

Proposed Procedures for Determining the Method Detection Limit and Minimum Level

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PROCEDURES

These procedures set the method detection limit (MDL) at the lowest result that can be reliably distinguished from a blank. This is functionally equivalent to the ISO/IUPAC term Critical Value, L_C . This is the normal censoring limit for analytical result reporting.

The Minimum Level (ML) is set at the lowest level that meets five conditions:

- Results from spikes at the ML must be above the MDL
- The ML must be at or above the lowest calibration level (or calibration verification standard for tests with a single point calibration).
- The ML must be at least two times the MDL
- The relative standard deviation of results from spikes at the ML must be less than 20%
- The average recovery of spikes at the ML must be within 50-150%

The Minimum level is the functional equivalent of the quantitation limit (L_Q) using international terminology.

1. Tests that always give a numerical result e.g., spectroscopic tests such as ICP-OES

- 1.1. Collect results for method blanks generated during routine operation of the method. The method blank must go through all preparation and analysis steps of the method. A minimum of 7 method blank results, each from a different preparation and analysis batch, is required in order to calculate an initial estimate of the method detection limit.
 - 1.1.1. If it is necessary to initiate analysis immediately, an initial estimate of the MDL may be made by analyzing 7 blanks in a single batch. The short term MDL must be replaced by a MDL determined from method blanks in a minimum of 7 different batches as soon as possible.
- 1.2. If a larger number of method blanks are available, then they should be used in the calculation. The objective is to estimate the true population standard deviation, σ . The larger the number of replicates used to calculate the sample standard deviation, s , the better the estimate will be. However, it is not necessary to use more than 100 results, as further improvements in the value of s are small relative to the data gathering and computing effort.
- 1.3. If multiple instruments are to be used for the same test, and will have the same reporting limit or minimum level (ML), a minimum of 7 method blank results must be used for each instrument and the combined results used to generate the standard deviation. If the laboratory wishes to determine different MDLs for different groups of instruments used for the same test (for example if only some of the instruments are capable of meeting certain compliance limits), then separate MDLs may be determined, but different MLs would have to be reported.

- 1.4. The data must not be filtered to the extent that “not detected” rather than numerical results are obtained for the blanks. Each result must have a numerical value. It is acceptable (and expected) that some results will have negative values.
- 1.5. Results associated with a known, spurious error that occurred during analysis should be discarded, or where appropriate, corrected. It is also acceptable to apply a statistically accepted outlier test, such as the Grubbs test. This data rejection must be performed with caution. Excessive rejection of data will result in a calculated MDL lower than can really be supported.
- 1.6. Calculate the sample standard deviation of the method blank results

$$s = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n - 1}}$$

Where:

X_i = a result obtained from the analysis of a method blank

\bar{X} = the mean of the method blank results

- 1.7. Calculate the MDL

$$MDL = \bar{X} + s K$$

Where:

K is a multiplier for a tolerance limit based on 99% coverage probability of 99% of the population of routine blanks and n-1 degrees of freedom. A table of values for k is provided in appendix A.

Note: In the case that a negative value for \bar{X} is obtained, substitute zero for \bar{X} in the equation for calculation of the MDL

- 1.8. Set the Minimum Level
 - 1.8.1. The lowest calibration standard (or low level calibration verification standard for tests with a single point initial calibration) must be at or below the Minimum Level.
 - 1.8.2. The Minimum Level must be at least 2 times the MDL.
 - 1.8.3. The standard deviation of the Minimum Level spikes must be less than 20% Relative Standard Deviation (RSD).

$RSD = (s / \bar{Y}) \times 100\%$, where \bar{Y} is the mean result from the spiked replicates

- 1.8.4. Analyze at least 7 spikes at the proposed Minimum Level. Calculate the lowest expected result from the Minimum level spikes. This must be above the MDL.

$$\text{Lowest Expected Result} = \bar{X}_s - (s \times t_{(n-1, 1-\alpha=0.99)})$$

Where \bar{X}_s is the mean result from the Minimum Level spikes
 $t_{(n-1, 1-\alpha=0.99)}$ is the Students t value appropriate for the 99th percentile and n replicates

1.9. Verification

1.9.1. Verification of the MDL

1.9.2. At least once per year repeat the calculation with the latest set of at least 20 and ideally 100 or more method blanks.

