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Calculating & Using Method Detection Limits

A Joint Presentation from
Water Environment Federation
&
American Public Health Association

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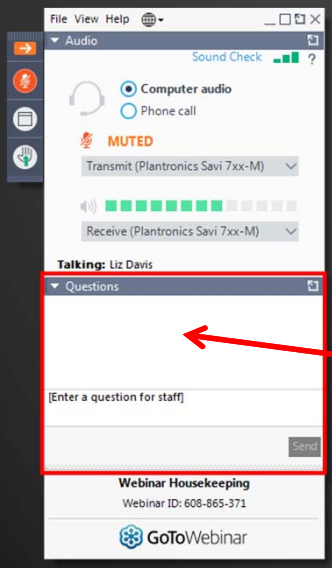
How to Participate Today



- **Audio Modes**
  - Listen using Mic & Speakers
  - Or, select "Use Telephone" and dial the conference (please remember long distance phone charges apply).
- **Submit your questions using the Questions pane.**
- **A recording will be available for replay shortly after this webcast.**

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Today's Moderator

Dale Baker
Laboratory Director and Environmental Coordinator

GARRETT COUNTY
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MARYLAND

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Today's Speakers

- History of Method Detection Limits & Regulatory Programs
  - Elizabeth Turner
- Evaluating Blanks
  - Jeff Bennett
- Calculating MDLs
  - Mary Johnson

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Our Next Speaker

Elizabeth Turner
Quality Program Manager

Pace Analytical®
ENVIRONMENTAL SCIENCES

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History of Method Detection Limits & Regulatory Programs

Elizabeth Turner

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Why Method Detection Limits?

- Make quantitation meaningful
- Needed for risk assessment
  - Regulatory Programs
  - Statistical analysis

Protection of human health and the environment to a large degree depends on the ability to measure accurately the presence or absence of contaminants of concern.

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Detection Limit

- Can you see me now? (10 pt)
- Can you see me now ? (12 pt)
- Can you see me now (18 pt)
- Can you see me now? (24)

At what font size can you see words?

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Analytical detection limits are:

- developed by statisticians,
- applied by analytical laboratories,
- and used by policy makers, regulators, and lawyers.

- Michael Brisson

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Lloyd Currie - 1968

- Introduced terms of – “critical level” (LC), “critical value” (CRV); the “detection decision”; with a 50% confidence level
- “minimum detectable value” (MDV), “detection limit” (LD) with a 99% confidence level
- “determination limit”, “minimum quantifiable value” (MQV); limit of quantitation” (LOQ); commonly “quantitation limit” (LQ) required precision, accuracy, false negative error rate and qualitative identification criteria for the intended purpose.

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Trace analyses for wastewaters

Method detection limit, a new performance criterion for chemical analysis, is defined as that concentration of the analyte that can be detected at a specific confidence level. Both theory and applications are discussed for reliable wastewater analyses of priority pollutants

John A. Glaser
Denis L. Foerst
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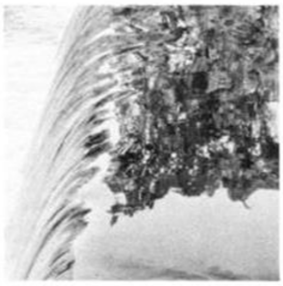

The development of trace analysis methodology brought with it a series of questions about method performance at low concentration levels of analyte (*1*, *2*, *3*). Under Section 304(h) of the Clean Water Act, as amended in 1977, (*4*) the Environmental Monitoring and

ority pollutants, it was incumbent on EMSL to develop method perfor-

detection limit should be related to the standard deviation of the measured values at or near zero concentration of the analyte (*11*).

There is no doubt that the detection limit is one of the most important performance characteristics of an analytical procedure. In most cases, a detection limit must be viewed as a temporary limit to current methodology.

Complete analytical system

Ostensibly, analysts do not directly observe concentrations of analyte. The measurements of the transducer signal, which are related to the analyte concentration, are actually observed. In any analytical system, information

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EPA - 1981

- Method detection limit (MDL) was first published in a paper by John Glaser and others at EPA's laboratory in Cincinnati in 1981 in Environmental Science and Technology
- MDL based on Currie's work
- Employs low-level spikes rather than backgrounds
- Uses Student's t-test to allow for varying number of replicates

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Various Procedures

- American Council of Independent Laboratories (ACIL) Proposed Procedures for Determining the Method Detection Limit and Quantitation Limit (ACIL procedure)
- Hubaux-Vos Detection Limit Procedure
- ASTM Interlaboratory Detection Estimate (IDE)
- EPA MDL, 40 CFR Part 136, Appendix B
- ASTM Interlaboratory Quantitation Estimate (IQE)
- EPA OGWDW Lowest Concentration Minimum Reporting Level (LC-MRL) for Quantitation
- ISO/IUPAC
- USGS LT-MDL

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EPA Method Detection Limit

- 1984 – 2017
- 40 CFR 136 Appendix B
- The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

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Procedure

- 7 low level spikes
- 2 – 10x the expected MDL
- MDL = $T_{(n-1,1-\alpha=0.99)}$ (S)
- Performed annually
- Usually done under ideal conditions

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Limitations of MDL Procedure 1.11

- Assumption of normal distribution and constant standard deviation
- Narrow estimate of method variability
- Assumption instrument variability is constant
- Assumption variability is the same for all instruments
- Assumption of normal distribution
- Focused on false negatives, ignored false positives

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EPA Must Change Procedure

- In 1999, several industry groups filed suit against EPA (Alliance of Automobile Manufacturers, et al. v. EPA, No. 99-1420, (D.C. Cir.)) – re: EPA Method 1631E
- October 2000, the parties reached a settlement agreement that required EPA to assess existing Agency and alternative procedures for determining detection and quantitation limits and sign a notice for publication in the **Federal Register** on or before February 28, 2003, and to invite comment on the assessment.

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EPA Must Change Procedure

- 2002 USEPA issues a Technical Support Document of Detection and Quantitation Regulations under the Clean Water Act (TSD).
- 2003 Draft revised MDL published
- 2003 Consensus letter submitted to Assistant Administrator of Office of Water signed by 31 parties urging EPA to consider a scientifically sound approach to the detection and quantification issue.
- 2004- proposed MDL procedure was withdrawn

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Federal Advisory Committee

- 2004 - **Federal Register** notice published that a neutral party is seeking a broad group of stakeholders willing to work together to define and address concerns about the way detection and quantitation values are calculated and used to support CWA programs.
- Formed in 2005
- Composed of state government, environmental laboratories, regulated industry, public utilities, the environmental community, and EPA
- To provide advice and recommendations on approaches for the development of detection and quantitation procedures and uses of these procedures in Clean Water Act program

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Committee Recommendations

December 2007 – 196 page Committee report

- A ≤ 1% false positive rate be used for detection.
- Need for Detection Limit and Quantitation Limit estimates that reflect normal, routine operations.
- Ongoing verification of detection limit and quantitation limit

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EPA Must Change Procedure

- 2009 EPA Pilot study for 200.7 and 625 concluded that additional data generated using other analytical methods and more laboratories are needed to fully assess the applicability of these procedures to Clean Water Act Programs
- 2010 TNI forms Environmental Methods Measurement Expert Committee based on a USEPA grant to address Calibration, Detection, Quantification and other measurement issues.
- 2013 TNI EMEC (renamed Chemistry committee) completes work on a MDL revision and submits to EPA
- 2014 EPA completes internal review of the revised MDL and makes minor modifications
- 2015 EPA publishes revised MDL as part of a Methods Update Rule
- 2017 Signed by EPA Administrator Scott Pruitt

