May 20, 2015

Water Docket, U.S. Environmental Protection Agency
Mail Code: 4203M
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Docket ID No. EPA-HQ-OW-2014-0797 ***"Clean Water Act Methods Update Rule for the Analysis of Effluent"***

The Environmental Laboratory Advisory Board (ELAB or Board) is a standing Federal Advisory Committee Act board that advises the U.S. Environmental Protection Agency (EPA or Agency). The Board's Charter states that it is to provide consensus advice, information and recommendations on issues related to EPA measurement programs and facilitate operation and expansion of a national environmental accreditation program.

ELAB is supportive of the Agency's efforts to implement changes to the available methods, proposed additional method choices, and method interpretation guidance in this update. The environmental testing community will welcome the additional flexibility these changes present. ELAB has prepared several comments and recommendations to support the Agency's efforts to increase analytical flexibility for testing performed under the Clean Water Act, which are included in the attached document. A summary of these comments/recommendations include:

- **Comment 1:** Comments and suggested edits on EPA Methods 624.1, 625.1 and 608.3, on which the Board previously provided comments to the Agency in 2013.
    - **Comment A:** General comments on use of qualified data.
    - **Comment B:** Proposed edits for Method 625.1.
    - **Comment C:** Proposed edits for Method 624.1.
    - **Comment D:** Proposed edits for Method 608.3.
- **Comment 2:** Comments and suggested edits to the proposed changes on method detection limits, as described in the Board's letter to the Agency dated January 31, 2014.
- **Comment 3:** Comments on proposed microbiological testing methods and procedures.
- **Comment 4:** Recommended edits to various tables, with the goal of providing consistency and additional clarity.
- **Comment 5:** Specific recommended edits to acrolein and acrylonitrile (in Method 624 and possibly Method 603) removal of pH requirement in preservation.

ELAB's specific comments follow this letter.

With regard to the Agency's request for comment on Alternate Test Procedures (ATP) and decision making: The Board recognizes that any decision to allow a Limited Use ATP method for compliance must come from the EPA Regional ATP Coordinator. This update offers good clarification in this regard. ELAB would suggest that the Agency choose the decision-making pathway described in the update: "The permitting authority could provide the initial review and approval, and then approved requests could be sent to the Regional ATP Coordinator for final review and approval." A pathway such as this would be a significant improvement to allow ATPs to be approved in a timely manner.

Regarding 40 CFR 136.7, ELAB would again recommend that the Agency include The NELAC Institute (TNI) Standard as an acceptable alternative to meeting the quality assurance and quality control elements included in the previous 40 CFR 136.7 revisions adopted in the 2012 MUR. The TNI Standard additionally provides applicable quality control measures for different methods, including chemistry, microbiological, toxicity and radiochemistry methods.

ELAB notes that many environmental organizations and laboratories will provide comments to the Agency on this Methods Update Rule. Because of the affiliations Board members have with certain organizations, the Board was able to review and acknowledges agreement with comments made by TNI, the Association of Public Health Laboratories, TestAmerica and Eurofins. ELAB concurs with and supports the comments made by these groups.

ELAB appreciates the opportunity to provide these comments to the Agency in support of this rule and applauds the Agency for providing measurement improvements that not only add flexibility to meet regulatory requirements but also continue to protect the nation's water quality.

Respectfully,

Patricia M. Carvajal
Chair, Environmental Laboratory Advisory Board

cc: ELAB Board
Lara Phelps, ELAB Designated Federal Official

Comment 1: Comments and Suggested Edits on EPA Methods 624.1, 625.1 and 608.3

The Board previously provided comments to the Agency on changes to Methods 624, 625 and 608. Although many of the recommendations from the Board have been adopted, several key items still could be addressed in the versions presented in this update.

A. General Comments on Methods 624.1, 625.1 and 608.3

Methods 608.3, 624.1 and 625.1 have statements related to the need to have acceptable quality control (QC) for all tests before the data can be "used for permitting or regulatory compliance purposes." To require that all QC results meet acceptance criteria before use in compliance or for regulatory decisions is unreasonable and may not be achievable (matrix interference, historically poor purger, etc.).

Further, there are instances in which data outside the acceptance range could be accepted. For example:

- If the laboratory control sample (LCS) or matrix spike failed low, the expected sample value would be greater than the reported value. If the reported value is greater than the decision point (i.e., compliance limit), then the actual concentration would be greater than the compliance level. In this case, noncompliance can be determined even when the QC failed.

- Another example would be a blank with contamination greater than one-tenth of any associated analyte. If the values of the associated analytes were less than the reporting limit, the data can be used to demonstrate compliance.

This requirement encourages permittees to demand that a laboratory not report data with qualifiers that indicate QC failures. This places undue pressure on a laboratory to either comply with a client's request or lose the client. Some laboratories may be inclined not to report failures, which is a serious data integrity issue. The data user should be allowed the flexibility of using data that fall outside the acceptance range for compliance when the failed QC does not affect decision of compliance/noncompliance.

Suggested Change: Add language that indicates: "The laboratory must take all reasonable measures to eliminate the QC failure. However, if the failure cannot be eliminated, report the results and the results of the failed QC. The result(s) must be appropriately qualified or have an accompanying narrative that clearly indicates the problem."

