Comments on Clean Water Act Methods Update Rule for the Analysis of Effluent

Prepared by:
The NELAC Institute
PO Box 2439
Weatherford, TX 76086

817-598-1624
www.nelac-institute.org

CONTACT: Jerry Parr, Executive Director; jerry.parr@nelac-institute.org

The NELAC Institute (TNI) is a 501(c)(3) non-profit organization whose mission is to foster the generation of environmental data of known and documented quality through an open, inclusive, and transparent process that is responsive to the needs of the community.

TNI manages the National Environmental Laboratory Accreditation Program (NELAP). Currently, 14 state agencies are recognized by TNI as Accreditation Bodies. TNI's Accreditation Bodies are responsible for ensuring the competency of environmental testing laboratories, including those analyzing waste water under the National Pollutant Discharge Elimination System (NPDES) program. Over 2000 laboratories are accredited under NELAP.

TNI also manages a Consensus Standards Development Program. TNI is accredited by the American National Standards Institute as a voluntary consensus standards organization and fully conforms to all requirements in OMB circular A-119.

In general, TNI applauds the Agency on ensuring the most current and reliable test methods are available to use. TNI specifically congratulates the Agency on proposing a new procedure for determining a Method Detection Limit (MDL) to replace the current procedure that is widely considered to be invalid. TNI's comments are organized into three areas, comments on the changes to Part 136, comments on the new 600 series methods, and comments on the new MDL procedure.

A. Changes to Sections 136.2 through 136.6

TNI supports the proposed changes to Sections 136.2 through 136.6 except for a few minor typographical errors and some document control issues.

Comment 1. Footnote 52

Recommendation: The citation to 300.1 (1997) should be changed to 300.1, Rev 1 (1999). The cover page to 300.1, Rev 1 should be changed and the text in the errata sheet incorporated into the method. This method should be posted on the OST website.

Discussion: Footnote 52 was proposed to be added. This footnote vaguely mentions 300.1-1 and then states "EPA Method 300.1 is Revision 1.0, 1997, including errata cover sheet April 27, 1999." Method 300.1-1, which was not in the docket or the OST website) is an exact copy of Method 300.1, Revision 1 published in 1997, except for the addition of the word 300.1-1 as a footer on the cover page and an errata sheet dated 1999 that appears as the second page. This errata contains minor changes to sections 4.1.1, 11.9, 9.3.2.2, 9.4.1.5, 9.4.3.2 and 9.4.3.3, which have all been made to the method. Thus, this method is not Revision 1 to Method 300.1. It is revision 1.1.

Comment 2. Table 1C, methods for analytes 35, 36, and 37 (dichlorobenzenes)

Recommendation: The approved EPA methods for these three analytes should be Methods 601, 602, and 624.1

Discussion: Table 1C shows Method 625.1 approved for 1,2-dichlorobenzene. This should be 624.1. The 2007 MUR removed Method 625 for dichlorobenzenes stating "significant losses of these volatiles can occur using the prescribed sample collection procedures in the LLE methods, resulting in relatively low recovery of these compounds" If this is true, 1625 should be not allowed either since the same analyte loss during storage could occur.

Comment 3. Errata Sheet for WET Methods

Recommendation: EPA should revise the Whole Effluent Toxicity methods manuals to reflect changes in two errata sheets.

Discussion: There are now two errata sheets associated with the Whole Effluent Toxicity Methods. One was referenced in the 2007 Method Update Rule and the second one in this proposed rule. Neither Table 1A nor the list of references in the text following Table 1H indicate the existence of these errata sheets. Laboratories who do not read the preamble would not know of the existences of this second errata sheet. These changes need to be incorporated into the methods. In the interim, the two errata sheets should be readily accessible on the OST website and footnotes 26, 27 and 28 to Table 1A should be revised to show that these errata sheets are part of the referenced methods.

