

**THE CALCULATION OF  
METHOD DETECTION LIMITS:  
AN ALTERNATIVE TO THE EPA PROCEDURE  
USING QUALITY CONTROL PRECISION DATA**

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# **CALCULATION OF METHOD DETECTION LIMITS: AN ALTERNATIVE TO THE EPA PROCEDURE USING QUALITY CONTROL PRECISION DATA**

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Traditional methods for the calculation of detection limits rely on the analyses in replicate of a limited number of samples on an aperiodic basis. An alternative method is presented that utilizes the precision results generated from the daily QA/QC routine. Advantages include avoided analytical costs, ready availability of an ongoing database, decreased uncertainty limits, and reduced analyst bias.

## **DEFINITION**

The Method Detection Limit (MDL) is defined as the "...minimum concentration of a substance that can be measured and reported with 99 percent confidence that the true value exceeds zero."<sup>1</sup> It is calculated as three (3) times the standard deviation of seven replicates of a sample with a low concentration of the analyte of interest.<sup>2</sup> The MDL is a property of the analytical procedure, sample matrix, and instrument used. It contrasts with the Instrument Detection Limit (IDL) in that it includes all steps from sample preparation to analytical completion.<sup>3</sup>

## **MOTIVATOR**

The cost of an MDL determination is nominally seven times the analytical cost, sometimes more since one sample may not provide sufficient data for a proper MDL calculation. This provides a motivation for an alternate procedure that uses quality control (QC) precision data generated as part of the laboratory quality assurance (QA) program to calculate a precision detection limit (PDL).

## **STATISTICAL CONSIDERATIONS**

An MDL is a statistic. It is an estimate that includes both systematic and random errors. As such it is one measurement from a population of measurements and has all of the statistical properties of measurements, such as average, standard deviation, and confidence limits.<sup>4</sup> When repeated determinations of an MDL are made, the plot of frequency versus deviation from average follows the Gaussian distribution.

It is the statistical properties of the MDL that allow for development of an alternative procedure. Most laboratories analyze 10 percent of all samples in duplicate as part of the QC practices. These duplicates are statistical estimates and include sampling and analytical variance (error).

This leads to a working hypothesis: there is no statistical difference in the variance of 'N' replicate subsamples from a population and 'N/2' samples collected in duplicate.<sup>5</sup>

### TEST OF HYPOTHESIS

To test this hypothesis, a computer model (Listing 1) was developed to randomly select pairs of values from a population of measurements. The population is a database of actual Biochemical Oxygen Demand (BOD) values. Pairs of values were randomly selected from the database and grouped into two collections. The standard deviations of each collection and of paired differences divided by two were calculated and compared (Table 1).

TABLE 1 ANALYTICAL MEASUREMENT ERROR HYPOTHESIS TEST RESULTS				
N	S(P)	S(1)	S(2)	S(1-2)
5	4.6	5.9	3.5	4.4
10	4.6	4.0	4.7	4.2
20	4.6	4.3	3.9	4.1
CONCLUSION: NO SIGNIFICANT DIFFERENCE IN TWO MEASURES OF ANALYTICAL ERROR.				
S(P)	= STANDARD DEVIATION OF TOTAL POPULATION			
S(1)	= STANDARD DEVIATION OF SET 1			
S(1-2)	= (STANDARD DEVIATION OF DIFFERENCES)/ $\sqrt{2}$			
N	= NUMBER OF RECORDS IN SET			

Based on 150 runs of the program, there were no statistically significant differences in the two measures of analytical error. As can be seen from Table 1, the measures of error for Sets 1 and 2 bracket the measure of error for the paired differences.

### PROCEDURE

In practice the EPA definition for MDL is:

the mean blank signal plus three times the standard deviation of seven replicates of a low level sample.

The QC Precision method definition for PDL is:

the mean blank signal plus three times the adjusted standard deviation of the differences of seven low level samples collected in duplicate.

- Procedure:
- 1) Select 7 low level QC duplicates with analyte concentrations between one and five times the estimated MDL.
  - 2) Exclude outliers and non-detectables.
  - 3) Calculate the standard deviation of differences.
  - 4)  $PDL = (Student's-t) \times (standard\ deviation) / 1.4$ .

(nb 1.4 = square root of 2)

It is not necessary to restrict the number of QC duplicates selected to seven. When more duplicates are selected, the student's-t number would decrease resulting in tighter confidence limits. Thus, by increasing the number of QC duplicates, the PDL potentially has a higher inter-laboratory comparability than the MDL.

### REAL DATA - ROBUSTNESS TESTING

The detection limits for a series of metals were determined by both procedures. With the possible exceptions of iron and lead, there were no statistically significant differences (Table 2).