The instances where reporting in this case can be addressed in the following sections of Method 624.1, 625.1 and 608.3:

Method 624.1

p. 9034

"8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance purposes…"

p. 9035

"8.5.2 . . . . Samples must be associated with an uncontaminated blank before they may be reported or used for permitting or regulatory compliance purposes."

p. 9038

"13.2.3 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,…"

Method 625.1

p. 9053

"8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance purposes…"

p. 9054

"8.5.2 . . . . Samples must be associated with an uncontaminated blank before they may be reported or used for permitting or regulatory compliance purposes."

p. 9058

"13.7 Matrix spike/matrix spike duplicate—…Results for the MS/MSD must meet the requirements in Section 8.3 before a result for an analyte in any unspiked sample in the batch may be reported or used for permitting or regulatory compliance purposes."

p. 9059

"15.2.3 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,…"

Method 608.3

p. 9013

"8.3.3 Compare the percent recoveries (P1 and P2) and the RPD for each analyte in the MS/MSD aliquots… If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance…"

p. 9013

"8.5.2 If any analyte of interest is found in the blank at a concentration greater than the MDL… Samples in a batch must be associated with an uncontaminated blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes. If retesting of blanks results in repeated failures, the laboratory should document the failures and report the problem and failures with the data."

p.9020

"15.6.2.4 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…"

"16.4 Recovery of the matrix spike and matrix spike duplicate (MS/MSD)…If the matrix spike recovery is still outside the range, the result for the unspiked sample may not be reported or used for permitting or regulatory compliance purposes…"

Furthermore, ELAB commends EPA's focus on data quality to demonstrate permit compliance. ELAB believes, however, that including data validation and data usability requirements within each method will, in the long term, result in a lack of harmony among methods. For example, approved methods EPA 1624B, EPA 1625B, SM 6200 B-2001, SM 6410 B-2000 and many other approved methods used for compliance do not include these requirements. ELAB believes that data validation and data usability has an important place as a stand-alone issue. The importance and complexity of data validation and data usability cannot and should not be described in one paragraph within a method. ELAB also believes that data usability is the responsibility of the data user.

Methods 608.3, 624.1, and 625.1, Sections 8.1.2.2.1: Is EPA requiring laboratories performing these methods to have a QC officer? ELAB believes that it is important for laboratories of all sizes to follow good quality assurance practices, but as this requirement is addresses a quality assurance issue, it does not belong in the method. Other approved methods do not include this requirement. Laboratory quality assurance issues could be better addressed under 40 CFR Parts 136.4, 136.5 or 136.6, and permittee reporting responsibilities could be best addressed under 40 CFR Parts 122 (122.41 k.4.ii) or 125.
Suggested Change: Remove from all three methods.

B. Proposed Edits for Method 625.1

7.2.1: Laboratories must be permitted to establish the range of calibration based on their sample requirements.
Suggested Change: Remove the reference to Table 1 and make the requirement be that the low calibration standard be at, or below, the laboratory's method limit (ML) or quantitation limit.

7.2.3: A relative standard deviation (RSD) of <35% is too high; the RSD should be <15% because with <35%, laboratories are using very poor curves.
Suggested Change: Use an RSD <20% or use another ICAL model and have the limit of the coefficient of determination be <0.98.

8.3: The requirement to analyze a Matrix Spike (MS)/Matrix Spike Duplicate (MSD) for each sample site puts a burden on the laboratory to track the different sample sites. This burden belongs on the data user. Although other options are provided, the leading statement says "must"; assessors will see this "must" and require laboratories to comply.
Suggested Change: ELAB suggests that the Agency adopt the same or similar MS/MSD language according to EPA SW-846 Method 8270D, Sections 9.6–9.9.

8.3.1: If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4), whichever concentration would be larger. When no information is available, the mid-point of the calibration may be used, as long as it is the same or less than the regulatory limit.
Suggested Change: Concentration of the specific analyte spike must be at or near the mid-point of the calibration.

8.3.2: For MS/MSD—Analyze one sample aliquot to determine the background concentration (B) of each analyte of interest. This only can occur if client submits enough sample.
Suggested Change: Remove this requirement as it is not practical.

15.2.2.2: Blank subtraction—If analytes are detected in the field blank, then that result should be reported, and the client can decide whether to subtract the blank concentrations. If detected at levels of concern in the reagent blank, the laboratory has a contamination issue.
Suggested Change: Remove this language.

C. Proposed Edits to Method 624.1

6.8: BFB standard—Prepare a solution of BFB in methanol as described in Sections 6.5 and 6.6. The solution should be prepared such that an injection or purging from water will result in introduction of ≤50 ng into the GC. BFB may be included in a mixture with the internal standards and/or surrogates.
Comment: If the concentration of BFB must be limited, then the statement concerning the concentration should be mandatory.
Suggested Change: …Prepare a solution of BFB in methanol as described in Sections 6.5 and 6.6.at a concentration such that an injection or purging from water will result in introduction of ≤50 ng into the GC. BFB may be…

7.3.1.3: Prepare a stock standard solution for each internal standard surrogate in methanol as described in Section 6.5, and prepare a solution for spiking the internal standards into all blanks, LCSs, and MS/MSDs. The spiking solution should be prepared such that spiking a small volume will result in internal standard concentrations near the mid-point of the calibration range. For example, adding 10 mL of a spiking solution containing the internal standards at a concentration of 15 mg/mL in methanol to a 5-mL aliquot of water would result in a concentration of 30 mg/L for each internal standard. Other concentrations may be used. The internal standard solution and the surrogate standard spiking solution (Section 6.7) may be combined, if desired. Store the solution at <6°C in fluoropolymer-sealed glass containers with a minimum of headspace. Replace the solution after 1 month, or more frequently if comparison with QC standards indicates a problem.
Comment: The example implies that the spiking solution must be such that the internal standard concentrations are near the mid-point of the calibration range.
Suggested Change: …and prepare a solution for spiking the internal standards into all blanks, LCSs, and MS/MSDs. Prepare the spiking solution such that spiking a small volume will result in internal standard concentrations near the mid-point of the calibration range…