Comment 4: Footnote 30 in Table 1A

Recommendation: Delete this footnote

Discussion: Footnote 30 states "The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection and analysis". This would place an undue burden on laboratories above what is required by Standard Methods. The footnote is erroneous. The verification section of SM 9222 D – 2006 states "Verify typical blue colonies and any atypical grey to green colonies as described in Section 9020 for fecal coliform analysis". SM Section 9020 regarding fecal coliform verification establishes a monthly verification of at least 10 blue colonies from one positive sample and to determine false negatives through verification of atypical colonies. The preamble states "SM 9222 D – 2006 specifies that the fecal coliform colonies should be verified "at a frequency established by the laboratory," which can be as low as zero. Under this QA/QC compendium associated with SM 9222 D – 2006, a minimum monthly verification is required so no lab using this method can set their verification frequency as low as zero.

B. Comments on Methods 608.3, 624.1 and 625.1

General Comments

The technical aspects of these methods represent a great improvement over the current methods. There is much more flexibility in the application of the methods to allow laboratories to take advantage of advancements in technology. The removal of specific procedural details help ensure laboratories can adjust the methods to fit their specific needs. The division of analytes into two groups, a default list that

is used for Quality Control purposes in lack of other specific guidance and an expanded list of additional analytes that may be measured is also useful.
The specific comments below are focused on these areas:

- Ensure these methods are somewhat comparable to similar methods to allow laboratories to meet the challenges of analyzing samples using different methods using one Standard Operating Procedure
- Correct inconsistencies among the three methods
- Correct technical errors
- Address inconsistencies between these methods and TNI's accreditation standard

MDLs and MLs

All three methods contain Method Detection Limits (MDLs) and Minimum Levels (MLs) for most of the default analytes, but not all. The MDLs are those published in the earlier versions of these methods, or in the case on Method 608.3, a comparable method. The MLs are the MDL multiplied by three.

Because the published MDLS were calculated using a procedure that is widely known to misrepresent the actual MDL that is achievable, these MDLs should be shown as guidance only and there should be no requirement for a laboratory to obtain MDLs that are at or below these numbers. Furthermore, since the ML is a simple multiplication of a number that may not be realistic, then this number may not be realistic as well. For example, the MLs for two compounds that are isomers of each other, anthracene and phenathrene are shown as 5.7 and 16.2 ug/L, differing by almost a factor of 3.

The MLs as published will create many logistical issues for laboratories in trying to customize calibration standards that are at or below these widely varying MLs because of the requirement that the low point of the calibration standard be at or below the ML. Because these MDL and ML values do not represent typical laboratory performance, they can be provided as guidance as to what is the expected sensitivity of the method but laboratories should not be required to achieve these levels.

Expanded Analyte Lists

The concept of having a default list of analytes, and then an expanded list is good. However, caution must be exercised to ensure the expanded lists are appropriate. For example, Table 2 in Method 624.1 lists methanol as an analyte. Methanol is used as the primary reagent in this method because under the normal conditions of the method, this analyte is not detectable. Another example is phthalic anhydride in Method 625.1. This compound decomposes in water to phthalic acid, and thus would never be measurable. Most of the analytes in these expanded tables have no published method performance data. If the Agency is to list an analyte in one of these tables, it should have some data to indicate the method is in fact capable of measuring the analyte.

Storage and Traceability of Standards

There are inconsistencies in the section on standards in terms of storage, traceability, and replacement. The table below highlights these differences.

608.3	624.1	625.1
Store neat standards or single	Store standard solutions at - 10	Store at <6 °C and protect from

analyte standards in the dark at -20 to -10 °C. Store multi-analyte standards at 4°C or per manufacturer's recommendations.	to -20°C, protected from light, in fluoropolymer-sealed glass containers with minimal headspace.	light.
Place a mark on the vial at the level of the solution so that solvent evaporation loss can be detected.		Check frequently for degradation or evaporation, especially just prior to preparing calibration standards from them.
Stock standard solutions must be replaced after 12 months or sooner if comparison with quality control check standards indicates a change in concentration.	Replace after one month, or sooner if the concentration changes by more than 10 percent.	Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions after one year, or sooner if comparison with QC check samples indicates a problem.
Analyze all standard solutions within 48 hours of preparation. Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions prepared by the laboratory or mixed with purchased solutions after one year, or sooner		

The differences appear to be arbitrary and these sections in the methods need to be revised for more consistency.