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EPA MDL Procedure 2

- 2017 Method Update Rule
- 40 CFR 136 Appendix B
- The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

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MDL Changes

- Initial study over 3 days
- Use of blanks
- The MDL now requires that the samples used to calculate the MDL are representative of laboratory performance throughout the year, rather than on a single date (MDLv)
- A laboratory has the option to pool data from multiple instruments to calculate one MDL that represents multiple instruments. (Not for Drinking Water)
- Recalculate every 13 months

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MDL Influenced By

- Sample Matrix
- Preparation Steps
- Instrument (age, maintenance)
- Technology (GC-MS ≠ GC-FID)
- Analyst Skill
- Environmental Conditions

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EPA MDL Procedure 2

- Analyze 7 blanks and 7 blanks prepared and analyzed in at least 3 batches over 3 separate days.
- Multiple Instruments
  - A minimum of two spiked samples and two method blank samples prepared and analyzed on different calendar dates.
- Calculate MDL_s and MDL_b
- MDL is higher of MDL_s and MDL_b
- TNI Tip – use LOQ for MDL spike

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MDL Verification Samples

- During any quarter in which samples are being analyzed, prepare and analyze a minimum of 2 spiked samples on each instrument, in separate batches, using the same spiking concentration used for the initial MDL study.
- Evaluate MDL_v against acceptance criteria
- Ensure that at least 7 spiked samples and 7 method blanks are completed for the annual verification.
- Missed a verification?

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Annual Verification

- Every 13 months recalculate MDL_s and MDL_b
  - Data from last 24 months
  - MDL verification spikes and method blanks
- The verified MDL is the greater of the MDL_s or MDL_b .
- If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged

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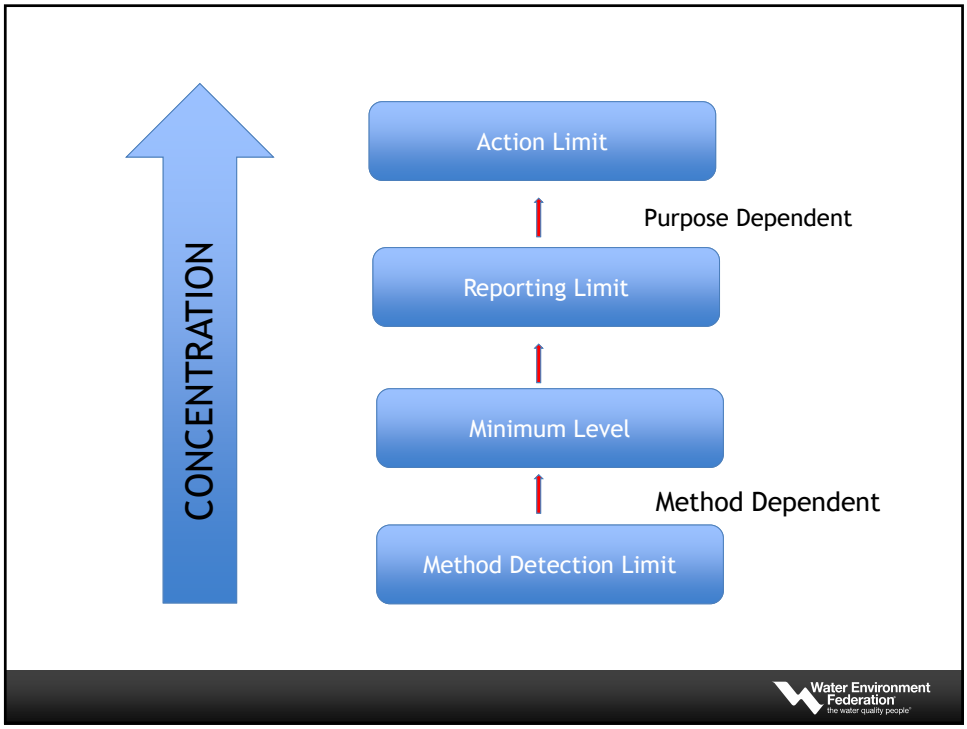

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Minimum Level

- The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.
- The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10n, where n is an integer.
- Minimum levels are used in some US EPA methods.

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Reporting Limits

- May or maynot be equal to quantitation limit
- Lowest standard must be at or below limit
- No federal method for determination
- Many states have own process for establishing for regulatory programs

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Regulatory Reporting Limits

Allowable concentration levels for a contaminant in a particular environmental medium (e.g., soil, air, or water) are often based on health-related risk assessments and are sometimes lower than levels that can be quantitated in a laboratory. For this reason, the lowest quantifiable level frequently becomes the de facto regulatory limit for monitoring and compliance purposes.

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Use in NPDES Permits

- MDLs serve as base for Reporting Limit
- Protective of Water Quality Standards
- State defined reporting limits
- Must use sufficiently sensitive method

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Reporting Limits for NPDES

- Southwest state – 3x MDL of most sensitive method for analyte or minimum level
- Central State- 5X method MDL
- Eastern state – 5X method MDL
- Eastern State – report everything to MDL

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Other Regulatory Uses

- Ambient monitoring (305)
- Pretreatment and Stormwater
- Water Quality Criteria
- 303(d) listing for Total Maximum Daily Loads
- Drinking Water monitoring (MCLs and reporting limits)
- Remediation (Protective Concentration Levels)

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Key Take Aways

- Detection ≠ Quantitation
- Detection limits will vary by laboratory
- Detection limits are utilized by regulators to assess:
  - Establish Permit Limits
  - Risk
  - Compliance

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Our Next Speaker

Jack Bennett
Technical Manager,
Analytical Laboratory

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Evaluating Blanks

Jack Bennett

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WEF Method Detection Limit Webinar

Jack Bennett
ALAB Technical Manager

July 16, 2020

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Lawrence Livermore National Laboratory

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Gathering Data

- The MDL must be calculated in the units that are reported for samples.
  - Not the units from the calibration curve.
  - Use the nominal sample weight or volume and take through all calculations.
- The results used for the MDL calculation must not be censored.
  - This really applies to blanks, although it could apply if the MDL spike is around the reporting limit.
  - Can't use "less than" or "Not Detected" or "zero" if the instrument gives a numerical result.
    - This is most common for metals, methods with "common" blank contaminants, and some automated wet chem methods.

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Gathering Data

- If you have a LIMS and normally do not report below the Reporting Limit (RL), create a LIMS test code without the logic to censor the data.
- If you don't have a LIMS, you can use a spreadsheet to do the calculations.
  - Many instruments have an option to export a file, which can be used to populate a calculations spreadsheet.
    - In Excel, the Legacy Wizard is (in my opinion) more user friendly than the new Wizard.
  - Its very important to keep up with "filing" the data as it is generated rather than gathering it once a year.
    - Especially important for blanks.

