

MEMORANDUM

To: Regional Water Engineers, Bureau Directors, Section Chiefs

Subject: Division of Water Technical and Operational Guidance Series (1.3.7)
ANALYTICAL DETECTABILITY AND QUANTITATION GUIDELINES FOR
SELECTED ENVIRONMENTAL PARAMETERS (Originator: Lawrence
Bailey)

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I. Purpose

The purpose of this TOGS is to provide guidance to Division of Water staff on the use and selection of analytical detection limits and quantitation limits in writing State Pollution Discharge Elimination System permits.

II. Discussion

Due to the extreme toxicity of some chemical substances it has been necessary to specify very low effluent concentration levels in SPDES discharge permits. These permit limits approach the detection limit of the analytical methods used in permit monitoring.

A major problem encountered in such a guidance document is defining what is meant by the terms detection limit or quantitation limit. One common definition requires the analysis of a series of "blank" samples (samples of laboratory pure water) for the analyte in question. The mean and standard deviation of the resulting instrument output signals are calculated and the detection limit is set equal to the mean plus 3 times the calculated standard deviation. What is actually being measured is the variation of the output signal. This variation is called "noise". Since 3 standard deviations represents the 99% confidence level, an output signal greater than or equal to the 3 standard deviation detection limit means that there is 99% confidence that the analyte concentration is greater than zero.

A report titled "Principles of Environmental Analysis" by the Subcommittee on Environmental Analytical Chemistry to the American Chemical Society's Committee on Environmental Improvement, that was published in the December 1983 edition of *Analytical Chemistry* proposed a "quantitation limit" which is equal to the mean plus 10 times the standard deviation. This limit would have a higher level of precision (approximately $\pm 30\%$) than is associated with the detection limit.

The USEPA has published in 40CFR Part 136 the procedure for determination of the "method detection limit" (MDL). This procedure involves the replicate analysis (seven replicates as a minimum) of a sample with an analyte concentration near but greater than zero. The standard deviation (s_c) at this concentration is then calculated. The MDL is then defined as

$$\text{MDL} = t_{n-1} \times s_c$$

where t_{n-1} is the Students t-Test value at the n-1 level and n is the number of replicates. For seven replicates, $t_{n-1} = 3.14$.

Therefore for seven replicates

$$\text{MDL} = 3.14 s_c$$

In keeping with these ideas the three terms, Method Detection Limit, Scan Detection Limit, and Practical Quantitation Limit are used in this guidance document and are defined as follows:

Method Detection Limit (MDL) - is the level at which the analytical procedure referenced is capable of determining with a 99% probability that the substance is present. This value is determined in distilled water with no other interfering substances present. The precision at this level is $\pm 100\%$. The MDLs presented here are either:

1. Those values listed in the published method
- or
2. If number one above is unavailable, they are values, rounded to one significant figure, that have been calculated from either precision information (3 times the standard deviation) published for the method; or 0.25 times the Practical Quantitation Limits published for the method; or they are values from some other referenced information source.

Scan Detection Limit (SDL) - is the MDL for a referenced analytical procedure that is capable of analyzing for several substances at one time and assuring correct identification of each. As with the MDL, the SDL is determined using distilled water, with only the substance or group of substances of interest added, and no interfering substances present. The SDL method for organic compounds uses a gas chromatograph equipped with a mass spectrometer detector (GC/MS). Mass spectrometer systems provide information on the molecular weight of organic pollutants but are less sensitive than other chromatographic detector systems used in the MDL methods. As a result, the SDL is generally higher than the MDL. For metals the instrument used for the measurements is an Inductively Coupled Plasma Emission Spectrometer (ICP). ICPs are capable of measuring several emission wavelengths at once thereby reducing interference problems, but are less sensitive than graphite furnace atomic absorption spectrometry, and as a result, also have generally higher SDLs.