Second Source Standards

Second source standards are used in many methods for organics and their primary purpose has always been to verify the identification and purity of the primary standard.[1] Method 608.3 uses a second source standard for this purpose. It is defined in the Reagents section of the method and used to verify the initial calibration. Methods 624.1 and 625.1 do not take this approach. Second source standard is not defined or listed in the Reagents section of each method, and rather than using this standard to verify the initial calibration, it is later equated with a laboratory control sample (Method 624.1) or a calibration check standard (Method 625.1) and is not used to verify the initial calibration, but instead is used as a daily calibration check. This is not the intent of a second source standard. Additional error can be brought into the analytical system because it is a different source and the calibration standards were prepared independently. These methods need to differentiate between a second source calibration check and a daily calibration check.

Instrument Calibration

The initial instrument calibration for Methods 624.1 and 625.1 reflect the best practices in use today, a minimum of 5 calibration points (6 for quadratic) and if a curve is used, then it must be inversely

weighted to concentration. Method 608.3 requires a minimum of 3 points but recommends 5. This should be changed to 5 for consistency. The methods then have RSD limits to be used to determine if an average response fact can be used. If these limits are not achieved, calibration curves may be used with the measure of fit using either relative standard error or correlation coefficient. For 35 years, this community has known the correlation coefficient is not a good statistic to be used for evaluating instrument calibrations.[2] As stated in the reference:

> One practice which should be discouraged is the use of the correlation coefficient (r) as a means of evaluating goodness of fit of linear models. Thorough statistical analysis of analytical calibration data should be used to provide optimal evaluation of results. The correlation coefficient is not an effective statistic for this purpose.

The initial calibration is to be verified each day by a calibration check standard. (This should not be called a Laboratory Control Sample in Method 624.1 to avoid confusion with that commonly used term.) The acceptance limits for this QC check are found in the QC Acceptance Criteria tables in the methods (608.3 - Table 4; 624.1 – Table 7; 625.1 – Table 6). These tables include all sample processing steps and in general, are way too lenient to be used for a calibration verification check. For example, the acceptance limits for benzo(ghi)perylene in Method 625.1 is 19-195%; the limits for chloromethane in Method 624.1 is D (for detected) to 205%. Using limits such as these will greatly increase the laboratory error and greatly increase the probability the laboratory will be able to achieve expected performance for QC samples.

Note: Method 608.3 is poorly organized, with part of the discussion of this QC check occurring in the Calibration section (Section 7) and part occurring in the System and Laboratory Performance section (Section 14).

These methods should be rewritten to establish a fixed QC limit for this calibration check, e.g., 30%, but with an allowance for corrective action and limited data reporting as described in the National Environmental Laboratory Accreditation Program (NELAP) laboratory accreditation standard and repeated below.

> If the continuing instrument calibration verification results obtained are outside the established acceptance criteria, corrective actions must be performed. If documented routine corrective action procedures are followed immediately with a calibration verification that is within acceptance criteria, analysis may proceed. If that calibration verification analysis is not within acceptance criteria the laboratory shall demonstrate acceptable performance, after additional corrective action measures, with two consecutive calibration verifications, or a new initial instrument calibration. If samples are analyzed using a system on which the calibration has not yet been verified, the results shall be qualified. Data associated with an unacceptable calibration verification may be fully useable under the following special conditions:
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> i. when the acceptance criteria for the continuing calibration verification are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or

ii. when the acceptance criteria for the continuing calibration verification are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.

