

## B. Definition and Procedure for the Determination of the Minimum Level of Quantitation (ML)

### 1.0 Definition

The minimum level of quantitation (ML) is the lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. It may be equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. It is functionally analogous to the "determination limit" described by Currie (1968) and the Limit of Quantification (LOQ) described by the American Chemical Society (Keith *et al.*, 1980, McDougal *et al.*, 1983) and Currie (1995).

**Note to Section 1.0:** The ML is directed at obtaining a 10% relative standard deviation for determination of an analyte in an environmental sample. This error may be reduced by making multiple determinations of the analyte in the sample.

### 2.0 Scope and Application

2.1 The ML is typically established by the organization that develops or modifies an analytical test method. A laboratory that employs the method would be expected to include calibration standards that encompass the ML when it calibrates an analytical system, unless a higher quantitation level is acceptable for a specific application. If an ML

is not specified in a method, a laboratory may use the ML procedure to establish the lowest calibration point.

2.2 This procedure is intended for use in EPA's Clean Water Act (CWA) programs. An alternative procedure may be used (e.g., from a voluntary consensus standards body) to establish the sensitivity of an analytical method provided the resulting quantitation limit meets the sensitivity needs (*i.e.*, data quality objective) for the specific application.

2.3 Laboratories are encouraged, but not required, to periodically demonstrate recovery of the target analyte near the published ML or laboratory-established ML by preparing a reference matrix sample spiked at the ML and analyzing it using all sample handling and processing steps described in the method. If the method does not provide acceptance criteria for such an ML standard, the laboratory can make an assessment of whether acceptance criteria for other spiked reference matrix samples (e.g., laboratory control samples, laboratory fortified blanks, ongoing precision and recovery samples, etc.) are appropriate to evaluate analyte recovery at the ML. Alternatively, the laboratory may develop its own acceptance criteria based on data gathered by the laboratory over time.

### 3.0 Procedure

3.1 The ML is based on 10 times the standard deviation of the results of replicate analyses of a matrix containing the analyte. The method detection limit (MDL) is also based on the same standard deviation, multiplied by the Student's *t*-value

appropriate for a 99% confidence level and corresponding degrees of freedom. Because the standard deviation may not be readily available, the ML is often calculated as a factor times the MDL.

3.1.1 Calculating the ML based on MDL study data

When available, obtain the actual standard deviation value from the MDL study and calculate the ML directly, as 10 times the standard deviation. If an iterative MDL study is performed, calculate the MDL as 10 times the pooled standard deviation.

3.1.2 Calculating the ML based on the MDL Assuming a single iteration of seven replicates is used to determine the MDL, the number of degrees of freedom is 6, and the Student's *t*-value is 3.143. Therefore, the MDL is:

$$MDL = 3.143 \times s$$

and the ML is:

$$ML = 10 \times s = \frac{10}{3.143} \times MDL \approx 3.18 \times MDL$$

3.1.3 If the MDL is calculated from other than seven replicates or using the iterative procedure, the factor of 3.18 will change, and the table below is used to establish the correct multiplier. For example, if an iterative MDL study is performed consisting of exactly 7 replicates in each iteration, the resulting pooled MDL would incorporate 12 degrees of freedom, and the equation for the ML above would be modified accordingly, using a multiplier of 3.73.

TABLE OF STUDENT'S *t*-VALUES AT THE 99% CONFIDENCE LEVEL AND ML MULTIPLIERS

Number of replicates for		Degrees of freedom (df)	$t_{(n-1, 1-\alpha=0.99)}$	ML multiplier
Single MDL (df=n-1)	Iterative MDL (df=n-2)			
7	N/A	6	3.143	3.18
8	N/A	7	2.998	3.34
9	N/A	8	2.896	3.45
10	N/A	9	2.821	3.54
11	N/A	10	2.764	3.62
12	N/A	11	2.718	3.68
13	14	12	2.681	3.73
14	15	13	2.650	3.77
15	16	14	2.624	3.81
16	17	15	2.602	3.84
17	18	16	2.583	3.87
18	19	17	2.567	3.90
19	20	18	2.552	3.92

**Note to Table:** Degrees of freedom = (n-1) if a single iteration MDL study is performed and (n<sub>h</sub> + n<sub>l</sub> - 2) if an iterative MDL study is performed; N/A indicates that the number of degrees of freedom in this row does not apply to an iterative MDL study.

### 4.0 Rounding

The ML may be used to establish the lowest calibration point for the analyte. Therefore, in order to facilitate the preparation of calibration standards containing the analyte without undue difficulty, the ML may be rounded to the

nearest multiple of 1, 2, or 5 × 10<sup>n</sup>, where n is an integer.

### 5.0 References

5.1 Currie, Lloyd A. (1968), Limits for Quantitative Detection and Quantitative Determination, *Analytical Chemistry* 40: 586-593.

5.2 Currie, Lloyd A. (1995), Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities, *Pure and Appl. Chem.* 67:10, 1699-1722.

5.3 Glaser, J.A., D.L. Foerst, J.D. McKee, S.A. Quave and W.L. Budde (1981), Trace

Analyses for Wastewaters, *Environ. Sci. Technol.*, 15:1426.

5.4 Keith, Lawrence H., *et al.* (1983), Principles of Environmental Analysis, *Analytical Chemistry* 55:14, 2210-2218.

5.5 McDougal, Daniel, *et al.* (1980), Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, *Analytical Chemistry* 52:14, 2242-2249.

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