Proposed Modification of V1M4 (Quality Systems for Chemical Testing), Section 1.5.2

The TNI Chemistry Committee has received input towards its further development of the 2016 Standard, resulting in the proposed modifications provided below. The rationale/justification for each proposed amendment is provided in the text boxes in BLUE font.

Stakeholders are invited to provide further input NO LATER THAN JULY 26. The committee will meet with the commenters if necessary, and further amendments may then be made to produce a Voting Draft Standard.

Input should be provided to the Chemistry Chair, Valerie Slaven at Valerie.Slaven@gmail.com, and should be limited to those sections highlighted through tracking.

1.5.2 Limit of Detection and Limit of Quantitation (however named)

Procedures used for determining limits of detection and quantitation shall be documented. Documentation shall include the quality system matrix type. All supporting data shall be retained.

1.5.2.1 Detection Limit (DL)

If a mandated test method or applicable regulation includes protocols for determining detection limits, they shall be followed. The laboratory shall document the procedure used for determining the DL. If the method or regulation does not contain specific directions for determination of the detection limit, the following requirements shall apply. DL determinations are not required for methods/analytes for which a detection limit is not applicable such as pH, color, odor, temperature, titrimetric, or dissolved oxygen. DL determinations based on spikes are not required for analytes for which no spiking solutions are available. If results are not reported below the limit of quantitation (LOQ), an initial DL determination is required, but ongoing verification is not.

1.5.2.1.1 Initial determination of the DL

The laboratory DL procedure, unless following a mandated test method or procedure, at a minimum, shall incorporate language addressing the following requirements:

a) the DL shall reflect current operating conditions;

b) the DL determination shall incorporate the entire analytical process~~, including sample preservations~~;

Removal of "including sample preservations" makes the section consistent with both the current version of 40 CFR Part 136 Appendix B and the pending updated version.

c) the DL determination shall include data from low level spikes and routine method blanks prepared and analyzed over multiple days; at least one spike~~d sample~~ and routine method blank~~s~~ must be analyzed on each applicable instrument; a minimum of seven replicates is required for both low level spikes and routine method blanks;

It was already a requirement for 7 replicates, but was not stated explicitly. This assures the wording of the standard is consistent with the referenced EPA MDL procedure that does explicitly require at least 7 replicates.

d) results from spiked samples used in the DL determination shall meet qualitative identification criteria in the method, and shall be above zero;

e) the DL procedure shall include criteria for and evaluation of false positive rates in routine method blanks;

f) the DL shall be determined for the analytes of interest in each test method in the quality system matrix of interest in which there are neither target analytes nor interferences at a concentration that would impact the results, or the DL shall be performed in the sample matrix of interest.

NOTE: One option is to follow the procedure found in R2014-MDL, a regulatory comment developed by the TNI Chemistry Expert Committee and published on the Committee's pages on the TNI website. This is identical to the MDL procedure published by the US Environmental Protection Agency in December 2016.

1.5.2.1.2 Ongoing verification of the DL

At a minimum, ongoing verification of the DL shall include assessments of spikes at or below the LOQ and of method blanks. A minimum of one (1) verification spike and one (1) blank shall be analyzed on each instrument during each quarter in which samples are being analyzed and results are being reported below the LOQ. The criteria listed in Section 1.5.2.1.1 shall be met for ongoing verification over the course of a year.

If the method is altered in a way other than routine maintenance and the change can be expected to elevate the detection limit, then a spike at or below the LOQ concentration and a blank shall be prepared and analyzed. If the spike at the LOQ concentration gives a result meeting qualitative identification criteria above zero, and the blank gives a result below the DL, then the DL is verified. If not, the DL shall be re-determined.

In the event that verification fails, the laboratory shall perform a new DL study within thirty (30) calendar days.

1.5.2.1.3 When a new DL is determined, the laboratory shall verify that the LOQ value is ~~at least three (3) times~~greater than the DL. If it is not, the laboratory shall raise the LOQ value to ~~at least three (3) times~~greater than the DL.

Although it is technically defensible for the LOQ to be at least 3 times the DL, this would cause problems with some methods (particularly drinking water), preventing laboratories getting a low enough reporting limit for some analytes. Just requiring the LOQ to be greater than the detection limit would be consistent with the 2009 standard. Additionally, the new 2016 standard, of which this will be a modification, has more rigorous LOQ verification requirements. Laboratories must set their LOQ at a level at which they could reliably analyze the sample. They must do it every quarter on every instrument, collect data spiked at that level, and demonstrate what their precision and accuracy are. There is also the additional requirement of measuring Relative Error in the calibration, so there will be additional controls.

