

More Ado About Next to Nothing

Bringing Minimum Petection Levels into Focus

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In the Beginning...

- Stack sampling was created, and an understanding of emissions levels came to pass. And it was good.
- Until someone asked..."How good is it?"
- And someone else asked... "How low can we measure and get reliable results that provide assurance that a given source is operating in a state of compliance with a low emissions limit while taking into account a host of variables?"





Emissions measurement levels and the CAA

- MACT floor process drives limits downward, sharply at times.
- New Source Floor (single best unit) often driven by MDL values
- Need to set limits where MDL results don't indicate non-compliance
- Must factor in variability of testing, analysis, and source operations
- All these elements are driving us to deal with MDL values head on.





What is Minimum Detection Level?

- Minimum concentration that can be measured with 99% confidence that the value is above zero.
- MDL ≥ blank
- Specific to sample matrix, test method, and analyte
- Generally expressed as mass/sample volume







How do labs determine a Minimum Detection Level?

- EPA Method 301, Section 15 and Table 4, Procedure 1
- Measure a blank sample, at least seven times
- Observe the standard deviation of the seven replicates
- Multiply that by the Student-T value for N-1 (six) data points (3.14) to determine MDL
- Multiply the MDL by the Student –T value again, or multiply the original Ds times ten to determine the Level of Quantitation (LOQ)





MDL realities

- Different from test method to test method
- Different from lab to lab
- May be different source to source
- Sometimes different "within" test method (Method 29)
- Some causes of variation are
 - Sample volume
 - Instrument calibration choice
 - Measurement scale
 - Measurement technique







Levels of "L" — Be advised

- MDL Minimum Detection Level What we really want to know
- LOQ 3x MDL = Practical Quantitation Level Where we can <u>reliably</u> measure.
 We <u>can</u> measure below this. Aka PQL
- RDL Representative Detection Level The average MDL achieved by a pool of measurements using the same approach. Used in MACT floor setting process.
- RL Reporting Limit What some labs consider to be their lowest reportable value, often much higher than MDL
 - NOT the "L" we are looking for
- EDL Specific to Dioxin/Furan tests and equivalent to MDL





RDL – A new term for the MACT floor world

- Represents the average MDL value for a given test method
- Gleaned from test reports representing the best performing sources
- Provides opportunity to use a local lab, not lab with lowest MDL
- Will always be a higher value than the lowest MDL in a source category
- Labs should be able to quantify at and above this mark





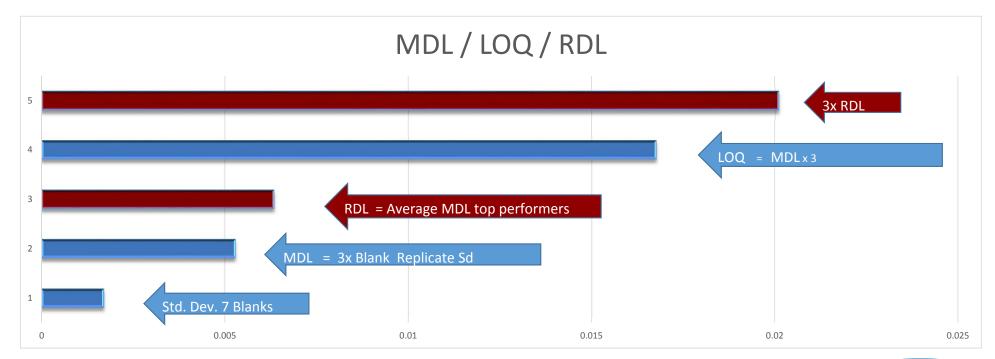
Certainty of Measurement

- At and above the LOQ, EPA Air test methods are +/- 15% to 20%
- Below the LOQ, uncertainty increases. At the MDL, uncertainty is generally about +/- 50%
- Below the MDL uncertainty increases rapidly as measurements approach zero, reported values may be +/- 100%





Visual representation of concepts







How best to avoid BDL values?