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Element	Dates Run / Spike Level, ug/g	7/24/2018 201812385A	7/24/2018 201812385B	7/24/2018 201812385C	7/26/2018 201812385D	7/26/2018 201812385E	7/26/2018 201812385F	8/2/2018 201812385G	8/2/2018 201812385H	Std. Dev	Spike MDL, ug/g	Spike/MDL <10 **	RL,ug/g	RL/MDL >2*	%R 50 - 150%*	**Initial MDL, ug/g**	RL/MDL >3***
Sb 206.836	5	4.9700	4.9800	4.3000	5.7300	5.4300	5.5400	6.9700	5.6000	0.7739	2.320	2.15	7.5	3.23	108.80	**2.456**	3.23
As 193.696	5	4.4000	5.4000	4.8000	5.7100	5.5700	4.7500	5.7500	4.7400	0.5244	1.572	3.18	7.5	4.77	102.80	**1.648**	4.77
Ba 233.527 Rad	4	4.0000	3.3200	3.7300	3.7300	4.1900	3.7000	3.8900	3.7600	0.2539	0.761	5.26	4	5.26	94.75	**0.971**	5.26
Be 313.107	0.04	0.0442	0.0380	0.0355	0.0357	0.0381	0.0407	0.0480	0.0419	0.0043	0.013	3.08	0.5	38.47	100.66	**0.017**	38.47
Cd 214.440	0.3	0.3110	0.3200	0.3160	0.2970	0.3030	0.2900	0.3260	0.3080	0.0120	0.036	8.35	0.3	8.35	102.96	**0.036**	8.35
Cr 205.560	2.5	2.4800	2.3900	2.4500	2.5100	2.4600	2.4400	2.4900	2.5100	0.0391	0.117	21.34	2.5	21.34	98.75	**0.117**	21.34
Co 228.616	2.4	2.4600	2.4000	2.4100	2.5000	2.4000	2.4200	2.5300	2.5000	0.0520	0.156	15.39	2.4	15.39	102.19	**0.156**	15.39
Cu 324.752	12	12.3000	12.4000	12.3000	12.8000	12.3000	12.2000	12.7000	12.7000	0.2326	0.697	17.21	18	25.81	103.85	**0.697**	25.81
Pb 220.353	1.6	1.6900	1.8400	1.7000	1.5900	1.6000	1.6600	1.3700	1.7000	0.1347	0.404	3.96	1.8	4.46	102.73	**0.404**	4.46
Mo 202.031	4	3.9600	3.9300	3.9900	4.1100	3.9000	3.8900	4.0100	3.9200	0.0725	0.217	18.40	4	18.40	99.09	**0.217**	18.40
Ni 231.604	10	10.6000	10.6000	10.6000	10.9000	10.5000	10.6000	10.7000	10.7000	0.1195	0.358	27.91	10	27.91	106.50	**0.358**	27.91
Se 196.026	6	5.6400	5.5000	7.1800	4.2500	5.5000	4.5000	4.0700	6.0900	1.0417	3.123	1.92	20	6.40	89.02	**3.123**	6.40
Ag 328.068	1.92	0.5570	0.5000	0.4930	0.5660	0.5760	0.5900	0.7030	0.6880	0.0770	0.231	8.32	1.92	8.32	30.42	**0.231**	8.32
Tl 190.801	1	1.1100	0.5650	1.0000	0.8100	1.0600	0.4920	1.0500	1.0800	0.2453	0.735	1.36	7	9.52	89.59	**0.919**	9.52
V 292.402	10	9.2100	9.4400	9.4000	10.2000	9.6400	9.5800	10.0000	10.0000	0.3471	1.041	9.61	10	9.61	96.84	**1.041**	9.61
Zn 213.857	10	11.6000	11.9000	11.7000	11.3000	11.1000	11.1000	11.1000	11.2000	0.3151	0.945	10.59	10	10.59	113.75	**1.837**	10.59

*=Not required to be evaluated in the MDL Procedure Revision 2
**= Use as guidance for determining future MDL spiking levels
***NELAC 2016 Requirement

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The Blank MDL – Why?

- The original MDL method was based on an assumption that the blanks were essentially zero.
  - Normal distribution tightly around zero.
- Without going into too much detail, Lloyd Currie's paper "Limits for Qualitative Detection and Quantitation: Application to Radiochemistry" Anal. Chem. 40, 586-593 (1968) was the seminal paper on the concept of detection limits.
- He proposed that the point where there was a random chance of a false positive being $\leq$ 1% was the Critical Level (L_c).

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The Blank MDL – Why?

- The concentration that gave that point was the Detection Limit (L_D).
- This figure from his paper illustrates the difference between the blank population and the detection limit population:

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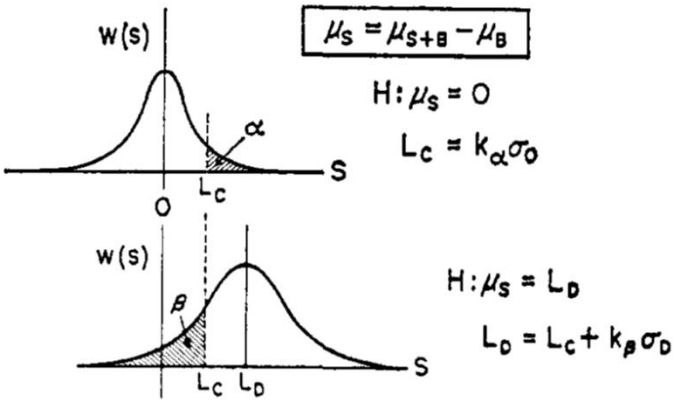

Figure 2. Hypothesis testing

Errors of the first and second kinds

"Limits for Qualitative Detection and Quantitation: Application to Radiochemistry" Anal. Chem. 40, 586-593 (1968)

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The Blank MDL – Why?

- Curries approach was to minimize false positives.
- When EPA produced their original MDL procedure in 1984, their approach was to minimize false negatives.
  - They set their procedure so that the MDL was at the L_C.
    - Blank < MDL/L_c < Currie L_D
- Blanks were not included in the EPA MDL calculation.
- As methods got more sensitive, labs were reporting false positives.
  - False positives can have consequences.

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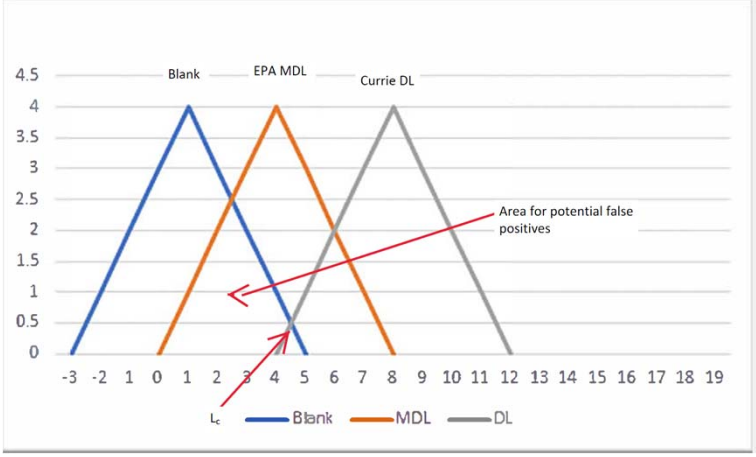
Potential of False Positives



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The Blank MDL – Why?

- In 1999, EPA was sued over a low-level mercury MDL method and lost.
- It took until 2016 for them to figure out a new MDL procedure.
  - Why not just use Curries procedure?
    - It is not practicable for a typical lab.
      - Need to run lots of samples.
- Including blanks in the procedure is a way to reduce false positives when reporting results below the RL.
- Not perfect, but not going to change.
- What else – can use for solids and other methods that can't practically be spiked.
  - Not a requirement, but (maybe) a "best practice".