7.3.2.1: Same comment as Method 625.1, Section 7.2.1—Make one ICAL standard at or near MDL? Is that point to be included in the curve? Why do we need to stretch the quantitation range down to the MDL? That will lead to some very poor data at the low end. Laboratories must be permitted to establish the range of calibration based on their sample requirements.
Suggested Change: Remove the reference to Table 1 and make the requirement that a low calibration standard be at, or below, the laboratory's ML or quantitation limit.

7.3.4: Same comment as Method 625.1, Section 7.2.3—An RSD of <35% is too high; the RSD should be <15% because with <35%, laboratories are using very poor curves; use <15% or use another ICAL model.
Suggested Change: Use an RSD <20% or use another ICAL model and have the limit of the coefficient of determination be <0.98.

7.4: States that the LCS is also the ICAL verification; this is inconsistent with other EPA methods.
Suggested Change: The ICV (initial calibration verification) needs to be from a second source; the LCS should be from the same source as the calibration standard.

8.1.4 and 8.3: The requirement to analyze an MS/MSD for each sample site puts a burden on the laboratory to track the different sample sites. This burden belongs on the data user. Although other options are provided, the leading statement says "must"; assessors will see this "must" and require laboratories to comply.
Suggested Change: ELAB suggests that the Agency adopt the same or similar MS/MSD language according to EPA SW-846 Method 8270D, Sections 9.6 – 9.9.

8.1.7: The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures (e.g., as qualifiers on results) and either avoid reporting results for analytes that failed or report the problem and failures with the data. Failure to report does not relieve a discharger or permittee of reporting timely results. Results for regulatory compliance must be accompanied by QC results that meet all acceptance criteria.
Comment: The last sentence implies that all results must meet acceptance criteria, which may not be achievable (matrix interference, historically poor purger, etc.). There are instances in which data outside the acceptance range could be accepted. For instance, if the LCS or matrix spike failed low, the expected sample value would be greater than the reported value. If the reported value is greater than the decision point (i.e., compliance limit), then the actual concentration would be greater than the compliance level. In this case, noncompliance can be determined even when the QC failed. This statement puts a heavy burden on the laboratory, and some laboratories may be inclined not to report failures, which would be a data integrity issue. The data user should be allowed the flexibility of using data that fall outside the acceptance range for compliance when the failed QC would not affect decision of compliance/noncompliance. This sentence is not found in 8.1.7 (p. 9052) of Method 625.1 and should be deleted from 624.1
Suggested Change: Delete the last sentence of 8.1.7.

8.3.1: If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger. When no information is available, the mid-point of the calibration may be used, as long as it is the same or less than the regulatory limit.
Suggested change: Concentration of the specific analyte spike must be at or near the mid-point of the calibration.

C. Proposed Edits to Method 608.3

6.3: Sodium sulfate—Sodium sulfate, reagent grade, granular anhydrous (Baker or equivalent), rinsed with methylene chloride (20 mL/g), baked in a shallow tray at 450°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate suitable for use.
Comment: Because sodium sulfate with a grayish cast is not suitable for use, it must be discarded or treated as noted.

Suggested Change: If, after heating, the sodium sulfate develops a noticeable grayish cast (resulting from the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and must be discarded or treated by extraction with methylene chloride (as opposed to simple rinsing) and baked at a lower temperature. This treatment may produce sodium sulfate suitable for use.

6.8.2.1: The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system. A separate standard near the MDL may be analyzed as a check on sensitivity, but should not be included in the linearity assessment. A minimum of six concentration levels is required for a non-linear (e.g., quadratic) calibration (Section 7.5.2 or 7.6.2). The solvent for the standards must match the final solvent for the sample extracts (e.g., isooctane or hexane).
Comment: A standard near the MDL should not be used in a calibration curve. The "should" should be changed to a "must."
Suggested Change: A separate standard near the MDL may be analyzed as a check on sensitivity but must not be included in the linearity assessment.

8.3.1: If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger. When no information is available, the mid-point of the calibration may be used, as long as it is the same or less than the regulatory limit.
Suggested Change: Concentration of the specific analyte spike must be at or near the mid-point of the calibration.

10.5.2.1: Place a 90-mm standard filter apparatus on a vacuum filtration flask or manifold and attach to a vacuum source. The vacuum gauge should read at least 25 in. of mercury when all valves are closed. Position a 90-mm C18 extraction disk onto the filter screen. Wet the entire…
Comment: If the extraction operates most effectively at vacuums of ≥25 inches of mercury, then the "should" should be a "must."
Suggested Change: Place a 90-mm standard filter apparatus on a vacuum filtration flask or manifold and attach to a vacuum source. The vacuum gauge must read at least 25 inches of mercury when all valves are closed. Position a 90-mm C18 extraction.

