[1] Native/labeled.
[2] Analysis of this pollutant is approved only for the Centralized Waste Treatment industry.
[3] Analysis of this pollutant is approved only for the Centralized Waste Treatment and Landfills industries.

TABLE 6—ACID EXTRACTABLE COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled Analog	Primary m/z [1]
p-cresol [2]	d_7	108/116

m/z = mass to charge ratio.
[1] Native/labeled.
[2] Analysis of this pollutant is approved only for the Centralized Waste Treatment and Landfills industries.

TABLE 7—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No.	Compound	Acceptance criteria			Calibration verification sec. 12.5 µg/mL)	On-going accuracy sec. 12.7 R (µg/L)
		Initial precision and accuracy section 8.2 (µg/L)		Labeled compound recovery sec. 8.3 and 14.2 P (percent)		
		s (µg/L)	X			
758	acetophenone [1]	34	44–167	.....	85–115	45–162
658	acetophenone-d_5 [1]	51	23–254	45–162	85–115	22–264
757	aniline [2]	32	30–171	.....	85–115	33–154
657	aniline-d_7 [2]	71	15–278	33–154	85–115	12–344
771	o-cresol [1]	40	31–226	.....	85–115	35–196
671	o-cresol-d_7 [1]	23	30–146	35–196	85–115	31–142
1744	p-cresol [2]	59	54–140	.....	85–115	37–203
1644	p-cresol-d_7 [2]	22	11–618	37–203	85–115	16–415
578	2,3-dichloroaniline [1]	13	40–160	.....	85–115	44–144
1330	pyridine [2]	28	10–421	.....	83–117	18–238
1230	pyridine-d_5 [2]	ns	7–392	19–238	85–115	4–621

s = Standard deviation of four recovery measurements.
X = Average recovery for four recovery measurements.
EGD = Effluent Guidelines Division.
ns = no specification; limit is outside the range that can be measured reliably.
[1] Analysis of this pollutant is approved only for the Centralized Waste Treatment industry.
[2] Analysis of this pollutant is approved only for the Centralized Waste Treatment and Landfills industries.

[49 FR 43261, Oct. 26, 1984; 50 FR 692, 695, Jan. 4, 1985, as amended at 51 FR 23702, June 30, 1986; 62 FR 48405, Sept. 15, 1997; 65 FR 3044, Jan. 19, 2000; 65 FR 81295, 81298, Dec. 22, 2000]

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the 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 in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, *i.e.*, a break in the slope of the standard curve.

(d) 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 initial 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 (blank) water, 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 method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) 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 detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

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

(2) The sample may be used as is for determining the method detection limit 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 method detection limit 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 a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement 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 method detection limit 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 inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit 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 desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in 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:

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

$$S = \left(S^2\right)^{\frac{1}{2}}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained

from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$MDL = t_{(n-1,1-\alpha=0.99)}$ (S)

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% 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% confidence interval estimates 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 (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

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

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

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute The final MDL according to the following equation:

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

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

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

LCL=0.72 MDL

UCL=1.65 MDL

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

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

Number of replicates	Degrees of freedom (n-1)	$t_{cn-1,.99)}$
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
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title ald 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 MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10

times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

APPENDIX C TO PART 136—DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY METHOD 200.7

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP–AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1–4] (For analysis of petroleum products see References 5 and 6, Section 16.0). This method is applicable to the following analytes:

Analyte	Chemical abstract services registry number (CASRN)
Aluminum (Al)	7429–90–5
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Boron (B)	7440–42–8
Cadmium (Cd)	7440–43–9
Calcium (Ca)	7440–70–2
Cerium[a] (Cr)	7440–45–1
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Iron (Fe)	7439–89–6
Lead (Pb)	7439–92–1
Lithium (Li)	7439–93–2
Magnesium (Mg)	7439–95–4
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Molybdenum (Mo)	7439–98–7
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Potassium (K)	7440–09–7
Selenium (Se)	7782–49–2
Silica[b] ($Si0_2$)	7631–86–9
Silver (Ag)	7440–22–4
Sodium (Na)	7440–23–5
Strontium (Sr)	7440–24–6
Thallium (Tl)	7440–28–0
Tin (Sn)	7440–31–5
Titanium (Ti)	7440–32–6
Vanadium (V)	7440–62–2
Zinc (Zn)	7440–66–6

[a] Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b] This method is *not* suitable for the determination of silica in solids.

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 §141.23 for drinking water), and the latest FEDERAL REGISTER announcements.

1.3 ICP–AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as ''direct analysis''. However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by ''direct analysis'' where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots