

TABLE OF F-STATISTIC VALUES

	F-statistic			
	6	7	8	9
6	3.055	3.014	2.983	2.958
7	2.827	2.785	2.752	2.725
8	2.668	2.624	2.589	2.561
9	2.551	2.505	2.469	2.440

4.8.4 When the process has been iterated and the results pass the F-test in section 4.8.3, the final MDL is calculated by pooling the results from the two iterations that passed the F-test. The pooled standard deviation is calculated as:

$$s_{\text{pooled}} = \sqrt{\frac{(n_h - 1)(s_h)^2 + (n_l - 1)(s_l)^2}{(n_h + n_l - 2)}}$$

Where:

$(s_h)^2$ = variance estimate from the higher spike concentration

$(s_l)^2$ = variance estimate from the lower spike concentration

n_h = number of sample aliquots used for the higher spike concentration

n_l = number of sample aliquots used for the lower spike concentration

4.8.5 The pooled MDL is calculated using the pooled standard deviation and the Student's t -value for $(n_h + n_l - 2)$ degrees of freedom (e.g., 12 degrees of freedom for two iterations with seven aliquots each).

$$\text{MDL}_{\text{pooled}} = s_{\text{pooled}} \times t_{(n_h + n_l - 2, 1 - \alpha = 0.99)}$$

Where:

s_{pooled} = pooled standard deviation of the results

$t_{(n_h + n_l - 2, 1 - \alpha = 0.99)}$ = Student's t -value appropriate for a 99% confidence level and $(n_h + n_l)$ aliquots

For 12 degrees of freedom, the t -value is 2.681. If more than seven replicates were used for either iteration, the appropriate t -value must be determined from the table given in section 4.7.

4.8.5 When verifying a method-, matrix-, program-, or study-specific MDL, the determined MDL is compared to the method-specified MDL, the MDL required to support a regulatory objective, or the MDL required to support an objective of a specific study or program. If the required MDL is not met for the analyte, make sure that all instrumentation and technical aspects of the process (reagent concentrations, temperature, clean glassware, proper dilutions, etc.) are checked and assessed to be working properly before a repeat of the analyses. If the second attempt fails, iteration at a more appropriate spiking level for that analyte is necessary until the requirement is met. If the regulatory, study, or program objective is not known, the MDL is verified if the determined MDL is less than or equal to the method-specified MDL.

4.9 Suspected Outliers

4.9.1 Results associated with a known, spurious error that occurred during analysis should be discarded, or where appropriate, corrected. Spurious errors include those that

arise through human error or instrument malfunction, such as transposing digits in a number while recording data, arithmetical errors when calculating results, double-spiking of an aliquot, or the presence of an air bubble lodged in a spectrophotometer flow-through cell. Recording or arithmetical errors can and should be corrected, and the corrective actions documented prior to use of results. Results associated with spurious errors that cannot be corrected will invalidate the measurement and should not be incorporated into the MDL determination.

4.9.2 If random or spurious errors are suspected, it may be appropriate to apply a statistically accepted analysis of outliers, such as Grubbs test described below. Any outlying result should be considered with care to identify potential causes. It is generally not an accepted practice to reject a value purely on statistical grounds. Therefore, EPA recommends that when the cause of a potential outlier cannot be attributed to spurious causes, the MDL test be repeated for the analyte(s) in which such an outlier occurs.

Note to Section 4.9.2: If more than seven aliquots are prepared and analyzed, results from all aliquots must be used in the MDL determination unless they have been determined to be outliers as described above. Given the small number of replicates typically used to determine the MDL, it is inappropriate to use a data set that contains more than one statistical outlier.

4.9.3 The use of Grubbs test for outliers is described below, followed by an example (section 4.9.4).

4.9.3.1 Rank the n observed data points in the order of increasing numerical value: $X_1 \leq X_2 \leq \dots \leq X_n$

4.9.3.2 Using the mean, \bar{X} , and standard deviation, s , from section 4.6, calculate:

$$T_1 = \frac{(\bar{X} - X_1)}{s} \quad \text{and} \quad T_n = \frac{(X_n - \bar{X})}{s}$$

Where:

X_1 = lowest observed value of X

X_n = highest observed value of X

4.9.3.3 Choose the larger of T_1 and T_n .

4.9.3.4 Compare the larger calculated value of T (e.g., T_1 or T_n) with the critical value appropriate for the number of observations (n) from the table below. If T is larger than the critical value in the table, then the smallest (when testing T_1) or largest (when testing T_n) observed data point is considered to be an outlier with 95% confidence.

TABLE OF CRITICAL VALUES FOR T IN THE GRUBBS TEST

Number of data points (n)	Critical values for T
7	2.020
8	2.126
9	2.215
10	2.290
11	2.355
12	2.412
13	2.462
14	2.507
15	2.549

4.9.4 Example application of the outlier test

4.9.4.1 Consider the following ranked data set with seven observations: 0.0449, 0.0458, 0.0462, 0.0469, 0.0471, 0.0475, and 0.0508.

4.9.4.2 Its mean, \bar{X} , is 0.0470, and its standard deviation, s , is 0.0019.

4.9.4.3 Calculate: $T_1 = (0.0470 - 0.0449)/0.0019 = 1.132$ and $T_n = (0.0508 - 0.0470)/0.0019 = 2.007$

4.9.4.4 Select the larger value: $T = \max\{1.132, 2.007\} = 2.007$

4.9.4.5 Compare T with the corresponding critical value in the second line of the table above, where $n=7$ and the critical value of $T = 2.020$.

Since the calculated value of T , 2.007, is not larger than the critical value in the table, 2.020, there is insufficient evidence to conclude that any of the observed data points is an outlier, and the MDL would be calculated from all seven results.

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.