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Blanks in the MDL Rev 2

- Initial MDL for Method Blanks:
  - Can use routine Method Blanks.
    - Must be within the last 24 months.
  - If no routine Method Blanks, at least 7 Method Blanks processed through the entire sample prep and analysis process on three separate calendar days.
    - If multiple instruments are used, must be run on all instruments.
    - A minimum of two blanks prepared on different days is required for each instrument.
    - Statistical outlier removal procedures should not be used.

Calculating the Initial Blank MDL (MDL_b)

- Three options:
  - Option 1 – No method blanks give numerical results, the MDL_b does not apply.
    - A negative number as a result is a numerical result.
    - Results below the current MDL or RL are numerical results.
    - An example of a non-numerical result is a chromatography method when a peak is not present.
  - Option 2 – Some (but not all) results give a numerical result, set the MDL_b to the highest method blank result.
    - If using routine method blank data and there are >100 method blanks, set the MDL_b to 99th percentile.
      - Estimating the 99th percentile is acceptable.

Calculating the Initial Blank MDL (MDL_b)

- Option 3 – All the method blanks give either positive or negative numerical results, calculate the MDL_b as:

$$MDL_b = \bar{x} + t_{students}\,(S_b)$$

where:

MDL_b = the MDL based on method blanks.

$\bar{x}$ = mean of the method blank results.

(use zero for the mean if the mean is negative)

$t_{students}$ = Students *t*-value for the 99th percentile.

S_b = Sample standard deviation.

- If existing data is being used and there are more than 100 method blanks, the 99th percentile value of the results can be used.

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MDL Study EPA MDL Procedure Revision 2

SDG

Students T Value	2.998			Instrument	ICP 6		Matrix	Soil/Solid		Method	EPA 3050B/6010B			
	Dates Run	7/24/2018	7/24/2018	7/24/2018	7/26/2018	7/26/2018	7/26/2018	8/2/2018	8/2/2018					
Element	Spike Level, ug/g	MDL BLK1	MDL BLK2	MDL BLK3	MDL BLK4	MDL BLK5	MDL BLK6	MDL BLK7	MDL BLK8	Std. Dev	Blank MDL, ug/g		RL, ug/g		Average LRB, ug/g
Sb 206.836	0	-0.7830	-0.7440	-0.0450	0.8210	0.7700	0.7110	-0.1320	1.1500	0.7463	2.456		7.5		0.22
As 193.696	0	-0.3040	0.8680	0.4180	0.1360	0.6470	-0.1760	0.0330	0.8100	0.4483	1.648		7.5		0.30
Ba 233.527 Rad	0	-0.7930	-0.4040	-0.6210	0.0194	-0.1380	0.1080	-0.0228	-0.1370	0.3238	0.971		4		-0.25
Be 313.107	0	0.0007	-0.0059	-0.0008	-0.0100	-0.0014	-0.0147	0.0022	-0.0014	0.0058	0.017		0.5		0.00
Cd 214.440	0	0.0032	-0.0100	-0.0136	-0.0080	-0.0239	-0.0176	0.0081	-0.0037	0.0106	0.032		0.3		-0.01
Cr 205.560	0	-0.0440	-0.0260	-0.0340	-0.0620	-0.0550	-0.0670	-0.0270	-0.0320	0.0162	0.048		2.5		-0.04
Co 228.616	0	-0.1400	-0.0479	-0.0391	0.0372	-0.0607	-0.0434	-0.0103	-0.0215	0.0503	0.151		2.4		-0.04
Cu 324.752	0	-0.0350	-0.1120	-0.1030	-0.1000	-0.1490	-0.1440	0.3630	0.1550	0.1817	0.545		18		-0.02
Pb 220.353	0	0.2000	0.0930	0.1150	0.0010	0.1010	0.0410	0.0490	-0.0140	0.0691	0.280		1.8		0.07
Mo 202.031	0	-0.0250	-0.0060	-0.0150	0.0190	-0.0470	-0.0690	0.0170	-0.0090	0.0300	0.090		4		-0.02
Ni 231.604	0	0.0110	-0.0120	-0.0010	0.0180	0.0020	0.0740	0.0310	0.0330	0.0269	0.100		10		0.02
Se 196.026	0	0.1110	0.2060	-0.5620	0.6040	0.1860	0.5820	-1.5600	-2.1500	1.0234	3.068		20		-0.32
Ag 328.068	0	-0.0470	-0.1050	-0.0380	-0.0300	-0.0560	-0.0730	0.0810	0.0430	0.0611	0.183		1.92		-0.03
Tl 190.801	0	-0.0280	-0.6060	-0.6820	-0.0410	-0.3700	-0.4410	0.0560	-0.6800	0.3064	0.919		7		-0.35
V 292.402	0	-0.0752	-0.1520	-0.0446	0.1720	-0.1290	0.0521	-0.1990	-0.2690	0.1413	0.424		10		-0.08
Zn 213.857	0	0.4500	1.5400	0.4800	0.4170	0.2030	0.2210	0.2120	0.0786	0.4626	1.837		10		0.45

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Ongoing Verification for Method Blanks

- The data only has to be collected if samples are being analyzed in a quarter.
  - There is guidance in the EPA MDL FAQ about low volume tests at https://www.epa.gov/cwa-methods/method-detection-limit-frequent-questions
- The verification / recalculation is done every 13 months ideally using data from the last 24 months.
  - Only use data from acceptable batches.
  - The 99th percentile value is not listed as an option for ongoing verification of methods with lots of blanks, however:
  - "The laboratory has the option to use only the last six months of method blank data or the fifty most recent method blanks, whichever criteria yields the greater number of method blanks".
- Must use data from all acceptable batches.

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Ongoing MDL Verification Criteria

- Fewer than 3% of the method blank results can have results greater than the existing MDL.
  - If more than 3% of the method blanks are greater than the existing MDL, must use the new verification MDL.
- MDL Evaluation Criteria:
  - If the verified MDL (i.e. MDL calculated using the verification data) is:
    - Within 0.5 to 2 times the existing MDL.
    - Fewer that 3% of the method blank results are above the existing MDL.
  - Then the existing MDL may continue to be used.
  - Otherwise, use the newly calculated verification MDL.
    - The verification MDL is the greater of the method blank MDL or the Spike MDL
  - However, if more than 5% of the MDL Verification Spikes do not return positive numerical results, then the original MDL must be re-performed using a higher spiking level.