1.5.2.2 Limit of Quantitation (LOQ)

If a mandated test method or applicable regulation includes protocols for determining quantitation limits, they shall be followed. The procedure used for determining the LOQ shall be documented by the laboratory. The laboratory shall select an LOQ for each analyte, consistent with the needs of its clients, and ~~at least three (3) times~~greater than the DL. An LOQ is required for each quality system matrix of interest, technology, method, and analyte, except for any component or property for which

See 1.5.2.1.3 comment above

spiking solutions are not available or a quantitation limit is not appropriate, such as pH, color, odor, temperature, dissolved oxygen, or turbidity.

a) Each selected LOQ shall be verified through analysis of initial verification samples. An initial verification sample consists of a spiked matrix blank at or below the selected LOQ.

b) All sample preservation, processing and analysis steps performed for routine sample analysis shall be included in the LOQ verification testing.

c) The LOQ must be at or above the lowest corresponding calibration standard concentration with the exception of methods using a single point calibration.

d) The laboratory shall establish acceptance criteria for accuracy for the LOQ verification spikes.

1.5.2.2.1 Initial verification of the LOQ

When first establishing an LOQ, or when an LOQ concentration has been selected that is lower than the concentration of the LOQ verification spikes previously performed, an initial verification shall be performed as follows:

a) A minimum of seven (7) blanks spiked at or below the LOQ concentration shall be processed through all steps of the method, including any required sample preservation. Both preparation and analysis of these samples shall include at least three (3) batches on three (3) separate days.

NOTE 1: Spiking slightly below the LOQ may help ensure that the results are also suitable for DL determination.

NOTE 2: If spiked blanks have been analyzed in order to generate a DL, the results may be used to perform the initial verification of the LOQ.

i. If there are multiple instruments that will be assigned the same LOQ, then these spiked blanks shall be distributed across all of the instruments.

ii. A minimum of two (2) spiked blanks prepared and analyzed on different days shall be tested on each instrument.

b) Existing data may be used if compliant with the requirements for at least three (3) batches, generated within the last two (2) years and representative of current operations.

c) The LOQ is verified if the following criteria are met:

i. All results are quantitative (above zero and meet the qualitative identification criteria of the method (e.g., recognizable spectra, signal to noise requirements, and presence of qualifier ions).

If a result from an LOQ verification sample is not above zero and/or does not meet the qualitative identification criteria in the method, the problem shall be corrected and the verification repeated, or the LOQ verification shall be repeated at a higher concentration.

ii. ~~Recovery~~ The mean recovery of each analyte is within the laboratory established accuracy acceptance criteria.

This is considered an editorial change for clarification purposes, since it was implicit that the initial LOQ have recoveries calculated based on the mean.

iii. The LOQ is ~~at least three (3) times~~greater than the established DL and at or above the spiking concentration.

If the LOQ is less than ~~three (3) times~~or equal to the DL, the LOQ shall be raised to ~~at least three (3) times~~greater than the DL.

NOTE: It is **not** necessary to repeat the LOQ verification at a higher concentration when it is necessary to raise the LOQ to ~~three (3) times~~greater than the DL.

See 1.5.2.1.3 comment above

d) The laboratory shall document the results of the initial LOQ verification as described in Section 1.5.2.4.

1.5.2.2.2 Ongoing verification of the LOQ

The laboratory shall prepare and analyze a minimum of one (1) LOQ verification sample spiked at the same concentration as the initial LOQ verification on each instrument during each quarter in which samples are being analyzed for each quality system matrix, method, and analyte.

~~a)~~ Results of each LOQ verification sample analysis shall be evaluated at the time of the testing and shall meet the qualitative identification criteria in the method and laboratory Standard Operating Procedure (SOP) and the quantitated result shall be greater than ~~zero~~the DL and meet the laboratory established accuracy criteria. If a continuing LOQ verification test does not meet this requirement, the laboratory shall take corrective action and document a technically valid reason for the corrective action~~.~~ Corrective action shall be either (i) correcting method or instrument performance and repeating the verification test, (ii) evaluating the laboratory established control limits to ensure they reflect current performance, or (iii) raising the spiking level (and the quantitation limit if the spiking level is above it) and repeating the initial verification study within thirty (30) calendar days of the initial failure. Any samples analyzed in a batch associated with a failing LOQ verification shall be reanalyzed or reported with qualifiers. ~~, or (ii) correcting method or instrument performance and repeating the verification test one time. In the event of second failure of a quarterly verification sample, the quantitation limit shall be raised and the initial study repeated within thirty (30) calendar days.~~

Concerns had been raised about the lack of a quantitative requirement in the on-going LOQ verification. There are insufficient data to specify accuracy limits in the standard, so it is now made incumbent on the laboratory to provide its own accuracy limits. The corrective action requirement is strengthened by requiring the laboratory to document its reason for corrective action. It is no longer stated that the quantitation limit shall be raised, because only one of several instruments may have failed.