1.9.3. Compare the variance of the new set of method blanks with that of the old using the F test

$$F = \frac{(s_h^2)}{(s_l^2)}$$

Where:

s_h^2 = Higher variance estimate

s_l^2 = Lower variance estimate

1.9.4. If the value of F is greater than the F-statistic at the 90th percentile then the MDL must be updated. If not then the MDL may be left unchanged (since there is no reason to expect that the populations are different) or the MDL may be updated using the pooled standard deviation from both studies.

1.9.5. Verification of the Minimum Level (ML)

1.9.6. Prepare and analyze at least one spike at the Minimum Level per quarter on each instrument.

1.9.7. At least once per year, determine the relative standard deviation at the Minimum Level, using the results collected from the initial and verification spikes combined. If it is more than 20% RSD double the Minimum Level and collect a new initial set of 7 spike replicates. The RSD of the Minimum Level spikes becomes a statement of precision at the Minimum Level, in the same way that the mid-level laboratory control spikes form a statement of precision at the mid level of the method.

1.10. Data reporting

1.10.1. Results are reported down to the MDL but are flagged as estimated if below the ML.

2. Tests that do not always give a numerical result, e.g., GC/MS

2.1. In order to generate sufficient data for tests that do not usually give a numerical result for a blank, we must use spiked replicates. The spike level must be at or

below the level that the laboratory intends to use as their ML (quantitation limit), but sufficiently high that qualitative detection is always obtained.

- 2.2. Generate an initial estimate of the lowest concentration at which qualitative identification is possible. The laboratory may use prior experience or consideration of the signal to noise to form this estimate
- 2.3. Test the estimate
 - 2.3.1. Analyze at least a single spiked blank at the estimated lowest concentration of reliable qualitative identification through the entire analytical procedure.
 - 2.3.2. If the analyte is not detected repeat the test at twice the concentration used in 2.3.1. Detected is defined as a quantitated result meeting all the qualitative identification criteria in the method.
- 2.4. If multiple instruments are to be used to perform the same test and the same reporting limit or minimum level will be used, then the test of the Minimum Level estimate must be performed on each instrument, and the highest value of the Minimum Level from all the instruments is used as the estimate.
- 2.5. Analyze a minimum of 7 replicates, divided between at least 3 different preparation and analysis batches, each spiked at the Minimum Level
 - 2.5.1. If multiple instruments are used for the test, at least two replicates in separate batches must be analyzed on each instrument
- 2.6. If the analyte is not detected in any one of the replicates, analyze a minimum of 7 replicates divided between 3 different preparation and analysis batches at twice the concentration. This new is concentration the Minimum Level estimate.

Calculate the relative standard deviation of the Minimum Level spikes. The RSD must be less than 20%. Also, calculate the average recovery of the spikes. The average recovery must be within 50-150%. If either of these two criteria are not met, double the level chosen for the Minimum Level and repeat the test. Set the Minimum Level at the lowest concentration that meets the five criteria for an acceptable Minimum Level.

Note that if the criteria of 20% RSD and 50% mean recovery are not met in the mid-level laboratory control samples then they would not be expected to in a quantitation level sample. Therefore for these analytes the Minimum Level is set at a concentration that reliably returns results above the MDL, and all results are qualified as estimated.

- 2.7. Estimate the MDL
 - 2.7.1. The MDL is determined according to the following equation.

$$MDL = s \times K$$

Where s is the standard deviation of the ML spikes

- 2.8. The Minimum Level as described above is the lowest level for reporting quantitative results, but data is normally reported down to the MDL. For example, if the ML is 2.0 and MDL is 0.6 then results are reported as follows (J is a flag indicating increased uncertainty in the results):

Instrument result	Reported Result
2.1	2.1
1.9	1.9J
0.91	0.9J
0.59	0.6J
0.54	<0.6 or 0.6U or DNQ
ND	<0.6 or 0.6U

