DATA POINTS
A STATISTICS Q&A

Detection Limits

Their Use and Importance

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Q What are detection limits and why are they important?

A Detection limits are of critical importance in both industrial and regulatory contexts. A DL for an analytical measurement system (AMS) is an estimate of the lowest concentration of a substance that can be reliably detected. As the concentration of a substance approaches zero, it becomes much more difficult to measure reliably. At some level close enough to zero, the measurement system may provide an unreliable estimate or fail to provide a result at all. DLs represent a statistically consistent methodology to estimate a figure of merit or capability of an AMS.

This figure of merit is often used as either a business or regulatory requirement. It is typically required that any method used to measure a trace product specification must have a DL that is equal to or less than the specification in question. For example, if a product is to contain no more than 1 ppb of chromium then its measurement method DL must be 1 ppb or less. FDA has DL requirements for validating an AMS in pharmaceutical applications. It is critically important for businesses, independent laboratories, and government laboratories to be able to perform to business specifications and/or regulatory requirements.

Additionally, specification requirements and regulatory limits sometimes challenge the current state of measurement system capability. For example, some chemicals in industrial wastewater are regulated by the U.S. Environmental Protection Agency at levels below the DL.[1] In these cases, a detection in a discharge stream is a violation and may trigger financial penalties for the regulated entity. This creates a perverse incentive for the regulated entity to justify the highest DL that the regulator will accept.

There are a very large number of DL concepts, methodologies, and related acronyms created by many different organizations, nationally and internationally, even radically differing between offices of the same federal agency. This diversity is driven in part by divergent interests and objectives. The following list of terms, while lengthy, is not complete. Some acronyms are nearly synonymous, but many are not. There are often alternative statistical methodologies and varying rule sets available for each acronym.

IDE: Interlaboratory Detection Estimate

IDL: Instrument Detection Limit

LCMRL: Lowest Concentration Minimum Reporting Level

LDL: Lower Detectable Limit

LLOD: Lower Limit of Detection

LOD: Limit of Detection

LOGD: Limit of Guaranteed Detection

LOQ: Limit of Quantification

MDL: Method Detection Limit

MRL: Minimum Reporting Level

PQL: Practical Quantification Limit

RL: Reporting Level or Reporting Limit

Let's examine a relatively simple low level detection limit concept, that of an IDL. Here are two of the available definitions: 1) Concentration that produces a signal that is equivalent to at least 3 times the standard deviation of the blank. 2) Concentration that is equivalent to 5 times the noise in the signal-to-noise ratio. Each has a wording that describes a statistical multiplier (3, 5, respectively) that converts a measure of the noise in the process of measuring an instrument signal into a concentration via a calibration relationship. In order to make the concept into a standard practice, one would have to pick a definition and also rigorously define how to react to every issue and exception encountered in routine practice.

For example, with the first definition, one might require that the standard deviation be based on a minimum of 20 or 25 independent blank measurements to justify the use of 3. Others might say that less than 20 is OK, but a Student's *t* multiplier should be used instead of 3. Still others may require an absolute minimum of 7 blanks no matter what the multiplier. In certain AMS, blanks are either not representative or not even measureable; what rule sets are required to still compute a reasonable IDL?

For example, with the second definition, alternate versions use multipliers other than 5 such as 2, 3, and 10. Which should be used? There are multiple definitions of the S/N ratio that provide different detection limits. Which should be used?

Some questions for both approaches are issues such as: What should detection limit estimation require with respect to calibration? Should only a single estimate of the detection limit be required or should multiple estimates be used? Should these estimates be averaged or should a particular estimated percentile be used?

The American Chemical Society provides the following quote, "Detection limits are controversial principally because of inadequate definitions and confusion of terms."[2] DLs are even more controversial because of their critical business and regulatory contexts. The complex and volatile mixture of statistics with business and regulatory requirements can make standardization of a methodology daunting because all likely parties at the table do not share fully common interests. Despite this, a robust and accepted standard for a key DL concept, the MDL, would be of great value to all stakeholders.

Against this backdrop, Committee D22 on Air Quality, with the active involvement of Committee E11 on Quality and Statistics, organized a Conference on Detection Limits in August 2016. The goal of the conference was to bring together as many of the stakeholders and points of view as possible and to lay the groundwork for greater consistency in terminology and methodology, going back to first principles as espoused by Lloyd Currie and others in the late 1960s.[3] A few of the key conclusions of the conference were:

- Terminology needs to be standardized and simplified.
- The requirements of both analytical and statistical communities need to be considered in a way that balances the need for statistical rigor with the need for understandable methodology that can be practically and consistently applied in the field.
- The methodology needs to evaluate the parameters that contribute to important sources of variance, bias, and error distributions. For low level measurements in particular, variation over time needs to be considered.
- The conference also identified data reporting as an issue, especially when the result is above zero but below the DL.

As a result, an ongoing effort involving Committees D22 and E11 is now underway to develop an ASTM guide that will provide a more consistent approach based on the ASTM consensus process and also to develop additional standards on laboratory detection and quantification. The D22 effort will focus on air quality and related methods, but the effort should lead to benefits in other areas. A second conference is being planned for October 2018.

REFERENCES

1. U.S. Environmental Protection Agency, "Memorandum: Guidance on Water Quality Based Effluent Limits Set Below Analytical Detection/Quantitation Limits," April 25, 2005, yosemite.epa.gov/r10/water.nsf/NPDES+Permits/Permits+Homepage/$FILE/ML-MDL-Policy-4-25-05.pdf.

2. American Chemical Society Committee on Analytical Reagents, Paul A. Bouis, Chair, *Reagent Chemicals: Specifications and Procedures*, 10th edition, Oxford University Press, 2006.

3. Currie, L.A., "Limits for Qualitative Detection and Quantitative Determination," *Analytical Chemistry*, Vol. 40, No. 3, 1968, pp. 586-593.

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