

Limit of Determination (LOD)

By necessity we must first review the history and terminology. Historically chemical analysts worked in a range of industries to provide data fit for purpose for that industry. Many methods were "wet" procedures, often delivering empirical data, i.e. following the method gave you that result, which may or may not have accurately reflected the concentration of the analyte. Such methods were often acceptable for the QC of manufactured products, when a significant amount of analyte was present, and LOD was usually less important than the accuracy of the test in ensuring that repeatable data could contribute to the necessary process controls.

As techniques developed and interest increased in trace analysis, both within products and the environment, the accuracy, i.e. how close is the result to the "actual" concentration? and the precision, i.e. how reproducible is the result? were identified as being crucial to determining the validity of the data. This led to the evolution of a whole range of terms and acronyms for different applications, which continue to develop while keeping analysts on their toes and confusing the end user.

LOD can mean limit of determination (what can accurately be measured) or limit of detection (what level can be seen but not necessarily accurately determined) and to these are added MRL (minimum reporting limit), MQV (minimum quantifiable value), LOQ (limit of quantification), MRV (minimum reporting value) and so the list continues. To further confuse this, the criteria used to determine the above values, by means of method validation, may differ depending on the application, i.e. how accurate or precise does the data have to be for the analyst to provide a robust LOD. Of particular importance is that the laboratory adopts a method that will produce an LOD meeting the requirements of the end user of the data; typically ten-fold lower than the level of interest, to give confidence that the result can be used with certainty.

The LOD calculation is founded on the observation that the relative standard deviation of a population of replicates increases as the concentration of the analyte decreases; a relationship described by American chemist William Horwitz. By setting values considered acceptable for the confidence level and the number of replicates to be tested, it is possible to establish from the calculated standard deviation the concentration limit at which these criteria are met, i.e. the level at which it is statistically proven that the analyte can be detected with that level of confidence.

The problems associated with unachievable LODs are acknowledged by the Environment Agency in their fact sheet issued 30 April 2008 and entitled "Groundwater trigger levels, minimum reporting values and limits of detection", which does say, "we accept the MRVs for certain list 1 substances published in our LFTGN 01 guidance cannot be reasonably achieved by a number of laboratories". However, laboratories must accept that there will be a continual expectation for lower and lower LODs, for elements and compounds that are potentially harmful to the environment.

Again, considering soils analysis the Agency accepts that, "the maximum value of the LOD usually regarded as being fit for purpose is 10% of the concentration regarded as the critical level of interest" (from MCERTS for soils, March 2006). However, in the same document it is also noted that, "the LOD of a method used to analyse highly contaminated samples may be higher than the LOD of a method used to analyse slightly contaminated samples"; this is also applicable to aqueous samples.

Laboratories routinely have to accommodate samples varying in levels of contamination, from clean surface waters to polluted gas works soils, and return fit for purpose data for analytes that can range from sub parts per billion to percent levels. This rigorously tests the ability of the analyst and the laboratory's systems and test methods, all adding to the challenges of providing fit for purpose LODs.

As a supplier of analytical data to the 'brownfield' industry, Chemtest constantly strives to provide UKAS and MCERTS accredited data in a timely and cost effective manner, in order to assist clients to meet their contractual obligations and to make meaningful risk assessments based on analytical results. To this end, our Bid Team and Technical Administrators ensure that our client's required specified LOD can be met, or otherwise consult the client to confirm that our achievable LOD is acceptable. In some cases a lower LOD is feasible, but not one determined to the criteria laid down in MCERTS. It is not uncommon to find that no laboratory can in fact meet a particular LOD with their accredited method and in these circumstances the client may choose either to accept an accredited method's higher LOD, or have data reported as non-accredited.

Further guidance comes from MCERTS for waters, July 2008, which states, "Ideally analysis of blank samples will produce normally distributed results scattered around the zero... However this may not always be possible and in some analytical systems negative or low results cannot be obtained. In these cases the blank sample may be spiked with a small amount of the determinand... This concentration should not exceed 5 times the LOD". For accreditation purposes, laboratories are required to provide robust data from running such blank or near-blank samples.

A typical LOD calculation (ANOVA) for one analyte, for one sample matrix may look like this:

Date	Batch	Replicate	Concentration mg l-1
28-Nov-07	Batch 1	A	0.073
28-Nov-07		B	0.081
29-Nov-07	Batch 2	A	0.108
29-Nov-07		B	0.076
29-Nov-07	Batch 3	A	0.077
29-Nov-07		B	0.074
30-Nov-07	Batch 4	A	0.081
30-Nov-07		B	0.083
30-Nov-07	Batch 5	A	0.080
30-Nov-07		B	0.072
03-Dec-07	Batch 6	A	0.092
03-Dec-07		B	0.089
04-Dec-07	Batch 7	A	0.044
04-Dec-07		B	0.049
04-Dec-07	Batch 8	A	0.052
04-Dec-07		B	0.055
05-Dec-07	Batch 9	A	0.071
05-Dec-07		B	0.068
05-Dec-07	Batch 10	A	0.066
05-Dec-07		B	0.070
06-Dec-07	Batch 11	A	0.075
06-Dec-07		B	0.077
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AVERAGE	0.073		
COUNT	22.00		
SD	0.015		
Blank			
	Mean	Sw	Var. (Sw2)
Batch 1	0.077	0.005656854	0.000032
Batch 2	0.092	0.022627417	0.000512
Batch 3	0.0755	0.00212132	0.000005
Batch 4	0.082	0.001414214	0.000002
Batch 5	0.076	0.005656854	0.000032
Batch 6	0.0905	0.00212132	0.000005
Batch 7	0.0465	0.003535534	0.000013
Batch 8	0.0535	0.00212132	0.000005
Batch 9	0.0695	0.00212132	0.000004
Batch 10	0.068	0.002828427	0.000008
Batch 11	0.076	0.001414214	0.000002
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Sum		0.000618	
m = 11		n = 2.00	
M0		0.0000562	
Pooled sw		0.00750	
LOD		0.038	
(LOD is 5.13 x Sw)			
Reporting Limit in SOP		0.05	



It should be borne in mind that once an LOD is established, it is also necessary to consider a method's fitness for purpose in other respects. In service there may always be significantly more of an analyte in the matrix, even when not contaminated and the contaminant, or the response from interfering compounds, may exceed the method's upper reporting limit or even the range of the detector. The sample will then need to be re-prepared, diluted or run by a different method. Under these circumstances, LOD is no longer the primary consideration.

In conclusion we recommend that all users of data consider and discuss what are appropriate LODs for the project, matrix and analyte with their chosen laboratory as they strive to consistently deliver robust data.