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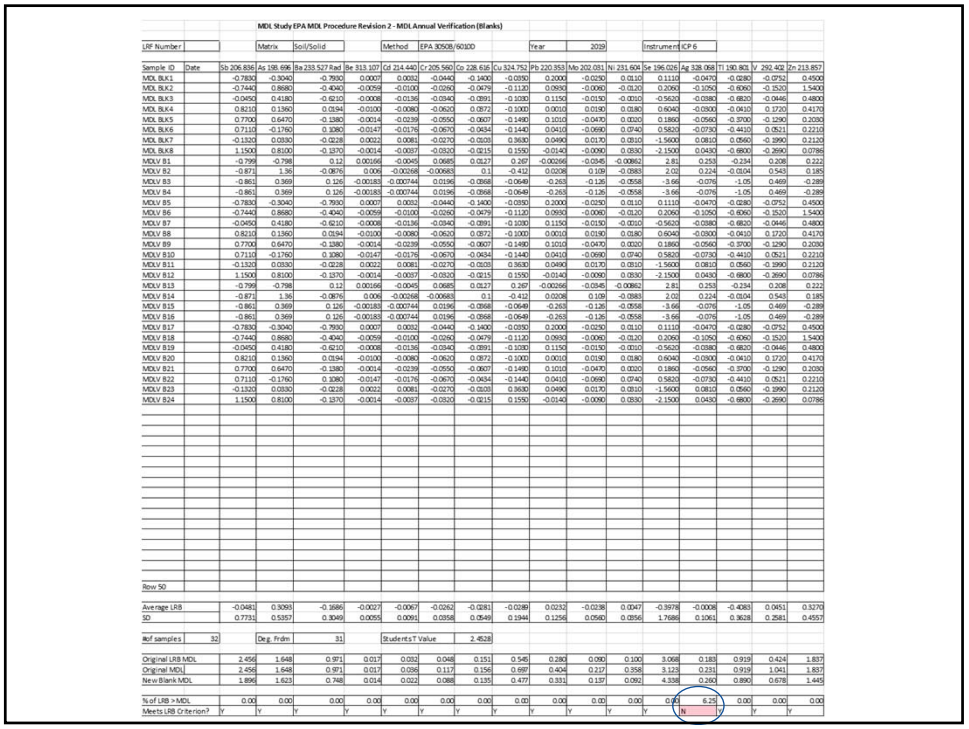

MDL Study EPA MDL Procedure Revision 2 - MDL Annual Verification (Blanks)

LRF Number			Matrix	Soil/Solid		Method	EPA 3050B/6010D			Year	2019		Instrument	ICP 6					
Sample ID	Date	Sb 206.836	As 188.696	Ba 233.527 Rad	Be 313.107	Cd 214.440	Cr 205.560	Co 228.616	Cu 324.752	Pb 220.353	Mo 202.031	Ni 231.604	Se 196.026	Ag 328.068	Tl 190.801	V 292.402	Zn 213.857		
MDL BLK1		-0.7830	-0.3040	-0.7930	0.0007	0.0032	-0.0440	-0.1400	-0.0350	0.2000	-0.0250	0.0110	0.1110	-0.0470	-0.0280	-0.0752	0.4500		
MDL BLK2		-0.7440	0.8680	-0.4040	-0.0059	-0.0100	-0.0260	-0.0479	-0.1130	0.0890	-0.0060	-0.0120	0.2060	-0.1050	-0.6060	-0.1520	1.5400		
MDL BLK3		-0.0450	0.4180	-0.6210	-0.0008	-0.0136	-0.0340	-0.0891	-0.1030	0.1150	-0.0150	-0.0010	-0.5620	-0.0380	-0.6820	-0.0446	0.4800		
MDL BLK4		0.8210	0.1360	0.0194	-0.0100	-0.0080	-0.0620	0.0872	-0.1000	0.0010	0.0190	0.0180	0.6040	-0.0300	-0.0410	0.1720	0.4170		
MDL BLK5		0.7700	0.6470	-0.1380	-0.0014	-0.0239	-0.0550	-0.0607	-0.1490	0.1010	-0.0470	0.0320	0.1860	-0.0560	-0.3700	-0.1290	0.2030		
MDL BLK6		0.7110	-0.1760	0.1080	-0.0147	-0.0176	-0.0670	-0.0434	-0.1440	0.0410	-0.0690	0.0740	0.5820	-0.0730	-0.4410	0.0521	0.2210		
MDL BLK7		-0.1320	0.0330	-0.0228	0.0022	0.0081	-0.0270	-0.0103	0.3630	0.0490	0.0170	0.0310	-1.5600	0.0810	0.0560	-0.3990	0.2120		
MDL BLK8		1.1500	0.8100	-0.1370	-0.0014	-0.0037	-0.0320	-0.0215	0.1550	-0.0140	-0.0090	0.0330	-2.1500	0.0430	-0.6800	-0.2690	0.0786		
MDLV B1		-0.799	-0.798	0.12	0.00166	-0.0045	0.0685	0.0127	0.267	-0.00266	-0.0045	-0.00862	2.81	0.253	-0.234	0.208	0.222		
MDLV B2		-0.871	1.36	-0.0876	0.006	-0.00268	-0.00685	0.1	-0.412	0.0208	0.109	-0.0383	2.01	0.224	-0.0104	0.543	0.185		
MDLV B3		-0.861	0.369	0.126	-0.00183	-0.000744	0.0196	-0.0368	-0.0649	-0.263	-0.126	-0.0558	-3.66	-0.076	-1.05	0.469	-0.289		
MDLV B4		-0.861	0.369	0.126	-0.00183	-0.000744	0.0196	-0.0368	-0.0649	-0.263	-0.126	-0.0558	-3.66	-0.076	-1.05	0.469	-0.289		
MDLV B5		-0.7830	-0.3040	-0.7930	0.0007	0.0032	-0.0440	-0.1400	-0.0350	0.2000	-0.0250	0.0110	0.1110	-0.0470	-0.0280	-0.0752	0.4500		
MDLV B6		-0.7440	0.8680	-0.4040	-0.0059	-0.0100	-0.0260	-0.0479	-0.1130	0.0890	-0.0060	-0.0120	0.2060	-0.1050	-0.6060	-0.1520	1.5400		
MDLV B7		-0.0450	0.4180	-0.6210	-0.0008	-0.0136	-0.0340	-0.0891	-0.1030	0.1150	-0.0150	-0.0010	-0.5620	-0.0380	-0.6820	-0.0446	0.4800		
MDLV B8		0.8210	0.1360	0.0194	-0.0100	-0.0080	-0.0620	0.0872	-0.1000	0.0010	0.0190	0.0180	0.6040	-0.0300	-0.0410	0.1720	0.4170		
MDLV B9		0.7700	0.6470	-0.1380	-0.0014	-0.0239	-0.0550	-0.0607	-0.1490	0.1010	-0.0470	0.0320	0.1860	-0.0560	-0.3700	-0.1290	0.2030		
MDLV B10		0.7110	-0.1760	0.1080	-0.0147	-0.0176	-0.0670	-0.0434	-0.1440	0.0410	-0.0690	0.0740	0.5820	-0.0730	-0.4410	0.0521	0.2210		
MDLV B11		-0.1320	0.0330	-0.0228	0.0022	0.0081	-0.0270	-0.0103	0.3630	0.0490	0.0170	0.0310	-1.5600	0.0810	0.0560	-0.3990	0.2120		
MDLV B12		1.1500	0.8100	-0.1370	-0.0014	-0.0037	-0.0320	-0.0215	0.1550	-0.0140	-0.0090	0.0330	-2.1500	0.0430	-0.6800	-0.2690	0.0786		
MDLV B13		-0.799	-0.798	0.12	0.00166	-0.0045	0.0685	0.0127	0.267	-0.00266	-0.0045	-0.00862	2.81	0.253	-0.234	0.208	0.222		
MDLV B14		-0.871	1.36	-0.0876	0.006	-0.00268	-0.00685	0.1	-0.412	0.0208	0.109	-0.0383	2.01	0.224	-0.0104	0.543	0.185		
MDLV B15		-0.861	0.369	0.126	-0.00183	-0.000744	0.0196	-0.0368	-0.0649	-0.263	-0.126	-0.0558	-3.66	-0.076	-1.05	0.469	-0.289		
MDLV B16		-0.861	0.369	0.126	-0.00183	-0.000744	0.0196	-0.0368	-0.0649	-0.263	-0.126	-0.0558	-3.66	-0.076	-1.05	0.469	-0.289		
MDLV B17		-0.7830	-0.3040	-0.7930	0.0007	0.0032	-0.0440	-0.1400	-0.0350	0.2000	-0.0250	0.0110	0.1110	-0.0470	-0.0280	-0.0752	0.4500		
MDLV B18		-0.7440	0.8680	-0.4040	-0.0059	-0.0100	-0.0260	-0.0479	-0.1130	0.0890	-0.0060	-0.0120	0.2060	-0.1050	-0.6060	-0.1520	1.5400		
MDLV B19		-0.0450	0.4180	-0.6210	-0.0008	-0.0136	-0.0340	-0.0891	-0.1030	0.1150	-0.0150	-0.0010	-0.5620	-0.0380	-0.6820	-0.0446	0.4800		
MDLV B20		0.8210	0.1360	0.0194	-0.0100	-0.0080	-0.0620	0.0872	-0.1000	0.0010	0.0190	0.0180	0.6040	-0.0300	-0.0410	0.1720	0.4170		
MDLV B21		0.7700	0.6470	-0.1380	-0.0014	-0.0239	-0.0550	-0.0607	-0.1490	0.1010	-0.0470	0.0320	0.1860	-0.0560	-0.3700	-0.1290	0.2030		
MDLV B22		0.7110	-0.1760	0.1080	-0.0147	-0.0176	-0.0670	-0.0434	-0.1440	0.0410	-0.0690	0.0740	0.5820	-0.0730	-0.4410	0.0521	0.2210		
MDLV B23		-0.1320	0.0330	-0.0228	0.0022	0.0081	-0.0270	-0.0103	0.3630	0.0490	0.0170	0.0310	-1.5600	0.0810	0.0560	-0.3990	0.2120		
MDLV B24		1.1500	0.8100	-0.1370	-0.0014	-0.0037	-0.0320	-0.0215	0.1550	-0.0140	-0.0090	0.0330	-2.1500	0.0430	-0.6800	-0.2690	0.0786		
Row 50																			
Average LRB		-0.0481	0.3093	-0.1686	-0.0027	-0.0067	-0.0262	-0.0281	-0.0289	0.0232	-0.0238	0.0047	-0.3978	-0.0008	-0.4083	0.0451	0.3270		
SD		0.7731	0.5357	0.3049	0.0055	0.0091	0.0358	0.0549	0.1944	0.1256	0.0560	0.0356	1.7686	0.1061	0.3628	0.2581	0.4557		
#of samples	32		Deg. Frdm	31		Students T Value		2.4528											
Original LRB MDL		2.456	1.648	0.971	0.017	0.032	0.048	0.151	0.545	0.280	0.090	0.100	3.068	0.183	0.919	0.424	1.837		
Original MDL		2.456	1.648	0.971	0.017	0.036	0.117	0.156	0.697	0.404	0.217	0.358	3.123	0.231	0.919	1.041	1.837		
New Blank MDL		1.896	1.623	0.748	0.014	0.022	0.088	0.135	0.477	0.331	0.137	0.092	4.338	0.263	0.890	0.678	1.445		
% of LRB >MDL		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.25	0.00	0.00	0.00		
Meets LRB Criterion?		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y	Y	Y		

