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STOPPING
WATER POLLUTION
AT ITS SOURCE

MISA

Municipal/Industrial Strategy for Abatement

ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL)

Environment
Ontario

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Minister

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ONTARIO MINISTRY OF THE ENVIRONMENT

ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL)

ANALYTICAL METHOD DETECTION LIMITS PROTOCOL

FOR

MUNICIPAL AND INDUSTRIAL STRATEGY FOR ABATEMENT (MISA)

PROGRAM

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Ministère de l'Environnement de l'Ontario
Évaluation des seuils de détection des méthodes d'analyse

Protocole relatif au calcul des seuils de détection des méthodes d'analyse pour la Stratégie municipale et industrielle de dépollution (SMID)

Ce protocole établit la marche à suivre pour évaluer la précision et le seuil de détection des méthodes d'analyse (SDM).

On analyse un nombre prédéterminé d'échantillons (soit de l'eau enrichie, soit des échantillons en double) suivant la méthode d'analyse prescrite et on utilise des formules statistiques courantes pour obtenir la précision.

On calcule ensuite le seuil de détection d'une méthode (SDM) en multipliant la précision par le facteur "Student's-t" approprié.

Ontario Ministry of the Environment

Estimation of Analytical Method Detection Limits (MDL)

Analytical Protocol

Introduction

This protocol is being established to ensure a consistent approach to the development of method detection limit estimates for the MISA program based on the use of fortified reagent (blank) water or evaluation of available routine within-run duplicate analyses.

It should be noted that when MDL estimates are developed using clean samples (i.e. reagent (blank) water) they represent an optimum achievable value. MDLs obtained in this fashion are very useful for establishing performance criteria and allowing comparison of interlaboratory method capabilities, but may not be applicable in defining the quantitation capability for other samples which introduce matrix effects.

The following protocol represents a modification to that documented in the Federal Register/Vol. 49, No. 209/ Friday, October 26, 1984/Appendix B to Part 136 - Revision 1.11.

This modification restricts the options listed in the original document and gives more direct instructions at other option points.

Definition

The method detection limit (MDL) is a statistically defined decision point such that measured results falling at or above this point are interpreted to indicate the presence of analyte in the sample with a specified probability, and assumes that there are no known sources of error in identification or biases in measurement.

For the purposes of this document, the MDL is defined as having a confidence limit of 99%. This confidence limit defines the multiplication factor used from Student's t-tables relating MDL to the analytical precision. This Student's t-value depends on the amount of data used to calculate the analytical precision. In general, analytical precision will depend on the analytical conditions and the sample matrix. When possible, precision will be determined by replicate analysis of typical low-level samples, with sufficient replication to provide a reasonable estimate.

Scope and Application

This protocol is designed for application to a wide variety of sample types ranging from reagent (blank) water fortified with a known concentration of analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The protocol 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 protocol was designed for application to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

There are four options available for estimating the analytical precision:

a) accumulation of a large number of in-run duplicate analyses of typical samples at levels not exceeding 10 times the estimated MDL;

b) accumulation of in-run duplicate analyses of laboratory reagent quality water spiked with a known amount of the target analyte(s) at levels not exceeding 10 times the estimated MDL;

c) analysis of eight replicate aliquots of a typical low level sample at levels not exceeding 10 times the estimated MDL;

d) analysis of a series of eight replicate aliquots of laboratory reagent quality water spiked with a known amount of the target analyte(s) at a level not exceeding 10 times the estimated MDL:

This protocol outlines the application of these approaches for the MISA program.

Organics Analytes (MISA Test Groups 16-24, 26 and 27)

This protocol requires that option d) be used. The fortification of laboratory reagent (blank) water with a known level of analyte is required to standardize the protocol for all laboratories and minimize the problems associated with analyzing duplicate or replicate samples or finding a standard "matrix" for organics analysis. The

analytical precision is established based on eight replicate analyses and the estimated MDL is derived from a combination of these measurements and the appropriate value from t-test tables. This option is not intended to assess the effect of matrix on the values obtained but rather to define a standardized approach in the development and application of interlaboratory performance criteria for the program. Proceed to step 1.

Conventionals, Metals and Inorganics
(MISA Test Groups 1-15 and 25)

This protocol allows any of the options a), b), c) or d) to be used. For option a) the laboratory should review recent data on in-run duplicates (data accumulated within the preceding 12-month period or less) and apply the formula as outlined in step 5b) to at least 40 data pairs. Proceed to step 5b) for option a) or b). Proceed to step 1 for option c) or d).

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 of 3:1.

   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. The use of commercially obtained or laboratory prepared organic free water or cold potable tap water is acceptable but clearly indicate what was used.

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 5 times, but not to exceed 10 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 5 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. Take eight 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 mesurement 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.

5. a) For option d), 8 replicates of spiked reagent water, calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

The formula for the mean:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

The formula for the variance (s^2):

$$s^2 = \frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n - 1}$$

The formula for standard deviation:

$$s = + \sqrt{s^2}$$

where:

X_i; i = 1 to 8, are the analytical results in the final method reporting units obtained from the 8 sample aliquots.

b) For option a), assessment of historic within run duplicate analysis data, calculate the variance (S^2) and the standard deviation (S) of the duplicate measurements as follows:

The formula for the variance (S^2):

$$S^2 = \frac{\sum_{i=1}^{n} (X_1 - X_2)_i^2}{2n}$$

The formula for the standard deviation(s):

$$S = + \sqrt{S^2}$$

where:

$(X_1-X_2)_i$; i = 1 to n are the analytical results of the n duplicate pairs X_1 and X_2. (Minimum of 40 pairs)

6. a) Compute the MDL as follows:

$$MDL = \left[t(n-1, \alpha = 0.01) \right] X \quad [S]$$

where:

MDL = the method detection limit

t (n-1, α = 0.01) = the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with the appropriate degrees of freedom.

S = standard deviation of the replicate analyses.

7.0 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 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.

Tables of Student's t Values at the 99 Percent Confidence Level

Number of Replicates	Degree of Freedom (n-1)	t (n-1)
7	6	3.143
8	7	2.998
9	8	2.897
10	9	2.821
11	10	2.764
16	10	2.603
21	20	2.528
26	25	2.485
31	30	2.457
∞	∞	2.369