13.8: Internal standard response—If internal standard calibration is used, verify that detector sensitivity has not changed by comparing the response (area or height) of each internal standard in the sample, blank, LCS, MS, and MSD to the response in the combined QC standard (Section 6.8.3). The peak area or height of the internal standard should be within 50% to 200% (1⁄2 to 2×) of its respective peak area or height in the verification standard. If the area or height is not within this range, compute the concentration of the analytes using the external standard method (Section 7.5).
Comment: Because the external standard method must be used when the response of the internal standard is not acceptable, the acceptance range must be stated.
Suggested Change: The peak area or height of the internal standard must be within 50% to 200% (1⁄2 to 2×) of its respective peak area or height in the verification standard. If the area or height is not within this range, compute…

15.6.2.3: …The results for each analyte in the MS/MSD samples should be reported from the same GC column as used to report the results for that analyte in the unspiked sample. If the MS/MSD recoveries and RPDs calculated in this manner do not meet the acceptance criteria in Table 4, then the analyst may use the results from the other GC column to determine if the MS/MSD results meet the acceptance criteria. If such a situation occurs, the results for the sample should be recalculated using the same GC column data as used

for the MS/MSD samples, and reported with appropriate annotations that alert the data user of the issue.
Comment: Reporting from the same GC column should be a requirement.
Suggested Change: …Report the results for each analyte in the MS/MSD samples from the same GC column as used to report the results for that analyte in the unspiked sample. If the MS/MSD recoveries and RPDs calculated in this manner do not meet the acceptance criteria in Table 4, then the analyst may use the results from the other GC column to determine if the MS/MSD results meet the acceptance criteria. If such a situation occurs, recalculate the results for the sample using the same GC column data as used for the MS/MSD samples and report with appropriate annotations that alert the data user of the issue.

Comment 2: Comments to the Proposed Changes to Method Detection Limit (MDL)

These comments are as described in the Board's letter to the Agency dated January 31, 2014 (see Reference: Background on MDL).

ELAB has reviewed the proposed update to the MDL included in the proposed Methods Update Rule. In ELAB's opinion, the proposed update is a considerable improvement to the current MDL procedure, and therefore the Board recommends that EPA adopt the proposed changes in full.

ELAB also suggests the following additions and modifications to the proposed procedure.

1. A minor clarification to the requirements when there are multiple instruments would be helpful. This could be added as a Section 2(b)(iii).
Suggested Language: (iii) The same prepared sample extract may be analyzed on multiple instruments so long as the minimum requirement of seven preparations in at least three separate batches is maintained.

2. The procedure does not discuss what actions should be performed by the laboratory if a new instrument is to be added to an existing group of instruments that have the same MDL. This is a common occurrence and guidance to the laboratories would be valuable. We propose adding the following language as a new Section 3(e).
Suggested Language: (e) If a new instrument is added to a group of instruments whose data is being pooled to create a single MDL, analyze a minimum of two spike replicates and two blank replicates on the new instrument. If both blank results are below the existing MDL, then the existing MDL_b is validated. Combine the new spike sample results to the existing spike sample results and recalculate the MDL_s as in Section 4. If the recalculated MDL_s is within a factor of three of the existing MDL_s, then the existing MDL_s is validated. If either of these two conditions is not met, calculate a new MDL following the instructions in Section 4.

3. For some tests, the requirement to analyze two spike samples per quarter on each instrument (Section 3(a)) may add up to a large number of analyses if there are a large number of instruments. For example, Method 608 will require separate analytical runs for five aroclors, the single component pesticides, toxaphene and technical chlordane. For the single component pesticides, it may be necessary to analyze more than one run at different concentrations to obtain data at the correct spiking concentration for each pesticide. Therefore, this adds up to nine different spike samples, multiplied by five different instruments, multiplied by two replicates on each instrument, or 90 analytical runs per quarter.
Suggested Change: Reduce the requirement to a minimum of one spike if there is more than one instrument, as this would still result in a minimum of eight replicates per year and more than that if there are more than two instruments

Comment 3: Comments on Proposed Microbiological Testing Methods and Procedures

ELAB acknowledges the update to newer versions of several microbiological methods, including *Standard Methods* 9221 and 9222 from 1997 to 2006 versions. This also will improve the QC measures used for these methods.

EPA Method 1680: For fecal coliform detection, the Agency is suggesting changing this sentence: "The predominant fecal coliform is *E. coli*." To this: "The predominant fecal coliform can be *E. coli.*" Data strongly suggests that *E. coli* is the predominant species in fecal coliform when samples are incubated at 44.5°C.
Suggested Change: Leave the original statement.

Comment 4: Recommended Edits to Various Tables

These comments are designed to clarify some of the instances of "should" that appear in the referenced citations. Historically, EPA has interpreted some instances of "should" as "must," resulting in confusion in the laboratory community. In the identified instances, it appears that the "should" (as defined by EPA) refers to something mandatory. The following comments are meant to clearly indicate to the laboratory community that some requirements are an essential part of the procedure.

NOTE: *Per EPA, "should" is defined as:* An action, activity or procedural step is suggested but not required.