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MDL Study EPA MDL Procedure Revision 2 - MDL Annual Verification (Spikes)

LRF Number			Matrix	Soil/Solid		Method	EPA 3050B/6010D			Year	2019		Instrument	ICP 6			
Sample ID	Date	Sb 206.836	As 193.696	Ba 233.527 Rad	Be 313.107	Cd 214.440	Cr 205.560	Co 228.616	Cu 324.752	Pb 220.353	Mo 202.031	Ni 231.604	Se 196.026	Ag 328.068	Tl 190.801	V 292.402	Zn 213.857
MDL 1		4.970	4.400	4.000	0.044	0.311	2.480	2.460	12.300	1.690	3.960	10.600	5.640	0.557	1.110	9.210	11.600
MDL 2		4.980	5.400	3.320	0.038	0.320	2.390	2.400	12.400	1.840	3.930	10.600	5.500	0.500	0.565	9.440	11.900
MDL 3		4.300	4.800	3.730	0.036	0.316	2.450	2.410	12.300	1.700	3.990	10.600	7.180	0.493	1.000	9.400	11.700
MDL 4		5.730	5.710	3.730	0.036	0.297	2.510	2.500	12.800	1.590	4.110	10.900	4.250	0.566	0.810	10.200	11.300
MDL 5		5.430	5.570	4.190	0.038	0.303	2.460	2.400	12.300	1.600	3.900	10.500	5.500	0.576	1.060	9.640	11.100
MDL 6		5.540	4.750	3.700	0.041	0.290	2.460	2.420	12.200	1.660	3.890	10.600	4.500	0.590	0.492	9.580	11.100
MDL 7		6.970	5.750	3.890	0.048	0.326	2.490	2.530	12.700	1.370	4.010	10.700	4.070	0.703	1.050	10.000	11.100
MDL 8		5.600	4.740	3.760	0.042	0.308	2.510	2.500	12.700	1.700	3.920	10.700	6.090	0.688	1.080	10.000	11.200
MDLV 1		4.600	6.370	4.170	0.054	0.308	2.470	2.550	12.300	1.910	3.960	10.700	5.120	2.090	1.220	10.100	11.400
MDLV 2		4.470	4.340	4.350	0.041	0.338	2.680	2.620	13.000	1.740	4.120	10.800	5.320	2.090	1.550	10.300	11.800
MDLV 3		4.600	6.370	4.170	0.054	0.308	2.470	2.550	12.300	1.910	3.960	10.700	5.120	2.090	1.220	10.100	11.400
MDLV 4		4.470	4.340	4.350	0.041	0.338	2.680	2.620	13.000	1.740	4.120	10.800	5.320	2.090	1.550	10.300	11.800
MDLV 5		5.25	4.98	4.24	0.0401	0.318	2.44	2.47	12.9	1.64	3.93	10.7	3.01	2.08	1.93	10.3	9.38
MDLV 6		4.970	4.400	4.000	0.044	0.311	2.480	2.460	12.300	1.690	3.960	10.600	5.640	0.557	1.110	9.210	11.600
MDLV 7		4.980	5.400	3.320	0.038	0.320	2.390	2.400	12.400	1.840	3.930	10.600	5.500	0.500	0.565	9.440	11.900
MDLV 8		4.300	4.800	3.730	0.036	0.316	2.450	2.410	12.300	1.700	3.990	10.600	7.180	0.493	1.000	9.400	11.700
MDLV 9		5.730	5.710	3.730	0.036	0.297	2.510	2.500	12.800	1.590	4.110	10.900	4.250	0.566	0.810	10.200	11.300
MDLV 10		5.430	5.570	4.190	0.038	0.303	2.460	2.400	12.300	1.600	3.900	10.500	5.500	0.576	1.060	9.640	11.100
MDLV 11		5.540	4.750	3.700	0.041	0.290	2.460	2.420	12.200	1.660	3.890	10.600	4.500	0.590	0.492	9.580	11.100
MDLV 12		6.970	5.750	3.890	0.048	0.326	2.490	2.530	12.700	1.370	4.010	10.700	4.070	0.703	1.050	10.000	11.100
MDLV 13		5.600	4.740	3.760	0.042	0.308	2.510	2.500	12.700	1.700	3.920	10.700	6.090	0.688	1.080	10.000	11.200
MDLV 14		4.600	6.370	4.170	0.054	0.308	2.470	2.550	12.300	1.910	3.960	10.700	5.120	2.090	1.220	10.100	11.400
MDLV 15		4.470	4.340	4.350	0.041	0.338	2.680	2.620	13.000	1.740	4.120	10.800	5.320	2.090	1.550	10.300	11.800
MDLV 16		4.9700	4.4000	4.0000	0.0442	0.3110	2.4800	2.4600	12.3000	1.6900	3.9600	10.6000	5.6400	0.5570	1.1100	9.2100	11.6000
Spike Level, ug/g		5	5	4	0.04	0.3	2.5	2.4	12	1.6	4	10	6	1.92	1	10	10
Std Dev		0.7234	0.6876	0.2962	0.0058	0.0136	0.0781	0.0731	0.2828	0.1388	0.0782	0.1073	0.9452	0.7019	0.3506	0.3908	0.5089
# of samples	24		Deg. Frdm.	23		Students T Value		2.4998									
Original MDL		2.456	1.648	0.971	0.017	0.036	0.117	0.156	0.697	0.404	0.217	0.358	3.123	0.231	0.919	1.041	1.837
New Spike MDL		1.808	1.719	0.741	0.014	0.034	0.195	0.183	0.707	0.347	0.195	0.268	2.363	1.755	0.876	0.977	1.272
Verification MDL		2.158	1.897	0.836	0.015	0.034	0.195	0.183	0.707	0.386	0.195	0.268	5.485	1.755	1.066	0.977	1.553
Do >95% of the spikes return a positive numerical result?		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Is the original MDL Verified?		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y	Y	Y
Use Verification MDL?															Y			

