Analytical Detection Limit Buzzwords Defined from a Chemist's Perspective

There are many statistical terms used in analytical chemistry. Many of these words are used daily, but not completely understood. Here is a primer on these statistical expressions, written by one of Lachat Instruments' Application Chemists.

It is important to note that all Lachat methods are developed according to standard work instructions and EPA requirements. There are criteria that must be met before any method can be published. These criteria are often defined in these statistical terms. Lachat hopes this short summary is helpful to your lab.

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Method Detection Limit

Published values for the Method Detection Limit (MDL) in Lachat methods seem to be a common source of confusion. It is important to note that the MDL for any given method is a STATISTICAL, and not a quantitative value.

The EPA defines MDL as "the minimum concentration of a substance that can be determined and reported with 99% confidence that the analyte concentration is greater than zero." This procedure is outlined in 40 CFR part 136. Method detection limits are matrix, instrument, and analyst specific. MDL's allow the analyst to compare different laboratories' capabilities with identical methods as well as different analytical methods within the same laboratory. The method detection limit can then be calculated according to the formula:

MDL = "Student's t value" x Standard Deviation

If the calculated MDL is less than $1/5^{th}$ of the standard used in its determination, a lower standard must then be used for the calculation.

Standard deviation is a signal to noise parameter. The calculated MDL can vary from day to day, depending on varying conditions in the lab, the instrument, or

the sample matrix. Worn pump tubes and expired reagents are several important things to note that can contribute to higher calculated MDLs.

Always remember when interpreting results, that the limit of detection or MDL is not a quantifiable value but is the lowest concentration of analyte that can be distinguished from a concentration of zero.

For more information, a very helpful perspective on MDL and other analytical detection limit information has been written by the Wisconsin Department of Natural Resources:

(http://www.dnr.state.wi.us/org/es/science/lc/OUTREACH/-Publications/LOD%20Guidance%20Document.pdf)

The **Limit of Quantitation**, (LOQ) in contrast, is approximately 2.5 to 5 times the MDL.

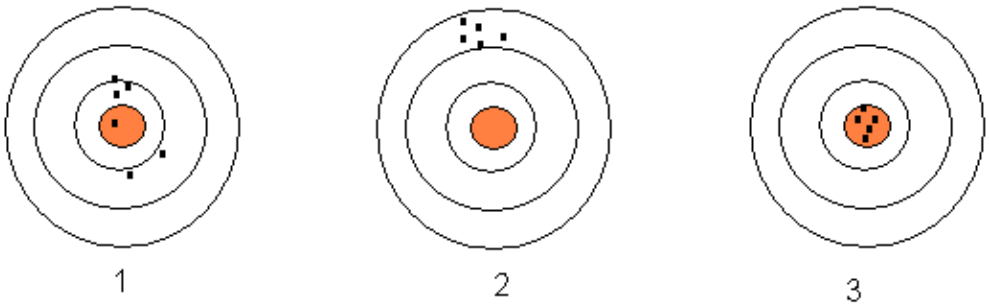
Note: This is because the standard used to determine the MDL cannot be more than 5X the MDL determined when using it. In the past, the USEPA mandated 10X, so many older methods may still have these lower MDL's.

Lachat method write-ups include the lowest concentration that can be quantified within +/-10% as the lowest, non-zero calibration standard. The calculated MDL is also used to determine spiking levels. Spikes are typically 5 to 50X the calculated MDL.

Repeating MDL testing at regular intervals can help ensure sure that your methods remain in control.

Precision and Accuracy

Accuracy: Defined by how close a determined value is to the true value
Precision: Defined by how close a set of repeated measurements come to one another. Precise results can still be inaccurate!



1) Neither accurate nor precise to the bull's-eye
2) Precise, but not accurate to the bull's-eye
3) Both accurate and precise to the bull's-eye

Lachat uses **%RSD** (% Relative Standard Deviation) as a measure of precision.