Citation: H. Corrections to 40 CFR Part 136, p. 8963: EPA proposes to make a number of clarifications and corrections to its whole effluent toxicity acute and chronic methods manuals (*Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*, EPA–821–R–02–012, October 2002). Clarifications include testing all concentrations rather than only high and low concentrations, definition of terms…pH and temperature measurements should be done at the beginning of the test (rather than only at the end of the test),…
Comment: If it is important enough to mention taking pH and temperature measurements at the beginning of the test, then the highlighted "should" must be changed to a "must."
Suggested Change: Clarifications include testing all concentrations rather than only high and low concentrations, definition of terms…pH and temperature measurements must be done at the beginning of the test (rather than only at the end of the test),…

Footnote 30 to Table IA, p. 8969 (and 27 of Table 1H, p. 8996): The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection and analysis.
Comment: If a wastewater treatment operator collects samples from the influent, the effluent after the chlorine contact chamber, and the outfall (total of three sampling sites), then the operator must confirm 10 colonies from each sampling location for a total of 30 colonies. The same language is used for surface water. No statement is included as to what a laboratory must do if the sample is negative for fecal coliforms. *Standard Methods* requires a frequency of once per month. The proposed requirement seems excessive. The requirement remains silent on whether the 10 colonies must be from the same culture plate, the results of which, according to all methods, leads to an adjustment in the actual result. The proposed requirement is not required for the comparable EPA or ASTM methods. The EPA method does not specify a frequency for verification. To be consistent, this footnote (if included) needs to apply to all membrane filter (MF) methods for fecal coliform.
Suggested Change: Ensure that a verification frequency applies to all MF methods for fecal coliform, and either remove the requirement or consider a reduced frequency. Clarify that the verification does not need to be performed on nonpositive samples and that the 10 colonies must be from the same plate, which is critical if multiple dilutions are performed. The 10 colonies should be a mix of presumptive positives and negatives.

Footnote 4 to Table IB, p.8981: For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non-platform graphite furnace atomic absorption determinations a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The procedure used should subject the sample to gentle, acid refluxing and at no time should the sample be taken to dryness…
Comment: This footnote sends mixed signals. It could be interpreted that the digestion for non-platform graphite furnace must follow Section 4.1.3. If this is not EPA's intent, the citation in parentheses should be changed to "such as" rather than "as specified in". If the cited method's method must be followed, the comment about gentle refluxing, as well as the caution of not allowing the sample to evaporate to dryness, is not needed as this is a requirement of the method. If, on the other hand, EPA intends to allow use of other nitric acid digestion methods and considers the gentle refluxing and evaporation-to-dryness requirement of Section 4.1.3 to be important enough to be mentioned, then the refluxing and evaporation-to-dryness comment should be a "must" not a "should."
Suggested Change: For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non-platform graphite furnace atomic absorption determinations, a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The digestion procedure must subject the sample to gentle acid refluxing. Do not allow the sample to be taken to dryness…

Footnote 6 to Table IB, p. 8981: Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as <20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.
Comment: The first sentence requires a study to demonstrate that manual digestion is not necessary. Therefore, if a selected analytical method does not require a distillation, the method must be followed. If the selected method is unclear, then the first sentence requires a study. The description is an example of how the study might be done.
Suggested Change: Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. Consult the analytical method regarding the need for distillation. If the method is not clear, a study must be performed to demonstrate that manual distillation is not required. The laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as <20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.

Footnote 29 to Table IB, p. 8981: Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides

such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na2S2O3 and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.
Comment: The sodium thiosulfate and sodium hydroxide buffer is identified as the reagent to be used to solubilize concentrations of silver at concentration ≤1 mg/L. Therefore, to obtain an accurate result, the outlined procedure must be followed. Furthermore, the standards must be prepared in the same buffer if an accurate result is to be achieved. This procedure should be mandatory, not advisory.
Suggested Change: Therefore, for levels of silver above 1 mg/L, dilute 20 mL of sample to 100 mL by adding 40 mL each of 2 M $Na_2S_2O_3$ and NaOH. Prepare standards in the same manner.

Footnote 31 to Table IB, p. 8981: For samples known or suspected to contain high levels of silver (e.g., in excess of 4 mg/L), cyanogen iodide should be used to keep the silver in solution for analysis. Prepare a cyanogen iodide solution by adding 4.0 mL of concentrated NH4OH, 6.5 g of KCN, and 5.0 mL of a 1.0 N solution of I2 to 50 mL of reagent water in a volumetric flask and dilute to 100.0 mL. After digestion of the sample, adjust the pH of the digestate to >7 to prevent the formation of HCN under acidic conditions. Add 1 mL of the cyanogen iodide solution to the sample digestate and adjust the volume to 100 mL with reagent water (NOT acid). If cyanogen iodide is added to sample digestates, then silver standards must be prepared that contain cyanogen iodide as well. Prepare working standards by diluting a small volume of a silver stock solution with water and adjusting the pH>7 with NH4OH. Add 1 mL of the cyanogen iodide solution and let stand 1 hour. Transfer to a 100-mL volumetric flask and dilute to volume with water.
Comment: The cyanogen iodide solution appears to be necessary to keep silver in solution a high levels (<4 mg/L). The described process would be necessary to ensure that an accurate result is obtained. The described procedure is written as if it must be followed; therefore, to be consistent, the first sentence should be changed to reflect that the process is mandatory, not suggested.
Suggested Change: For samples known or suspected to contain high levels of silver (e.g., in excess of 4 mg/L), use cyanogen iodide to keep the silver in solution for analysis. Prepare a cyanogen…

Footnote 60 to Table IB, p. 8982: Analysts should be aware that pH optima and chromophore absorption maxima might differ when phenol is replaced by a substituted phenol as the color reagent in Berthelot Reaction ("phenol-hypochlorite reaction"') colorimetric ammonium determination methods. For example when phenol is used as the color reagent, pH optimum and wavelength of maximum absorbance are about 11.5 and 635 nm, respectively—see, Patton, C.J. and S.R. Crouch. March 1977. Anal. Chem. 49:464–469. These reaction parameters increase to pH > 12.6 and 665 nm when salicylate is used as the color reagent—see, Krom, M.D. April 1980. The Analyst 105:305–316.
Comment: Although an analyst may or may not be aware of the difference, this footnote should be a statement.
Suggested Change: The pH optima and chromophore absorption maxima might differ when phenol is replaced by a substituted phenol as the color reagent in Berthelot Reaction ("phenol-hypochlorite reaction") colorimetric ammonium determination methods.