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Takeaways:

- Develop a system to keep track of when MDLV's are due.
  - This is especially important for low volume tests.
- Automate the calculations as much as possible.
  - Spreadsheets work nicely, and there is more than one way to get to your desired result.
    - Figure a way that makes sense to you.
  - Remember to (ideally) have someone else check your calculations.
- Start with an easy test.

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This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Lawrence Livermore National Laboratory

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Our Next Speaker

Mary Johnson
Laboratory Manager

Rock River Water Reclamation District

Water Environment Federation
the water quality people

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Calculating MDLs

Mary Johnson

Water Environment Federation
the water quality people

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A Tool for Calculating MDLs

Analyte:	Analyte Name			
Spike Conc:		(spike concentration must be a numerical value)		
Units:	units			
Method:	Method Reference or SOP			
Replicate	Test Date	Analysis Result	units	Percent Recovery
1			mg/L	#DIV/0!
2			mg/L	#DIV/0!
3			mg/L	#DIV/0!
4			mg/L	#DIV/0!
5			mg/L	#DIV/0!
6			mg/L	#DIV/0!
7			mg/L	#DIV/0!
8			mg/L	#DIV/0!
Average		#DIV/0!		#DIV/0!
Std Dev		#DIV/0!		#DIV/0!
Deg of Freedom		-1		
t(n-1)		#NUM!		
MDL_s = MDL based on spiked samples				#NUM!
MDL_b = MDL based on blanks				0.016
MDL is greater of MDL_s and MDL_b				#NUM!

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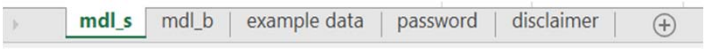
Spreadsheet Tabs



mdl_s:
spreadsheet for calculating mdl based on spiked samples

mdl_b:
spreadsheet for calculating mdl based on blank samples

example data:
spreadsheet with sample data used in this presentation

password:
spreadsheet with password for unlocking mdl_s and mdl_b

disclaimer:
as stated

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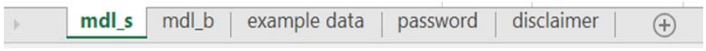
A Disclaimer

These spreadsheets were put together by members of the Association of Public Health Laboratories and the WEF Laboratories Practices Committee. The authors have attempted to align procedures with the EPA's *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 (EPA821-R-16_006)*.

The authors make no representation or warranty of any kind, whether expressed or implied, concerning the accuracy, completeness, suitability, or utility of any information or process presented here, nor do they assume any liability.



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MDL Calculation

The MDL is the greater of MDL_s and MDL_b

$MDL_s = t_{(n-1,\ t\text{-}\alpha=0.99)} * S_s$

$MDL_b = X + (t_{(n-1,\ t\text{-}\alpha=0.99)} * S_b)$

You need a minimum of 7 spiked samples for the MDL_s calculation and 7 blank samples for the MDL_b calculation.

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MDL_s

$MDL_s = t_{(n-1,\ t\text{-}\alpha=0.99)} * S_s$

Where

MDLs	=	the method detection limit based on spiked sample
$t_{(n-1,\ t\text{-}\alpha=0.99)}$	=	Students t-value at 99% for standard deviation with n - 1 degrees of freedom
S_s	=	standard deviation of the spiked samples

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Data Needed: Spiked Samples

- Minimum of seven spiked samples
- Must use most recent available data
- Data must be from at least three separate batches analyzed on three separate days
- Data must have been generated within last 24 months
- Analysis results must be a numerical value greater than zero
- No statistical outlier data removal for initial MDL

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Spiked Samples: Practicalities

- Spiking level is typically 2 – 10 times the expected MDL
- Analyzing two MDL samples each quarter is a practical way to collect enough data to calculate the MDL each year.
- Use only data associated with acceptable calibration and batch QC.

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Example Data: MDL_s

A laboratory tests for ammonia using a specific ion meter. Each quarter they analyze two 0.100 mg/L ammonia samples. The results of these analysis are used to calculate MDLs.

test date	mg/L Ammonia
1/1/2019	0.095
2/1/2019	0.091
4/1/2019	0.087
5/1/2019	0.088

test date	mg/L Ammonia
7/1/2019	0.104
8/1/2019	0.095
10/1/2019	0.088
11/1/2019	0.096

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It's Easier with a Spreadsheet

Analyte:	Ammonia			
Spike Conc:	0.100 mg/L			
Method:	SOP 301, Ammonia by Specific Ion Electrode (SM 4500-NH3 D)			
Replicate	Test Date	Analysis Result	units	Percent Recovery
1			mg/L	0.0
2			mg/L	0.0
3			mg/L	0.0
4			mg/L	0.0
5			mg/L	0.0
6			mg/L	0.0
7			mg/L	0.0
8			mg/L	0.0
Average		#DIV/0!		0.0
Std Dev		#DIV/0!		0.0
Deg of Freedom		-1		
t(n-1)		#NUM!		
MDL_s = MDL based on spiked samples				#NUM!

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MDL_s Calculation

#VALUE!	A
	Analysis Result
1	
2	
3	
4	
5	
6	
7	
8	
Average =	#DIV/0!
Std Dev =	#DIV/0!
Deg of Freedom =	-1
t(n-1) =	#NUM!
MDL =	#NUM!