Quality Control

All three methods have an appropriate level of Quality Control (QC) checks embedded in the methods, and as discussed in more detail below, there are only a few minor issues related to these QC checks that need to be addressed. However, fundamental to this discussion is a new concept that is not contained in Part 136 and has never been subjected to public comment. This phrase "Results from tests performed with an analytical system that is not in control (i.e., that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results." This statement would ensure these methods are never selected since alternative methods exist for all analytes that do not carry this very stringent clause. This statement also supersedes other language elsewhere in the existing proposed method in the QC section.

If the Agency truly believes all QC checks must always be met, then this language should be added to Part 136 and subjected to public review and comment. Such a requirement would be impossible to achieve for many reasons, and would greatly lead to laboratory fraud if implemented.
The specific recommendations below on each QC check recognize that sometimes all a laboratory can legitimately do is report the sample results along with the QC results and let the regulated entity and permitting authority determine the appropriate course of action.

Demonstration of Capability

The earlier versions of these methods indicated this test was to be per analyst. This has now been changed to laboratory. The current accepted industry practice, and a requirement for laboratory accreditation under NELAP, is per analyst. To be in harmony with many other methods, current practice and NELAP, the DOC should be per analyst. The inclusion of an MDL study as part of this DOC is appropriate and consistent with current industry practice and a requirement in NELAP. However, to require laboratories to meet MDLs published in these methods that may or may not reflect the true MDL is inappropriate. The Agency should either conduct new MDL studies using these revised methods with the new MDL procedure, or drop the requirement to achieve the published MDLs. The DOC should be verified on an annual basis. The NELAP standard allows flexibility in meeting this requirement:

> The laboratory shall have a documented procedure describing ongoing DOC that includes procedures for how the laboratory will identify data associated with ongoing DOCs. The analyst(s) shall demonstrate on-going capability by routinely meeting the quality control requirements of the method, laboratory SOP, client specifications, and/or this Standard. If the method has not been performed by the analyst in a twelve (12) month period, an Initial DOC shall be performed. It is the responsibility of the laboratory to document that other approaches to ongoing DOC are adequate.
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> This on-going demonstration may be one of the following:

a) acceptable performance of a blind sample (single blind to the analyst) or successful analysis of a blind performance sample on a similar method using the same technology;

b) another initial DOC;

c) at least four (4) consecutive laboratory control samples with acceptable levels of precision and accuracy. The laboratory shall determine the acceptable limits for precision and accuracy prior to analysis. The laboratory shall tabulate or be able to readily retrieve four (4) consecutive passing LCSs or reference sample(s) for each method for each analyst each year;

d) a documented process of reviewing QC samples performed by an analyst or groups of analysts relative to the quality control requirements of the method, laboratory SOP, client specifications, and/or this Standard. This review can be used to identify patterns for individuals or groups of analysts and determine if corrective action or retraining is necessary;

e) if a) through d) are not technically feasible, then analysis of real-world samples with results within a predefined acceptance criteria (as defined by the laboratory or method) shall be performed.

Blanks

Given that the definition of the MDL is "the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results" it is not reasonable to expect all blank results will be less than the MDL. Also, since the reporting section of these methods all require results less than the ML to be reported as <ML, there would never be a reported results that is greater than the MDL and less than the ML. This section should be rewritten to mimic the language in the NELAP standard:

The source of contamination shall be investigated and measures taken to minimize or eliminate the problem and affected samples reprocessed or data shall be appropriately qualified if:

a) the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the method or by regulation, AND is greater than 1/10 of the amount measured in the sample;
b) the blank contamination otherwise affects the sample results as per the method requirements or the individual project data quality objectives; and
c) a blank is determined to be contaminated. The cause shall be investigated and measures taken to minimize or eliminate the problem. Samples associated with a contaminated blank shall be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases the corrective action shall be documented.

Laboratory Control Samples

These methods introduce a troubling concept in allowing duplicate measurements of the LCS to occur with the laboratory able to use the second results to demonstrate compliance if the first one fails. This

"pick and choose" concept is not allowed under NELAP. A better approach is to use the marginal exceedances concept developed by Tom Georgian of the US Army Corps of Engineers that is contained in the NELAP Standard and described below:

> Allowable Marginal Exceedances. If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (three standard deviations), but within the ME limits. ME limits are between three (3) and four (4) standard deviations around the mean. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than eleven analytes.
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> The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

> If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. Laboratories shall have a written procedure to monitor the application of marginal exceedance allowance to the LCS.