Footnote 4 to Table IC, p. 8987: Method 624.1 may be used for quantitative determination of acrolein and acrylonitrile, provided that the laboratory has documentation to substantiate the ability to detect and quantify these analytes at levels necessary to comply with any associated regulations. In addition, the use of sample introduction techniques other than simple purge-and-trap may be required. QC acceptance criteria from Method 603 should be used when analyzing samples for acrolein and acrylonitrile in the absence of such criteria in Method 624.1.
Comment: Because Method 624.1 has no acceptance criteria for acrolein and acrylonitrile, and no other criteria sources are mentioned (e.g. laboratory-developed acceptance criteria), the Method 603 criteria

should be mandatory.
Suggested Change: …Use the QC acceptance criteria from Method 603 when analyzing samples for acrolein and acrylonitrile in the absence of such criteria in Method 624.1.

Footnote 17 to Table II, p. 9002: Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.
Comment: A sample for dissolved mercury must be filtered within 24 hours. The options are in the laboratory or in the field. Therefore, both should be requirements, with the laboratory being the preferred option.
Suggested Change: A sample collected for dissolved trace level mercury must be filtered within 24 hours of collection. If filtration is performed in the field, it must be filtered in a designated clean area in accordance with procedures given in Method 1669.

Appendix A to Part 136—Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater
Method 608.3—Organochlorine Pesticides and PCBs By GC/HSD
Method 624.1—Purgeables by GC/MS
Method 625.1—Base/Neutrals and Acids by GC/MS

Comments related to two or more of the cited methods:

Cleaning Glassware: Method 608.3 (p. 9004–9005) and Method 625.1 (p. 9047)

Method 608.3, 3.2: Glassware must be scrupulously cleaned (Reference 4). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400°C for 15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Volumetric labware should not be heated excessively or for long periods of time. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.
Method 625.1, 3.2: Glassware must be scrupulously cleaned (Reference 5). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400°C for 15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Volumetric labware should not be heated above 90°C. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with solvent-rinsed or baked aluminum foil.
Comment: In Method 608.3 heating volumetric labware is an expressed concept with no guidance for defining “excessive heating”; Method 625.1 places a limit above which volumetric labware cannot be

heated. Both are expressed as options rather than requirements. Because excessive heating of volumetric labware can potentially change the accuracy of the container, increase the measurement uncertainty, and affect the accuracy of the reported value, the statements should be requirements, not options. The last sentence in both Methods 608.3 and 625.1 describes methods to store glassware to minimize accumulation of dust or other contaminants and is written as a requirement. Therefore the sentence before should be a requirement, not an option.
Suggested Changes: Recommend that the Agency define the temperature and time requirements and harmonize the language for both Methods 608.3 and 625.1.

Automatic Samplers: Method 608.3 (p. 9005) and Method 625.1 (p. 9048)

Method 608.3, 5.1.2: Automatic sampler (optional)—the sampler must use a glass or fluoropolymer container and tubing for sample collection. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize the potential for sample contamination. An integrating flow meter is required to collect flow proportional composites. The sample container must be kept refrigerated at <6°C and protected from light during compositing."
Method 625.1, 5.1.2: Automatic sampler (optional)—the sampler must incorporate a pre-cleaned glass sample container. Samples must be kept refrigerated at <6°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportioned composites.
Comment: The requirement is to minimize contamination from the compressible tubing. Unless other methods to minimize sample contamination are used, rinsing the compressible silicone rubber tubing as described should be considered mandatory.
Suggested Change: Minimize the potential for sample contamination by the compressible tubing by cleaning the tubing before use. Rinse compressible tubing by thoroughly rinsing the tubing with methanol, followed by repeated rinsing with reagent water. Alternative cleaning techniques may be used as long as the technique does not cause the tubing to lose elasticity or contaminate the sample.

Calibration Standards—ML: Method 608.3 (p. 9008), Method 624.1 (p. 9031) and Method 625.1 (p. 9049)

Method 608.3, 6.8.2.1: Prepare calibration standards for the single-component analytes of interest and surrogates at a minimum of three concentration levels (five are suggested) by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration of the analyte near the ML in Table 1 or 2. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Tables 1 or 2 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values do not exceed the MLs in Table 1 and 2, and provided that the resulting calibration meets the acceptance criteria in Section 7.5.2.
Method 624.1, 7.3.2.1.1: Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding appropriate volumes of one or more stock standards to a fixed volume (*e.g.,* 40 mL) of reagent water in volumetric glassware. Fewer levels may be necessary for some analytes based on the sensitivity of the MS. The concentration of the lowest calibration standard for an analyte should be at or near the ML value in Table 1 for an analyte listed in that table. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from

a commercial vendor, again, provided that the ML values does not exceed the MLs in Table 1, and provided that the resulting calibration meets the acceptance criteria in Section 7.3.4, based on the RSD, RSE, or R2."
Method 625.1, 7.2.1: Prepare calibration standards for the analytes of interest and surrogates at a minimum of five concentration levels by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration near the ML for the analyte in Table 1, 2, or 3. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1, 2, or 3 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values do not exceed the MLs in Tables 1, 2, or 3, and provided that the resulting calibration meets the acceptance criteria in Section 7.2.3, based on the RSD, RSE, or Region 2.
Comment: All three discussions on calibration standard preparation state that one of the calibration standards should be near the ML. The discussions continue with emphasis on the standard concentration and the need to have a standard that is less than (or equal to?) the ML in the published tables. Based on the discussion, there must be one standard near the ML.
Suggested Changes:
Methods 608.3, 624.1 and 625.1: Change language in all of the methods to: One of the calibration standards must be at the concentration of the analyte that does not exceed the ML in use in the laboratory.