DNQ = Detected, not quantitated

- 2.9. Blank Check – There may be some analytes included in these methods that have frequent numerical blank results, for example common laboratory contaminants. For these analytes calculate a detection limit based on the method blanks as described in section 1.6. Use the greater of this value and the value determined in section 2.6 as the MDL.
- 2.10. Verification
- 2.10.1. At least once per quarter, verify the ML on each instrument by analyzing a reference matrix spiked at the ML. If the analyte is not detected perform instrument maintenance and repeat the test. If the analyte is still not detected, repeat the test at a spiking level 2 times higher and adjust the MDL and ML accordingly.
- 2.10.2. There is no need to repeat the MDL determination unless major changes to the method or the instrumentation result in the expectation of a different MDL. However, if the initial estimate of the ML and MDL were made using data gathered over a relatively short period they should be replaced with a new estimate incorporating the monthly verification samples once a years worth of data has been collected.
- 2.11. Data reporting
- 2.11.1. Data may be reported down to the value of the MDL determined in section 1.7 or 2.7.

3. Demonstration of Sensitivity

- 3.1. For some applications it is not necessary to demonstrate the absolute lowest limit of detection. For example, the analysis may be appropriate if sensitivity is

demonstrated at the level equal or less than that required by a sensitivity criterion in a method. In these cases a full detection limit study is not necessary and method sensitivity may be demonstrated using the following procedure.

- 3.2. Analyze four blank or matrix samples spiked at or below the level at which sensitivity demonstration is required. (The matrix may be a reference matrix or a matrix applicable to a particular site of project).
- 3.3. Measure the mean and standard deviation of the results.
- 3.4. Compare the mean and standard deviation with acceptance criteria in the method. If no acceptance criteria are available then recovery must be greater than or equal to 40% and the relative standard deviation must be less than or equal to 50% or a full detection limit determination according to sections 1 or 2 must be performed.
- 3.5. Gather additional data as the method is performed and calculate the detection limit according to sections 1 or 2 once sufficient data is available.

Appendix A

K and t values for n replicates

n	K	t	n	K	t
7	6.101	3.143	54	2.993	2.399
8	5.529	2.998	55	2.985	2.397
9	5.127	2.896	56	2.977	2.396
10	4.829	2.821	57	2.97	2.395
11	4.599	2.764	58	2.963	2.394
12	4.415	2.718	59	2.956	2.392
13	4.264	2.681	60	2.949	2.391
14	4.138	2.650	61	2.943	2.390
15	4.031	2.624	62	2.936	2.389
16	3.939	2.602	63	2.93	2.388
17	3.859	2.583	64	2.924	2.387
18	3.789	2.567	65	2.919	2.386
19	3.726	2.552	66	2.913	2.385
20	3.67	2.539	67	2.907	2.384
21	3.619	2.528	68	2.902	2.383
22	3.573	2.518	69	2.897	2.382
23	3.532	2.508	70	2.892	2.382
24	3.494	2.500	71	2.887	2.381
25	3.458	2.492	72	2.882	2.380
26	3.426	2.485	73	2.877	2.379
27	3.396	2.479	74	2.873	2.379
28	3.368	2.473	75	2.868	2.378
29	3.342	2.467	76	2.864	2.377
30	3.317	2.462	78	2.86	2.376
31	3.295	2.457	79	2.851	2.376
32	3.273	2.453	80	2.847	2.375
33	3.253	2.449	81	2.843	2.374
34	3.234	2.445	82	2.839	2.374
35	3.216	2.441	83	2.836	2.373
36	3.199	2.438	84	2.832	2.373
37	3.182	2.434	85	2.828	2.372
38	3.167	2.431	86	2.825	2.372
39	3.152	2.429	87	2.821	2.371
40	3.138	2.426	88	2.818	2.370
41	3.125	2.423	89	2.815	2.370
42	3.112	2.421	90	2.811	2.369
43	3.100	2.418	91	2.808	2.369
44	3.088	2.416	92	2.805	2.368
45	3.077	2.414	93	2.802	2.368
46	3.066	2.412	94	2.799	2.368
47	3.055	2.410	95	2.796	2.367
48	3.045	2.408	96	2.793	2.367
49	3.036	2.407	97	2.79	2.366
50	3.027	2.405	98	2.787	2.366
51	3.018	2.403	99	2.784	2.365
52	3.009	2.402	100	2.782	2.365
53	3.001	2.400			