In addition, the method should allow for the circumstances described below.

> Samples analyzed along with an LCS determined to be "out of control" shall be considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes.
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> i. when the acceptance criteria for the positive control are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; or
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> ii. when the acceptance criteria for the positive control are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level with data qualifying codes.

Matrix Spikes

The 1984 versions of these methods required matrix spikes to be analyzed, but for those analytes that did not meet the QC criteria, a QC check sample could be used to demonstrate laboratory control. The requirement to not use results for compliance purposes only applied if the results from both the MS and QC check failed. This practice is consistent with the long-standing understanding of the purposes of the LCS and MS[3,4]. This section should be revised to be consistent with the earlier versions of the method and accepted practice, where the LCS is used to document laboratory performance and the MS used to document the performance of the method on that matrix.

Accuracy Assessment

The 1984 version of these methods, and the proposed revisions both contain a requirement to generate statements of accuracy for wastewater. This section does state what this statement is to be used for and it is unclear as to whether this is for all wastewaters from multiple sources, or segregated by discharger. In any event, there does not seem to be any use for this requirement. This section references 136.7 (c)(1)(viii), but that section merely states "Control charts (or other trend analyses of quality control results)," which could be many other charts such as LCS.

Reporting

The requirement to report quantitative data down to the ML to three significant figures is not appropriate given the precision of these methods. The requirement to report results less than the ML as <ML is not consistent with accepted practice and reflects a lack of understanding of the relationship of the MDL and ML. The mathematical relationship of these two numbers is based on Currie's Limit of Detection L_D and Limit of Quantitation L_Q.[5] Results above the ML should be reported as quantitative results. Results below the ML, but above the MDL should be shown as detected, typically with a quantitative value and a data qualifier to indicate the result is an estimate only. Results below the MDL should be reported as ND, not detected, at the stated MDL. The methods allow for blank subtraction. This sentence should be removed as such a technique increases the measurement uncertainty due to the uncertainties of both the sample and blank results.

Specific Method Comments

Method 608.3
The requirement to report an analyte as not detected if the results from two columns differ by more than a factor of 2 if an "interferent" is not detected will be difficult to implement and likely lead to false negative results.

Method 624.1
The recommendation to go down to mass range of 25-250 for four analytes ignores the fact that the recommended characteristic ions for these four analytes are all above m/z 50 and going below m/z 35 introduces many interferences. See the table below:

Analytes recommended for low mass scan and m/z	**Interferences below m/z 35**
Acrolein (m/z 56, 55, 58)	Methanol (m/z 29, 31, 32)
Acrylonitrile (m/z 53, 52, 51)	Nitrogen (m/z 28)
Choloromethane (m/z 50, 52)	Oxygen (m/z 32)

Vinyl chloride (m/z 62, 64)	Argon (m/z 40)

The requirement to achieve a 25% resolution between 1,2-dibromoethane (characteristic ions 107 (109, 188)) and chlorobenzene (characteristic ions 112 (77, 114)) ignores the fact that GC/MS can correctly identify and measure these two compounds even if they coelute. The same principle applies to most other target analytes. Any requirement for GC resolution can only apply to compounds that have the same characteristic ions.

Methods 624.1 and 625.1

The change in the requirement for relative intensities from ± 20% to -50% to +200% will likely increase false positives. The new requirement appears too broad and is not consistent with other similar methods. The statement to account for "m/z's present in the acquired mass spectrum" presumes mass spectra are obtained, but this is not a requirement if the laboratory uses extracted ion current profiles for identification and quantification as allowed by the method and furthermore could lead to false negatives due to the practical difficulty of meeting this requirement where the analyte is obscured by high concentrations of interferences.

References:

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