Comment 5

On June 19, 2014, ELAB sent a letter to EPA advising removal of the pH 4–5 preservation requirement for acrolein and acrylonitrile. ELAB continues to request this method change as part of the Methods Update. A copy of the contents of this letter is included below in the references section (Reference: Letter to EPA Advising Removal of the pH 4–5 Preservation Requirement for Acrolein and Acrylonitrile).

Reference: Background on MDL

The detection limit of an analytical procedure is a critical property and vital to understanding the capability of the method and the range of data quality objectives that can be supported. The MDL serves the purpose of determining the single laboratory detection limit for methods approved under 40 CFR 136, and the importance of accurate estimates can hardly be overstated because incorrect compliance decisions are likely to result from an inaccurate estimate. Unfortunately, the current MDL procedure is widely recognized to have serious flaws that can and do result in incorrect detection limit estimates.

There have been previous efforts to update or replace the MDL procedure. In 2003, EPA issued a proposed update that was withdrawn after receiving considerable negative comment during the public review period. Subsequently, a federal advisory committee developed a replacement for the MDL that was generally considered technically sound, but implementation difficulties were such that it was never implemented.

In the Board's opinion, The NELAC Institute procedure strikes a good balance between technical validity and ease of implementation. Detailed comments are provided below, and suggestions for language changes are included marked as revisions in the attached copy of the procedure.

Definition: ELAB supports the change in definition to reference method blanks rather than zero. For the purposes of determining compliance, it is important to identify the lowest level that can be reliably distinguished from a blank rather than zero.

Section 2.a Selection of spiking level: Changing the initial spiking level from 1 to 5 times the estimated MDL to 2 to 10 times is beneficial. Spiking at only 1x the MDL is likely to result in many results below the MDL (i.e., the spiking level would be too low). It may be helpful to point out that spiking levels 10x the anticipated MDL should only be needed if the specific analyte is a poor performer in terms of recovery.

Section 2.b Blanks: The Board strongly supports including an assessment of blanks in the MDL procedure. As the objective is to identify the lowest level that can be distinguished from a blank, using actual blank data makes sense.

Section 2.b.i Multiple instruments: The guidance for multiple instruments is valuable. This is a very common situation, and lack of previous guidance has resulted in a wide and confusing range of different approaches.

Section 2.c.iii Computation of the MDL based on blanks: ELAB supports calculation of the MDL based on blanks as mean plus Student's *t* times the standard deviation. Incorporation of the mean is very important.

Section 2.d Set the MDL: The Board believes that EPA should consider favoring the blank-calculated MDL over the spike-calculated MDL, assuming that there is more blank data than spike data.

Section 3. Ongoing data collection: ELAB believes that spreading data collection over time is important, and the requirement for a minimum of two spikes per quarter is a reasonable compromise between collecting sufficient data and having a procedure that is not too onerous. See the note above for a recommendation that the requirement be reduced to one spike per quarter per instrument if there are multiple instruments. EPA may want to consider providing clearer guidance regarding what is meant by "per quarter."

Section 4. Ongoing annual verification: Although an annual recalculation of the MDL is not in the current procedure, the Board believes that this recalculation (annual verification) is a sound practice for maintaining MDLs that reflect the current capability of the laboratory; therefore, ELAB believes that it is a good addition to the procedure. EPA may wish to consider clarifying the annual requirement. For example, "recalculation of the MDL must be performed within 13 months of the previous MDL determination or recalculation."

Section 4.f. Adjustment of the MDL: No justification is provided for the factor of three used as a limit for determining whether the current MDL needs to be adjusted. Some degree of justification would be useful and ELAB notes that the upper 99% confidence interval for a population standard deviation based on six degrees of freedom is 2.98.

Addressing Previous Objections to the MDL

ELAB has reviewed objections to the 2003 MDL update that were received in the public comments, with a view to determining whether they have been addressed in the new draft. Many comments were received on each of the following general issues.

Variability:

Long-Term Variability—The new draft does a good job of incorporating longer term variability.

Interlaboratory Variability—There is no additional material covering interlaboratory variability; however, the procedure is intended as a single laboratory detection limit determination. Recently, EPA has set MDLs based on the highest MDL from participating laboratories, after removal of outliers, and the same approach could be used with the new draft. Another option for estimating the interlaboratory variability would be to calculate a pooled MDL from a large population of laboratories. ELAB would be able to assist EPA in gathering this data once the revised MDL has been in use for a year or more.

Analyte Concentration, Calibration and Analytical Range—Determining the spiking concentration is similar in the current and new drafts, but the new draft has the benefit that there are steps to verify the MDL determined.