Practical Quantitation Limit (PQL) - is the lowest level that can be measured within specified limits of precision and accuracy during routine laboratory operations on most effluent matrices. For this document these numbers are:

1. Those values listed in the published method
- or
2. If number one above is unavailable, they are values, rounded to one significant figure, that are equal to 4 times the published MDL; or 4 times the unrounded MDL that was calculated from precision information published for the method; or values from some other referenced information source.

This should result in a precision of about $\pm 30\%$.

Three types of permit situations were anticipated in preparing this guidance document. They were:

- Case 1) - Discharges to groundwater or surface water where the intent is that the permitted substance **MUST** be non-detectable or the water quality limit is less than the lowest MDL for the parameter.
- Case 2) - The water quality limit is above the PQL for the parameter.
- Case 3) - The water quality limit is between the MDL and the PQL.

For Case one the permit writer is advised to use the stated numerical MDL value for the most sensitive technique.

For Case two the permit writer is advised to use the derived water quality limit.

For Case three the permit writer is advised to use the derived water quality limit understanding that the precision at this level will be greater than that at the MDL but less than the precision at the PQL.

The following are specific examples of situations for each of these cases and the permit limit that would be selected:

- Example #1- A discharge to groundwater has the potential to contain benzene. Groundwater regulations require benzene to be "non-detectable" in the discharge. The permit would therefore be written as benzene non-detectable by USEPA Method 602 (MDL = $0.2\mu\text{g/L}$).
- Example #2- A water quality review has determined that a discharge should be limited at $100\mu\text{g/L}$ of total cyanide. The permit would therefore be written with a total cyanide limit of $100\mu\text{g/L}$ since Method 335.2 has a PQL below that limit.
- Example #3- A water quality review has determined that a discharge should be limited to $0.01\mu\text{g/L}$ of r-BHC. The permit limit may be set at $0.01\mu\text{g/L}$ by USEPA Method 608 (understanding that the precision at this level will be greater than that at the MDL but less than the precision at the PQL).

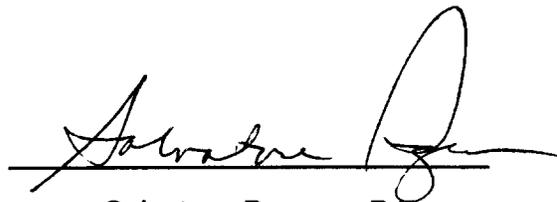
Example #4- A water quality review has determined that a discharge should be limited to $0.1\mu\text{g/L}$ of silver. The permit limit would be set at $0.2\mu\text{g/L}$ which is the MDL of Method 272.2 since that is the most sensitive method for silver.

Example #5- A water quality review has determined that a discharge should be limited to $0.5\mu\text{g/L}$ of chloroform. The permit limit would be set at $0.5\mu\text{g/L}$ by Method 601 since that is greater than the PQL for this method.

In any instance, where absolute identification of an organic pollutant is necessary, confirmation using the mass spectrometer and/or a second gas chromatography column, which has approximately the same MDL as the first column, is available. The permit writer always has the option of selecting from any of the listed methods that satisfy all concerns.

III. Guidance

The Division of Water has prepared a guidance document entitled "Analytical Detectability and Quantitation Guidelines for Selected Environmental Parameters" (prepared December 1988). This document, a list of environmental parameters with associated detection and quantitation limits, has been prepared as a guide for Division of Water permit writers to use in setting permit limits that are analytically determinable. The list contains 396 parameters of environmental interest. Additional parameters will be added periodically. Because of matrix interferences, the detection/quantitation limits included may not apply to all dischargers at all times. It is the policy of the Division of Water that this document shall be used in the establishment of wastewater discharge permit limits utilizing the procedures described herein.



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cc: Dr. Banks
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* Available from the NYS Department of Environmental Conservation, Division of Water Bureau of Technical Services and Research, 50 Wolf Road, Albany, New York 12233-3502. There is a fee of \$250.00 for this document.