$$\%RSD = \frac{StdDev}{mean} \times 100$$

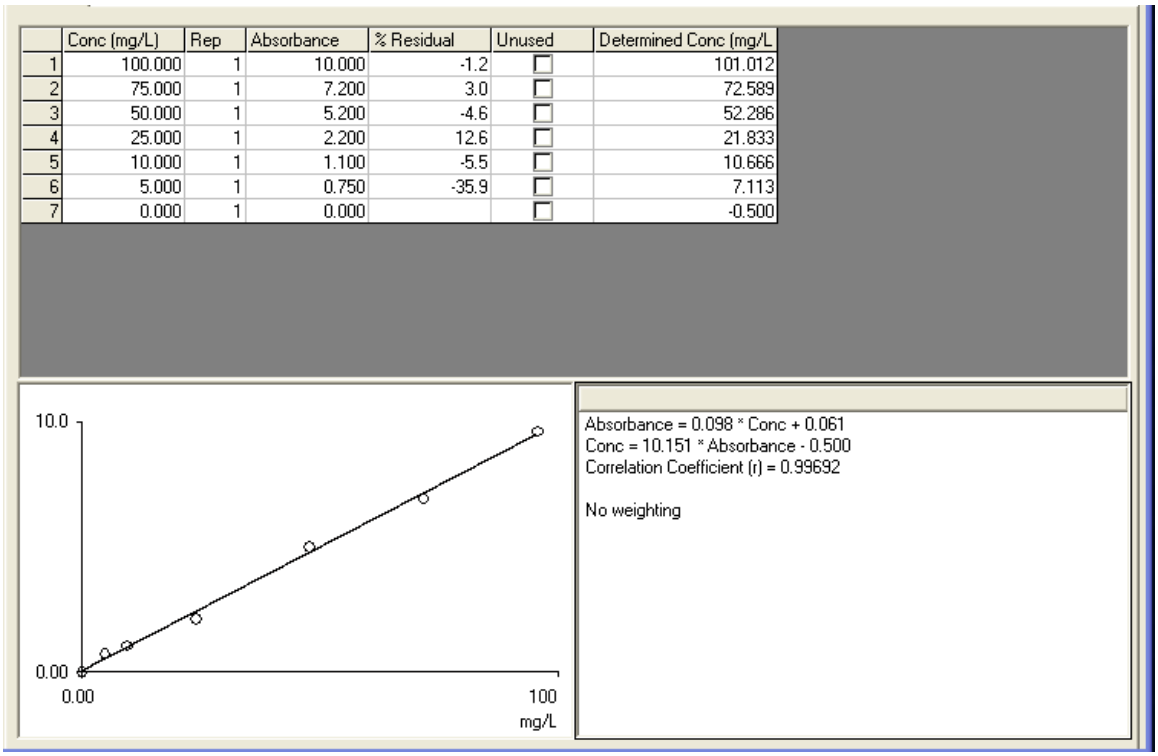
This determination is typically made using 10 replicates of a mid-range standard. Accuracy is measured by **%residual**.

Calibrations: Correlation and Residual

A **correlation coefficient** is a number between -1 and 1, which measures the degree to which two variables are related. If there is perfect linear relationship with positive slope between the two variables, we have a correlation coefficient of 1; if there is positive correlation, whenever one variable has a high (low) value, so does the other. If there is a perfect linear relationship with negative slope between the two variables, we have a correlation coefficient of -1; if there is negative correlation, whenever one variable has a high (low) value, the other has a low (high) value. A correlation coefficient of 0 means that there is no linear relationship between the variables.

Residual (or error) represents unexplained (or residual) variation after fitting a regression model. It is the difference (or left over) between the observed value of the variable and the value suggested by the regression model.

It is important to note that a calibration can have a good correlation coefficient (0.995 or greater), but not be a "good" calibration. Residuals for a calibration should never exceed +/- 10%. When a standard has a high residual, this will affect the determination of a sample that is near that concentration.



	Conc (mg/L)	Rep	Absorbance	% Residual	Unused	Determined Conc (mg/L
1	100.000	1	10.000	-1.2	☐	101.012
2	75.000	1	7.200	3.0	☐	72.589
3	50.000	1	5.200	-4.6	☐	52.286
4	25.000	1	2.200	12.6	☐	21.833
5	10.000	1	1.100	-5.5	☐	10.666
6	5.000	1	0.750	-35.9	☐	7.113
7	0.000	1	0.000		☐	-0.500

For example, using this calibration, a sample that has a concentration near 5 ppm will be read as nearer to 7 ppm, and one near 25 ppm will read closer to 22!

Using a 5 ppm standard to determine an MDL in this case would give a very high value.

If you are having difficulty understanding your results or would like further explanation on the application of these terms, please contact Lachat Technical Support.

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