Definitions: Many concerns were raised regarding the definition of the MDL. ELAB believes that adjusting the definition to refer to blanks, and clarifying that the MDL is based on results rather than true concentrations, will be beneficial in removing some of the current confusion. The MDL does not purport to be equivalent to the IUPAC limit of detection, but is more similar to the critical level because it only controls false positives.

Precision and Bias: Concerns were raised especially concerning bias, and the new draft addresses these well by incorporating the mean of the blanks into the MDL_b calculation.

Error Types: The current MDL does nothing to control false negatives. The revised draft addresses false negatives to some extent through the requirement that the ongoing spikes return positive results. The Board would encourage EPA to consider further control of false negatives through a subsequent effort to provide better definition of a single laboratory quantitation limit, which could be used to replace the minimum level.

Iterative Procedure: There were many complaints regarding the proposed iterative procedure in the 2003 proposed update. This iterative procedure has fortunately been removed from the current draft and replaced with ongoing evaluations of the MDL.

Outlier Testing: There were various comments both in favor and opposed to outlier testing. The new draft does not include an outlier test, but the nonparametric option for method blanks could be considered a useful alternative.

Spike Levels: The new draft includes options and requirements for adjusting spike levels if needed based on the ongoing data collection.

Use of Blanks: Many comments concerned the lack of consideration of blanks in the 2003 draft; these are fully addressed in the new draft.

Number of Replicates: Some comments noted that more replicates would be desirable. The new draft still allows starting with seven replicates (a reasonable compromise), but in most cases many more replicates would soon be available through the ongoing data collection.

Tolerance vs. Confidence Intervals: Some comments stated that tolerance intervals should be used for the MDL. This is a point of contention between statisticians, and ELAB does not take a position on which is preferable. However, retaining Student's *t* will certainly make implementation of the new draft easier, and in many cases, the increased number of replicates will reduce the difference between the confidence and tolerance intervals. Also, the use of nonparametric statistical tools when possible eliminates this contentious issue.

Sensitivity Check: Comments in favor of a sensitivity check are addressed by the requirement for ongoing data collection and the requirement that the spikes return positive detections.

Reference: Letter to EPA Advising Removal of the pH 4–5 Preservation Requirement for Acrolein and Acrylonitrile

June 19, 2014

Mr. Adrian Hanley
U.S. Environmental Protection Agency
1200 Pennsylvania Ave, NW
Mail Code 4303T
Washington, DC 20460

Re: Analysis Requirements and pH Preservation for Acrolein and Acrylonitrile Methods

Dear Mr. Hanley,

The Environmental Laboratory Advisory Board (ELAB or Board) is a standing Federal Advisory Committee Act board that advises the U.S. Environmental Protection Agency (EPA or Agency). The Board's Charter states that it is to provide consensus advice, information and recommendations on issues related to EPA measurement programs and facilitate operation and expansion of a national environmental laboratory accreditation program.

ELAB welcomed EPA's revision of Method 624 for the determination of acrolein and acrylonitrile in the last Methods Update Rule (MUR) published on May 18, 2012. In addition to the changes made in 2012, the Board would like to recommend supplementary changes to the method that could be addressed in the upcoming MUR in 2014.

1. **The recommended preference of Method 624 versus Method 603.**

   Section 1.2 of Method 624 states that Method 624 may be extended to screen for acrolein and acrylonitrile, but that the preferred method is Method 603. ELAB suggests changing this statement to "…acrolein and acrylonitrile should preferably be analyzed by Method 624." Method 624 is superior to Method 603 for this testing and used by the laboratory community more often than Method 603. Some of the rationalization to promote Method 624 over Method 603 includes:

   - Method 603 uses a flame ionization detector. This is a nonselective detector and will respond to any organic compound. If acrolein and acrylonitrile are present in a sample, there also is the possibility of finding significant concentrations of various other hydrocarbons. Hence, the potential for false positives and false negatives caused by interferences can be high.
     - For example, a false negative could be caused by the presence of a large, masking hydrocarbon eluting at a slightly different retention time than acrolein or acrylonitrile, making it difficult to see the target peak when present at a lower concentration.
   - The purge conditions in Method 603 (85^{o}C for 15 minutes) can transfer very large quantities of water to the instrument, which hinders the analysis of acrolein and acrylonitrile.

2. Preservation requirement for acrolein and acrylonitrile.

The Board has discussed the pH preservation requirement and provides information (attached) to support ELAB's suggestion that EPA consider the removal of preservation at pH 4–5. Removal of the pH requirement for acrolein and acrylonitrile will:

- Eliminate the problem of field adjustment of samples to pH 4–5, which is very challenging.
- Facilitate implementation and management of method specifications by laboratories.
- Reduce cost to laboratories without compromising data quality.
- Provide harmonization with SW-846 Update V, Chapter 4, which no longer contains the preservation requirement of pH 4–5 for acrolein and acrylonitrile.

Failure of laboratories to comply with the current pH requirement often results in data of good quality being unnecessarily invalidated. ELAB suggests that EPA consider removing the pH preservation requirement for acrolein and acrylonitrile and instead make the preservation requirement identical to that for purgeable aromatic hydrocarbons, which preserves samples below pH 2.

Thank you for your consideration. The Board looks forward to your comments and feedback on this issue. Please know that you are welcome to attend any of ELAB's monthly teleconferences to discuss these topics in detail.

Respectfully,

Patsy Root
Chair, Environmental Laboratory Advisory Board

cc: ELAB Board
Attachments: "*Proposed Changes to table II Preservation Requirements*"