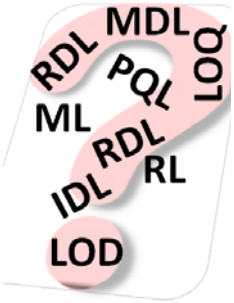
LOD & LOQ Unplugged -The complex and confounding relationship between calibration, the LOD, and the LOQ



The list of acronyms associated with the conceptual detection and quantitation limits is a veritable alphabet soup with an overabundance of "D"s and "L"s.

The NELAC (TNI) program has its own list of concepts and definitions, as do the EPA, a number of federal programs, and even various states. To further complicate things, the EPA has recently proposed a wholesale change to the "MDL" protocol, the first in over 30 years. But at the end of the day, in this state, we are bound by our administrative code. So, while we can appreciate the difficulty in juggling this multitude of concepts, definitions, and protocols for labs that operate nationwide, our programs depend on us to follow our administrative rule. It's as unrealistic to request that the LabCert program accept the Department of Defense's procedures as it is for us to request that they accept ours. In the absence of a nation-wide consensual approach to these issues, satisfying multiple regulatory entities is simply the price of doing business in the national arena. LabCert's primary mission directive is to support the internal DNR programs. Our approaches to these issues serve as the foundation of each environmental programs' determination of whether or not an action level has been exceeded, or a trigger point has been tripped requiring additional monitoring.

Actually, the cart may have been placed before the horse on this issue. While the issues of detection and quantitation are important, one could make a solid argument that they are both meaningless in the absence of a robust calibration. We focus intently on details of the LOD and LOQ, yet there are no equivalent detailed requirements of the calibration which is required to obtain these values. But that's a whole different article. We need to talk about two very basic concepts (detection and quantitation) and the very critical bridge —calibration— between them.

We first have to define our terms. Again, there are numerous definitions out there, but in this state, we are bound by our administrative code. It's also important to keep these definitions centered on your radar screen.

LOD
"Limit of detection" or "LOD" means the lowest concentration or amount of analyte that can be identified, measured, and reported with confidence that the concentration is not a false positive value. For department purposes, the LOD approximates the MDL and is determined per 40 CFR Part 136 Appendix B.

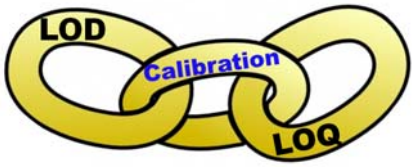
LOQ
"Limit of quantitation" means the lowest concentration or amount of an analyte for which quantitative results can be obtained.

Stripped of its entourage of endless theories and opinions, the LOD is simply the point at which an analyte is present and that it is not a false positive; the LOQ is simply the point at which quantitative results are obtained. *Note that there is no implied accuracy or precision associated with the LOQ (although many try to incorporate it)*. It's that simple. One is the point at which you can conclusively state that "X" is present, and the other is the point at which you can definitively state how much "X" there is.

While it could be interpreted that the LOD is not a measurable result, that would be an incorrect assertion. We recognize that values between the LOD and the LOQ represent a gray area where quantitation is uncertain. We get it; our programs get it. In fact, if one looks at the hierarchy of decision making process determining whether a particular action limit or standard has been exceeded, the LOD and LOQ are significant parts of the assessment process. That also explains why the LabCert program staff must remain focused on our administrative rule requirements, regardless of what other programs are doing.

Calibration Points

Quite frequently our auditors get an earful about LODs and how unrealistic they are. But just as frequently, when auditors review



calibration data they find that the questionable LOD or LOQ are directly related to how the calibration was constructed. Years ago when Flame AA (FLAA) was still in vogue we used to see LODs in the 1 to 10 ppb range and calibrations beginning at 500 or 1000 ppb. Then we'd find that the low calibration standard was associated with an almost imperceptible instrument response. Newsflash; those LODs were not realistic. Things have improved over the years (*and FLAA has almost gone the way of the 8-track*), but we can still trace a number of LOD problems to the calibration.

Bottom up – not top down.

Our administrative rule tethers the LOD to the LOQ and then the LOQ to the calibration. Some programs have apparently adopted a top-down approach where a calibration standard is established as the LOQ and then the LOD is derived as some fraction of the LOQ. While a top-down approach is often preferred over a bottom-up one, in this case we need to start from the bottom (the LOD) and work our way up, because the LOD is the piece of the puzzle that is developed via a strict formula. Everything else can be definitively related to the LOD.

Even Siri has trouble with "near"

The principal deficiency that auditors encounter is that, instead of mathematically relating their LOQ to their LOD, labs simply establish their LOQ as the concentration of the lowest calibration standard, or ½ their lowest calibration standard. This practice does not meet administrative code requirements and therefore is not acceptable.

The Lab Cert program does not allow labs to indiscriminately establish their LOQ based on any point in their calibration . Our program establishes the LOD and then states that the LOQ must be "related" to the LOD. While some may disagree, by "relate" our intent was that the relationship be mathematically defined (*and stating that the LOQ must be greater than the LOD does not satisfy this requirement*). One only needs to go back to the original treatise on LOD/LOQ *("Principles of Environmental Analysis" Analytical Chemistry, 1983, Vol. 55, pp. 2210-2218*) to see that the most recognized relationship between the LOD and LOQ is that the LOQ is statistically 10/3 times the LOD. Then, where analyses are being performed down to the LOD (which is a requirement of most of the agency's environmental programs), the lowest point in the calibration is required to be "**near**" the LOQ. Admittedly, that is a poor choice of terms, but it affords us some flexibility. The intent here is clearly "in close proximity to". If you're going to meet somebody "nearby", it certainly wouldn't involve a 30-minute drive. The underlying point here is that, with the exception of a few technologies (e.g., ICP), the further away from the LOQ the lowest calibration point, the more difficulty one will have in establishing a reasonable LOD.

LabCert Requirements

The LabCert program has recently developed a resource (2015LOD_LOQ_Clarity) which should help clarify the critical requirements for labs as it relates to LOD, LOQ, and calibration.