- Employ a multi-pointed approach before the test:
 - Require MDL determination for each analyte
 - Lower the Detection Level with more sensitive technology
 - Collect more sample where mass is the target
 - Westlin/Merrill memo
 - MPG
 - Be aware that more sample is not always the right answer (concentration)
- Post test:
 - Scrutinize reported data for proper MDL values, not RL or LOQ





Where to expect low values

- Baghouse emissions of PM Especially membrane bags and cartridge type filters
- Thermal oxidizer exhausts of VOC or organic HAP
- Some Dioxin/Furan congeners will be BDL
- HCl emissions on outlet of a wet scrubber
- Clean fuel sources
 - Natural gas turbine and boiler PM emissions
- Sources that are mostly ambient air
 - Rooftop vent(s)



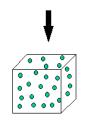




Moving the MDL downward

 Concentration based analyses can only improve by lowering measurement range/calibration precision to increase sensitivity

 Mass based analyses may improve detection by collecting more sample (more sample ≈ more mass) and using analysis with improved sensitivity



Every approach has its lower limitations





Westlin/Merrill Memo

- Determine sample collection needs for mass/volume test methods
- Outlines RDL's for Metals, D/F, PM, and HCl
- Will be updated as more RDL's are developed
- Included in your packets

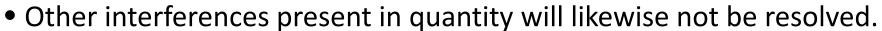
	RDL (ug)	3 x RDL	3 x RDL Concentrations (ug/dscm)			
		(ug)	1 dscm test	2 dscm test	3 dscm test	4 dscm test
HCl/Cl2 (Method 26A)	6.0E+1	1.8E+2	1.8E+02	9.0E+01	6.0E+01	4.5E+01





Caveats to common solutions

- Mass measurements often benefit by collecting more sample
 - This is not a panacea.
- Many sample techniques collect condensed moisture
 - May dilute the sample you are trying to concentrate
 - More problematic with high moisture sources
 - Test durations > 8hrs not feasible







What about DLL data?

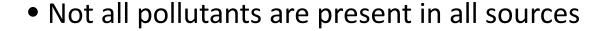
- Detection Level Limited
 - Example Method 29 for mercury has 5 analytical fractions.
 - Detection of Hg in three fractions, and BDL values in two others can happen.
 - Sum of all five fractions will exceed the MDL, so DLL values are valid.

Hg Fraction	Mass	MDL
Filter	1.2	.03
HNO3 + Rinse	0.61	0.09
Mid-Imp	<0.09	0.09
KMnO4	0.52	0.11
HCl Rinse	<0.11	0.11
Total:	≤2.53	0.43





Is BDL data always bad?





- Key is to use due diligence so BDL has real meaning
 - "If it was there, we'd have seen it."
- Helpful to rule out pollutants that don't need regulation





Policy Decisions regarding Minimum Detection Levels

- A concerted effort should be made to quantify emissions above the MDL level. Appropriate sample volume, instrument range, and sampling technique/method.
- The detection limit should always be reported with the analytical results.
- The detection level should be used to determine compliance whenever BDL data is reported.
- If there are multiple sample fractions in a train, the sum of the fractions (either all of the detections limits or a mix of measured quantities and detection limits) should be used to determine compliance.
- If there are multiple compounds combined in one limit (e.g. total metals, VOC, etc.), the sum of the numbers for each compound (either all of the detection limits or a mix of measured quantities and detection limits) should be used to determine compliance.

Office of Air Quality Planning and Standards



Summary

- Always request an MDL value and accept no substitutes
- Not all "DL's" are created equal
- Expect some MDL variability from lab to lab, method to method, etc.
- More volume = more mass (in general)
- Lower concentration requires greater sensitivity
- Some test methods have expected MDL values in them (26A, 29)
- Sometimes a compound of interest just isn't there
- DLL data is ok

