

2. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision by performing the following operations.

(a) Perform four replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water (see paragraph 8 under "Reagents" above).

(b)(1) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented in paragraph 2(b)(2) below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analyses to be considered under control.

(2) Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 mg./l. to 50 mg./l. sulfide, the mean concentration from four replicate analyses must be within the range of 72 to 114 percent of the true value.

3. The Method Detection Limit (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in appendix C to part 425.

4. A minimum of one spiked and one duplicate sample must be run for each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (see paragraph 3 above for MDL samples) and at  $x$  when  $x$  is the concentration found if in excess of the MDL. Spike recovery must be 60 to 120 percent for the analysis of a particular matrix type to be considered valid.

5. Report all results in mg./liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

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#### APPENDIX C TO PART 425—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT<sup>1</sup>

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured and reported with 99 percent confidence that the analyte concentration is greater than

<sup>1</sup>Source: "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268

zero and determined from analysis of a sample in a given matrix containing analyte.

#### *Scope and Application*

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

#### *Procedure*

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered in making the estimate.

(b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

(c) The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, *i.e.*, a break in the slope of the standard curve.

(d) The concentration value that corresponds to known instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent water (blank), prepare a laboratory

standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (Recommended between 1 and 5 times the estimated MDL.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated MDL, proceed to Step 4.

If the measured concentration of analyte is less than the estimated MDL, add a known amount of analyte to bring the concentration of analyte to between one and five times the MDL. In the case where an interference is coanalyzed with the analyte:

If the measured level of analyte is greater than five times the estimated MDL, there are two options:

(1) Obtain another sample of lower level of analyte in same matrix if possible.

(2) The sample may be used as is for determining the MDL if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If blank measurements are required to calculate the measured level of analyte, obtain separate blank measurements for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated MDL before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL can be calculated from data obtained at many times the real MDL even though the background concentration of analyte is less than five times the calculated MDL. To insure that the estimate of the MDL is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower MDL. Take two aliquots of the sample to be used to calculate the MDL and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in the desirable range for determining the MDL, take five additional

aliquots and proceed. Use all seven measurements to calculate the MDL.

(2) If these measurements indicate the sample is not in the correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance ( $S^2$ ) and standard deviation ( $S$ ) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1} \left[ \sum_{i=1}^n X_i^2 - \left( \frac{\sum_{i=1}^n X_i}{n} \right)^2 \right]$$

$$S = (S^2)^{0.5}$$

where: the  $x_i$ ,  $i = 1$  to  $n$  are the analytical results in the final method reporting units obtained from the  $n$  sample aliquots and

$$\sum_{i=1}^n X_i^2$$

refers to the sum of the  $X$  values from  $i = 1$  to  $n$ .

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1, 1-\alpha=.99)} (S)$$

where:

MDL=the method detection

$t_{(n-1, 1-\alpha=.99)}$ =the student's  $t$  value appropriate for a 99 percent confidence level and a standard deviation estimate with  $n-1$  degrees of freedom. See Table.

$S$ =standard deviation of the replicate analyses.

(b) The 95 percent confidence limits for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ( $X^2/df$ ) and calculated as follows:

$$MDL_{LCL} = 0.69 MDL$$

$$MDL_{UCL} = 1.92 MDL \quad \text{where } MDL_{LCL} \text{ and } MDL_{UCL} \text{ are the lower and upper 95 percent confidence limits respectively based on seven aliquots.}$$

7. Optional iterative procedure to verify the reasonableness of the estimated MDL and calculated MDL of subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimated MDL in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If the current MDL determination is an iteration of the MDL procedure for which the spiking level does not permit qualitative identification, report the MDL as that concentration between the current spike level

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and the previous spike level which allows qualitative identification.

(c) If the current MDL determination is an iteration of the MDL procedure and the spiking level allows qualitative identification, use  $S^2$  from the current MDL calculation and  $S^2$  from the previous MDL calculation to compute the F ratio.

$$\text{if } \frac{S_A^2}{S_B^2} < 3.05$$

then compute the pooled standard deviation by the following equation:

$$S_{\text{pooled}} = \left[ \frac{6S_A^2 + 6S_B^2}{12} \right]^{0.5}$$

$$\text{if } \frac{S_A^2}{S_B^2} > 3.05,$$

respoke at the last calculated MDL and process the samples through the procedure starting with Step 4.

(d) Use the  $S_{\text{pooled}}$  as calculated in 7b to compute the final MDL according to the following equation:

$$\text{MDL} = 2.681 (S_{\text{pooled}})$$

where 2.681 is equal to  $t(12, 1 - \alpha = .99)$

(e) The 95 percent confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$\text{MDL}_{\text{LCL}} = 0.72 \text{ MDL}$$

$$\text{MDL}_{\text{UCL}} = 1.65 \text{ MDL}$$

where LCL and UCL are the lower and upper 95 percent confidence limits respectively based on 14 aliquots.

*Reporting*

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with the MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, report the mean recovery, and indicate if the MDL determination was iterated.

If the level of the analyte in the sample matrix exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

REFERENCE

Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., "Trace Analysis for Wastewaters," Environmental Science and Technology, 15, 1426 (1981).

TABLE OF STUDENTS' T VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t(n-1, 1-\alpha=.99)$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
		2.326

[53 FR 9186, Mar. 21, 1988]

**PART 426—GLASS MANUFACTURING POINT SOURCE CATEGORY**

**Subpart A—Insulation Fiberglass Subcategory**

Sec.

426.10 Applicability; description of the insulation fiberglass subcategory.

426.11 Specialized definitions.

426.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

426.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

426.14 [Reserved]

426.15 Standards of performance for new sources.

426.16 Pretreatment standards for new sources.

426.17 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).