capability.

Main changes to the MDL proposed by EPA in the February 19, 2015 Federal Register

- The revised MDL procedure requires ongoing quarterly MDL verification and annual recalculation. Currently, laboratories can run MDL samples once a year under the most ideal circumstances (i.e., immediately after the instrument has been serviced or after an annual maintenance routine); this could result in artificially low MDLs. Quarterly evaluation will determine if the MDL has significantly drifted during the year, and also help verify that the results obtained are reasonable.

New MDL Determination Procedure

- Estimate the Initial MDL using one of the following:
  - The mean plus three times the standard deviation of a set of method blanks.
  - The concentration value that corresponds to an instrument signal/noise in the range of 3 to 5.
  - The concentration equivalent of three times the standard deviation of replicate instrumental measurements of spiked blanks.
  - 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.
  - Instrumental limitations.
  - Previously determined MDL.
  - It is recognized that the experience of the analyst is important to this process. However, the analyst should include some or all of the above considerations in the initial estimate of the MDL.

New MDL Determination Procedure

- Select a spiking level, typically 2–10 times the estimated MDL (Spiking levels in excess of 10 times the estimated detection limit may be required for analytes with very poor recovery)
- Process a minimum of 7 spiked blank samples and 7 method blank samples through all steps of the method, including any sample preservation. Both preparation and analysis of these samples must include at least three batches on three separate calendar dates. Existing data may be used if compliant with the requirements for at least 3 batches and generated within the last 2 years.

New MDL Determination Procedure

- If there are multiple instruments that will be assigned the same MDL, then the samples must be distributed across all of the instruments.
- A minimum of two spiked samples and two method blank samples prepared and analyzed on different calendar dates is required for each instrument.
- Evaluate the spiking level: If any result for any individual analyte from the spiked blank samples does not meet the method qualitative identification criteria or does not provide a numerical result greater than zero then repeat the spikes at a higher concentration.

New MDL Determination Procedure

- Compute the MDL_S (MDL based on spiked blanks) as follows:

$$MDL_S = t(n-1, 1-\alpha=0.99)\ S_S$$

Where:

MDLs = the method detection limit based on spiked blanks

t(n-1, 1-α=0.99) = the Student's t-value appropriate for the single tailed 99^{th} percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_S = sample standard deviation of the replicate spiked blank sample analyses.

New MDL Determination Procedure

- **Compute the MDL_b (MDL based on method blanks) as follows:**

A. If none of the method blanks give numerical results for an individual analyte, the MDL_b does not apply. A numerical result includes both positive and negative results, including results below the current MDL.

New MDL Determination Procedure

- **Compute the MDL_b (MDL based on method blanks) as follows:**

B. If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result.

New MDL Determination Procedure

- **Compute the MDL_b (MDL based on method blanks) as follows:**

C. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the blank results.

- For "n" method blanks where n ≥ 100, sort the method blanks in rank order. The (n×0.99) ranked method blank result (round to the nearest whole number) is the MDL_b . For example, to find MDL_b from a set of 164 method blanks where the highest ranked method blank results are . . . 1.5, 1.7, 1.9, 5.0, and 10, then 164×0.99 = 162.36 which rounds to the 162nd method blank result. Therefore, MDL_b is 1.9 for n = 164 (10 is the 164^{th} result, 5.0 is the 163^{rd} result, and 1.9 is the 162^{nd} result).

New MDL Determination Procedure

- **Compute the MDL_b (MDL based on method blanks) as follows:**

D. If all of the method blanks for an individual analyte give numerical results, calculate the MDL_b as:

$$MDL_b = \bar{x} + t(n-1, 1-\alpha=0.99)\, S_b$$

Where:

MDL_b = the MDL based on method blanks

$\bar{x}$ = mean of the method blank results

$t(n-1, 1-\alpha=0.99)$ = the Student's t-value appropriate for the single tailed 99^{th} percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_b = sample standard deviation of the replicate blank sample analyses.

New MDL Determination Procedure

- **Set the greater of MDL_s or MDL_b as the initial MDL.**

New MDL Determination Procedure

- **Ongoing Data Collection**
  - During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked blanks on each instrument, in separate batches if available, using the same spiking concentration used in Section 2. If any analytes are repeatedly not detected in the quarterly spike sample analysis, this is an indication that the spiking level is not high enough and should be adjusted upward.

New MDL Determination Procedure

- **Ongoing Data Collection**
  - –Ensure that at least 7 spiked blanks and 7 method blanks are completed for the annual verification.
  - –At least once per year, re-evaluate the spiking level.

New MDL Determination Procedure

- **Ongoing Data Collection**
  - If more than 5% of the spiked blanks do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level must be increased and the initial MDL re-determined following the procedure in Section 2.
  - If the method is altered in a way that can be reasonably expected to change the detection limit, then re-determine the initial MDL according to Section 2, and the ongoing data collection restarted.

New MDL Determination Procedure

- **Ongoing Annual Verification**
  - At least once per year, re-calculate MDL_s and MDL_b from the collected spiked blank and method blank results using the equations in section 2.
  - Include data generated within the last 2 years, but only data with the same spiking level.
  - Include the initial MDL spiked blanks if within two years.

New MDL Determination Procedure

- **Ongoing Annual Verification**
  - Only use data associated with acceptable calibrations and batch QC. Include all routine data, with the exception of batches that are rejected and the associated samples reanalyzed. If the method has been altered in a way that can be reasonably expected to change the detection limit, use only data collected after the change.
  - The verified MDL is the greater of the MDL_s or MDL_b. If the verified MDL is within a factor of 3 of the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL.

New and Old MDL examples

Spiked Blank Result (ug/L)	Blank Result (ug/L)
1.38	0
1.39	0
1.45	0
1.35	0
1.28	0
1.35	0
1.42	0
Recovery (%)	-
137.4	

True value 1.0 ug/L

Old MDL (ug/L)	New MDL (ug/L)	
	MDL_S	0.173
	MDL_b	na
0.173	**MDL**	**0.173**

New and Old MDL examples

Spiked Blank Result (ug/L)	Blank Result (ug/L)
1.38	0.62
1.39	0.21
1.45	0.24
1.35	0.51
1.28	0
1.35	0
1.42	0
Recovery (%)	-
137.4	

True value 1.0 ug/L

Old MDL (ug/L)	New MDL (ug/L)	
	MDL_S	0.173
	MDL_b	0.62
0.173	**MDL**	**0.62**

New and Old MDL examples

Spiked Blank Result (ug/L)	Blank Result (ug/L)
1.38	0.62
1.39	0.21
1.45	0.24
1.35	0.51
1.28	0.51
1.35	0.35
1.42	0.42
Recovery (%)	-
137.4	

True value 1.0 ug/L

Old MDL (ug/L)	New MDL (ug/L)	
	MDL_S	0.173
	MDL_b	0.883
0.173	**MDL**	**0.883**

Evaluate Reports

Analyte	Units	Result	PQL
Cadmium	ug/l	234000	0.2
BOD	mg/L	2400	2.0

Thank You

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