Average:
=average(A1:A8)

Standard Deviation
=stdev(A1:A8)

(n – 1) Degrees of Freedom
=count(A1:A8)-1

Students $t_{(n-1,\ t\text{-}\alpha=0.99)}$
=ABS(TINV(2*0.99,A9))

MDL
$MDL_s = t_{(n-1,\ t\text{-}\alpha=0.99)} * S_s$
= A12 * A10

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MDL_s Calculation

	A
	Analysis Result
1	0.095
2	0.091
3	0.087
4	0.088
5	0.104
6	0.095
7	0.088
8	0.096
Average =	0.093
Std Dev =	0.006
Deg of Freedom =	7
t(n-1) =	2.998
MDL_s =	0.017

In this example, the MDL_s calculation produced an MDL_s of 0.017 mg/L.

$MDL_s = t_{(n-1,\ t\text{-}\alpha=0.99)} * S_s$

$= 2.998 * 0.006$

$= 0.017$

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Where to find Students t values

EPA's Method Detection Limit Publication:

EPA 821-R-16-006

NIST.gov website:

https://www.itl.nist.gov/div898/handbook/eda/section3/eda3672.htm

Or just use the spreadsheet function for Students t.

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Organize Your Information

Analyte:	Ammonia			
Spike Conc:	0.100 mg/L			
Method:	SOP 301, Ammonia by Specific Ion Electrode (SM 4500-NH3 D)			
Replicate	Test Date	Analysis Result	units	Percent Recovery
1	1-Jan-19	0.095	mg/L	95.0
2	1-Feb-19	0.091	mg/L	90.5
3	1-Apr-19	0.087	mg/L	87.0
4	1-May-19	0.088	mg/L	88.0
5	1-Jul-19	0.104	mg/L	104.0
6	1-Aug-19	0.095	mg/L	94.6
7	1-Oct-19	0.088	mg/L	88.0
8	1-Nov-19	0.096	mg/L	96.0
Average		0.093		92.9
Std Dev		0.006		5.7
Deg of Freedom		7		
t(n-1)		2.998		
MDL_s = MDL based on spiked samples				0.017

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Is Your MDL Reasonable?

Is the calculated MDL > 0 ?

Is the calculated MDL > 0.1 * spike concentration?

Is the spike concentration > calculated MDL?

Is the spike concentration between 1 and 10 times the MDL?

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Is Your MDL Reasonable?

In our example, for ammonia by specific ion electrode:

Spike Concentration = 0.100 mg/L
Average of eight replicates = 0.093
Standard deviation = 0.006
MDL_s = 0.017

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Is Your MDL Reasonable?

- ✓ Is the calculated MDL > 0 ?

  0.017 > 0
- ✓ Is the calculated MDL > 0.1 * spike concentration?

  0.017 > 0.1 * .100
- ✓ Is the spike concentration > calculated MDL?

  0.100 > 0.017
- ✓ Is the spike concentration between 1 and 10 times the MDL?

  0.017 < 0.100 < 0.17

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Do your spike results make sense?

Replicate	Percent Recovery
1	95.0
2	90.5
3	87.0
4	88.0
5	104.0
6	94.6
7	88.0
8	96.0
Average	92.9
Std Dev	5.7
Deg of Freedom	
t(n-1)	

Does the % recovery for each replicate make sense?

Are all spike results within ± 2 standard deviations of the mean?

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We're not done yet.

Remember: the MDL is the greater of MDL_s and MDL_b

We still need to calculate MDL_b

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Data Needed: Method Blanks

- Minimum of seven method blanks
- Must use most recent available data
- Data must be from at least three separate batches analyzed on three separate days
- Data must have been generated within the last 24 months.

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How should we evaluate method blank data?

- If none of the method blanks give numerical results, MDL_b does not apply
- If some, but not all, of method blanks give numerical results, MDL_b is the highest method blank result. If more than 100 method blanks, set MDL_b to number no less than 99th percentile.
- If all method blanks have numerical results, $MDL_b = X + (t_{(n-1,\ t\text{-}\alpha=0.99)} * S_b)$

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MDL_b

$$MDL_b = X + (t_{(n-1,\ t\text{-}\alpha=0.99)} * S_b)$$

Where

MDL_b	=	the method detection limit based on blank samples
X	=	mean of the method blank results
$t_{(n-1,\ t\text{-}\alpha=0.99)}$	=	Student's t-value at 99% for standard deviation with n-1 degrees of freedom
S_b	=	standard deviation of the method blank analyses

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Example Data: MDL_b

Continuing our ammonia analysis example, let's assume the laboratory tested ammonia twelve times the previous year and thus have 12 blank results.

test date	mg/L Ammonia
1/1/2019	0.0029
2/1/2019	0.0123
3/1/2019	0.0000
4/1/2019	0.0060
5/1/2019	0.0071
6/1/2019	0.0058

test date	mg/L Ammonia
7/1/2019	0.0069
8/1/2019	0.0109
9/1/2019	0.0058
10/1/2019	0.0087
11/1/2019	0.0023
12/1/2019	0.0054

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MDL_b Calculation

	A	B	C	D
	test date	analysis result		
1			average =	#DIV/0!
2			S_b, std dev =	#DIV/0!
3			count =	0
4			deg of freedom =	-1
5			students $t_{(n-1)}$ =	#NUM!
6				
7			MDL_b =	X + $t_{(n-1)}(S_b)$
8			=	#DIV/0!
9				
10				
11				
12				

Average:
=IF(average(B1:B12)<0,
0,average(B1:B12))

Standard Deviation
=stdev(B1:B12)

Count:
=count(B1:B12)

Degrees of Freedom
=D3-1

Students t
=ABS(TINV(2*0.99,D4))

MDL_b
= X + ($t_{(n-1,\ t\text{-}\alpha=0.99)}$ *S_b)
= D2 + (D3 * D4)

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MDL_b Calculation

test date	analysis result		
1/1/2019	0.00290	average =	0.0062
2/1/2019	0.01230	S_b, std dev =	0.003
3/1/2019	0.00000	count =	12
4/1/2019	0.00600	deg of freedom =	11
5/1/2019	0.00710	students $t_{(n-1)}$ =	2.718
6/1/2019	0.00580		
7/1/2019	0.00690	MDL_b =	X + $t_{(n-1)}(S_b)$
8/1/2019	0.01090	=	0.016
9/1/2019	0.00580		
10/1/2019	0.00870		
11/1/2019	0.00230		
12/1/2019	0.00540		

In this example, the MDL_b calculation produced an MDL_b of 0.016 mg/L.

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So what is the MDL?

The MDL is the greater of MDL_s and MDL_b

For our example:

$MDL_s = 0.017$

$MDL_b = 0.016$

So our MDL = 0.017 mg/L

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MDL vs. RL

MDL – Method Detection Limit

RL - Reporting Limit

The RL is the smallest concentration that is reported by a laboratory. The RL may be the lowest standard used when making a calibration curve.

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References

Definition and Procedure for the Determination of the Method Detection Limit, Revision 2
EPA 821-R-16-006

Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs Final Report 12/28/07

ANALYTICAL DETECTION LIMIT GUIDANCE & Laboratory Guide for Determining Method Detection Limits
Wisconsin DNR, PUBL-TS-056-96

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