<b>TABLE 2 COMPARISON OF TWO DL CALCULATION PROCEDURES, INCLUDING 95% CONFIDENCE LIMITS</b>						
	DETECTION LIMITS IN UG METAL/L					
	MDL (df = 6)			PDL (df = 20)		
	DL	U <sub>5</sub>	L <sub>5</sub>	DL	U <sub>5</sub>	L <sub>5</sub>
AG	2	4	1.5	2	3	1.4
CD	0.3	0.6	0.2	0.4	0.5	0.3
CR	8	17	5	5	7	4
CU	20	45	15	20	30	14
FE	300	700	200	100	140	80
NI	10	24	7	10	14	8
PB	6	13	4	2	3	1.4
ZN	30	70	20	20	30	14
MDL = EPA METHOD DETECTION LIMIT			U <sub>5</sub> = UPPER 95% LIMIT			
PDL = QC PRECISION DETECTION LIMIT			L <sub>5</sub> = LOWER 95% LIMIT			

When the method was applied to MDLs from two different laboratories for the same series of metals, the differences were not statistically different except for two analyses: silver and chromium (Table 3).

<b>TABLE 3 COMPARISON OF PDLs FOR TWO LABORATORIES</b>		
	PDL (ug metal/L)	
	LAB 1	LAB 2
CD	0.5	0.4
CU	18	20
CR	0.4	5
FE	60	100
PB	2	2
NI	3	10
AG	0.07	2
ZN	14	20

If differences were due to either methodology or the sample matrices, then these two analyses should exhibit similar anomalies when comparisons are made using the EPA MDL.

Accordingly, MDL and PDL ratios were calculated for the two labs (Table 4).

<b>TABLE 4 COMPARISON BETWEEN LAB DETECTION LIMIT RATIOS</b>		
	MDL RATIO	PDL RATIO
CD	3	1
CU	1	1
CR	80	10
FE	10	2
PB	6	1
NI	10	3
AG	20	30

<b>TABLE 4</b>		
<b>COMPARISON BETWEEN LAB DETECTION LIMIT RATIOS</b>		
	MDL RATIO	PDL RATIO
ZN	3	1
AVERAGE:	16	6
STANDARD DEVIATION:	26	10
MDL RATIO = RATIO OF DLS OF LAB1/LAB2 BY EPA MDL PROCEDURE		
PDL RATIO = RATIO OF DLS OF LAB1/LAB2 BY QC PRECISION PROCEDURE		

A ratio of '1' indicates an exact agreement between the two labs. The average ratio for the EPA MDLs was 16, the average for the PDLs was 6. The difference is statistically significant and is a consequence of using a larger sample size (20 instead of 7). The ratios for the two problem analyses, chromium and silver, were far from '1' by both procedures, indicating that the differences were inherent in the analytical procedures used.

The calculation is dependent on selecting low level samples and should demonstrate a sensitivity to the initial estimate. Selecting from total suspended solids results over a range of 2 to 10 mg/L, the PDLs ranged from 3.9 to 3.6, a 10 percent difference (Table 5).

<b>TABLE 5</b>					
<b>SENSITIVITY OF PDL TO INITIAL ESTIMATE</b>					
BOD		TSS		AMMONIA	
ESTIMATE	PDL	ESTIMATE	PDL	ESTIMATE	PDL
2	1.6	2	3.9	0.02	0.019
5	2.1	5	3.5	0.05	0.022
10	2.4	10	3.6	0.10	0.022

Ammonia results were tested over a 5-fold range with a difference between the low and high estimates of 20 percent. When BOD results were evaluated, the difference between the low and high estimates was 50 percent and was statistically significant. This was not a consequence of estimate based sensitivity but sample size; the larger the BOD sample, the lower the PDL (Table 6).

<b>TABLE 6</b>	
<b>BOD PDL VS. SAMPLE VOLUME</b>	
<b>VOLUME (mL)</b>	<b>PDL (mg BOD/L)</b>
30	2.4
100	1.7
200	1.4

Since the MDL is a property of the analytical method and sample matrix, temporal variance should not occur unless the method or the matrix changes. PDLs were determined for total suspended solids data over a 15-month period in 3-month intervals, a test for which the matrix and analytical method were fairly well defined (Table 7).

<b>TABLE 7</b>	
<b>TEMPORAL VARIANCE OF PDL FOR TOTAL SUSPENDED</b>	
<b>DATE RANGE</b>	<b>PDL (mg/L)</b>
1/88 - 3/88	3.6
4/88 - 6/88	3.7
7/88 - 9/88	3.5
10/88 - 12/88	3.4
1/89 - 3/89	3.5
	Mean 3.5
	S 0.1

The relative standard deviation of the MDLs was less than 3 percent.

## **CONCLUSIONS**

The advantages of using QC duplicates for the determination of detection limits are:

- Data is immediately available
- Additional analytical costs are avoided
- Temporal variance is minimized

- Inter-laboratory comparison enhanced
- Tighter 95 percent confidence limits

## REFERENCES

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