8. Method Detection Limits

   8.1 Verify the method detection limit (MDL) for each analyte using low-level estuarine or fresh water containing the analyte at approximately the current detection limit. The water sample may be spiked with reagent water if necessary to make the concentration approximately 1 – 5 times the current method detection limit.

   8.2 Alternatively, determine the MDL in reagent (blank) water by preparing a laboratory standard (i.e., analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the current method detection limit.

   8.3 Analyze at least seven replicate aliquots of water *which have been prepared individually* (e.g., digested) and subjected to the entire analytical method. It is recommended that some of the replicates be analyzed on a different day to include the day-to-day variability in the MDL determination.

   8.4 Perform all calculations defined in the method and report concentrations in appropriate units.

   8.5 If a blank measurement is required to calculate a particular analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

   8.6 Calculate the MDL as follows: (Online calculator available at: http://www.chemiasoft.com/mdl_by_epa.html)

   $$MDL = (t)(S), \text{ where:}$$

   S = the standard deviation of the replicate analyses,
   t = Student's t value for n-1 degrees of freedom at the 99% confidence limit; where
       t = 3.143 for six degrees of freedom

   8.7 MDLs should be determined every 12 months or whenever a significant change in method, instrument, operator, or instrument response occurs, or a new matrix is encountered.

   8.8 MDLs should always be calculated using the same calibration curve that would be used for typical sample analysis. If more than one instrument or calibration range is used in the lab, determine the MDL on the instrument that will be used to report low-level results, under realistic conditions.

   8.9 A table of MDL and PQL values shall be submitted annually. When values change, a revised table of MDL and PQL values and their effective dates should be included with the next data submittal.

9. Practical Quantitation Limits

   9.1 The method quantitation limit (MQL or PQL) is approximately 3.18 (MDL); or:

   MQL = 10 (S), where S = the standard deviation of the replicate analyses as described in subsection C.8.6 above.

   9.2 The lowest calibration standard concentration must be at or below the PQL (see subsection C.5.2.4).

   9.3 Analytical results between the MDL and PQL shall be quantified. Report the numerical value and qualify with the appropriate qualifier code "G".

Students' *t* Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602

To: OW-Docket@epa.gov

From: Mary Ellen Ley (mley@chesapeakebay.net)

Attention: Docket ID # EPA-HQ-OW-2014-0797

On behalf of the Chesapeake Bay Program Data Integrity Workgroup, please consider the following comments in response to the February 19th Federal Register 40 CFR Part 136 – Clean Water Act Methods Update Rule for the Analysis of Effluent; Proposed Rule

The Chesapeake Bay Program is an EPA-led regional partnership of federal and state agencies. Program Partners collect surface water nutrient and solids samples for multiple data analyses and modeling uses using many of these methods. Program staff also use NPDES data as direct input into watershed and water quality model. The Chesapeake Bay Program has a long-standing analytical methods and quality assurance workgroup that seeks the best available methods and practices to obtain its data. The comments submitted below represent the concurrence of this group on the proposed revisions to 40 CFR Part 136.

§ 136.3(a) Identification of Test Procedures, Table IB – List of Approved Inorganic Test Procedures

1. Agree with the proposal to approve new versions of methods currently approved from *Standard Methods for the Examination of Water and Waste* as long as there are no substantive changes.

2. Support the addition of USGS Methods I-2547-11 and I-2548-11 and NECi Method N07-00303 (Nitrate Reductase Methods) for the analyses of nitrate and nitrite. Two of our laboratories routinely use these methods and generate data that are comparable to results from the cadmium reduction technique.

Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit

1. The group agrees with proposed changes for determining the MDL and supports the adoption of the proposed changes in whole. Some of the reasons are that:

   a. The procedure accounts for measurement bias as well as precision. Verification of the MDL using the method blank MDL calculation is simple and straightforward and should result in more realistic MDL determinations;

   b. Replicates are processed as samples and analyzed on three different days. This will simulate day-to-day variability;

   c. The quarterly checks and the use of the quarterly results for the annual determination is less burdensome on the laboratories and will produce more representative estimates;

   d. A MDL determination is required for each instrument; and

e. The specifications for determining the MDL in a sample matrix are reasonable.

2. In the preamble of the final rule, please explain the rationale in Appendix B, section (4)(e), that states "If the verified MDL is within a factor of 3 of the existing MDL and fewer than 3% of method blank results … are above MDL, then the existing MDL may optionally be left unchanged".

Thank you for making these improvements.