February 21, 2013

Mr. Lemuel Walker, Jr.
U.S. Environmental Protection Agency (MC 4303T)
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

**Reference:** Comments to proposed revisions of

- **EPA Method 624A_Draft 6-11-12**: For the determination of **volatile organic** pollutants by purge and trap gas chromatography combined with mass spectrometry (GC/MS)
- **EPA Method 625A_Draft 6-10-12:** For the determination of **semivolatile** organic pollutants by extraction and GC/MS

Dear Mr. Walker,

The Environmental Laboratory Advisory Board (ELAB, or the Board), a Federal Advisory Committee to the U.S. Environmental Protection Agency (EPA), is providing the attached response to EPA's November 2012 request for comment on proposed revisions to EPA Methods 624 and 625.

For your consideration, ELAB respectfully submits the comments and suggestions found in the attachment on the proposed revisions of these methods. These comments represent a summary of the feedback from ELAB members and their stakeholders who are familiar with using these methods for compliance monitoring. As such, some sections have more than one comment or position.

The general feedback was overwhelmingly positive; specifically, these revised versions allow for far more flexibility than the original versions. Given that these methods are quite dated, however, ELAB strongly suggests that the Agency consider updating the information contained in the tables and figures in both methods to reflect current technologies and laboratory practices. In terms of where such efforts can be directed, please note the specific comments within the text for each method.

The Board appreciates the opportunity to share its feedback with you and would be happy to further discuss any of the comments with you at your convenience. Please contact me directly at ashields@lawrenceks.org or ELAB's Designated Federal Official, Lara Phelps, at phelps.lara@epa.gov to arrange for further discussion.

Respectfully,

Aurora Shields
Chair, Environmental Laboratory Advisory Board

## Specific Comments – EPA Method 625A_Draft 6-10-12

**Please note** that these comments are *by section* within EPA Method 625A_Draft 6-10-12

1.5 Method detection limits (MDLs) are determined according to the procedure delineated in Appendix B to 40 CFR 136. Each laboratory will determine their MDLs and reporting limits but must meet client requirements. Guidance on minimum MDLs should be provided.

2.1 Extraction at a single acid pH should be allowed if only analytes in Tables 1 and 2 are required; there is plenty of validation data from the Contract Laboratory Program (CLP).

4.1 As of 2013, the Occupational Safety and Health Administration requires that Material Safety Data Sheets (MSDS) comply with the Globally Harmonized System for Chemical Information and Labeling, and the official term for MSDS becomes "Safety Data Sheet"; change MSDS to SDS with a definition.

4.2 Please use “chemical fume hood” rather than just “hood.”

5.1.1 Delete “generally 1L or 1 quart” as this is an unnecessary specification.

5.1.2 Refrigerating samples and maintaining temperature at < 6°C during compositing may not be possible or practical. What if samples are collected in effluent stream with an automated sampler? That sampler will be at ambient temperature unless it has the ability to refrigerate the samples.

5.2.6 Please change to two-ball micro rather than macro.

6.7 Suggest that alternate stock solution concentrations may be used.

6.13 Clarify: Sulfur removal—copper powder (bright, non-oxidized) or tetrabutyl ammonium TBA sulfite reagent.

7.2.1 Should one instrument calibration (ICAL) standard be made at or near the 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.

Suggest that the low standard be at or below the quantitation limit.

7.2.2.5 Clarify: Replace the column or a short section of the front end of the column and repeat the test . . . Break off part of the front of the column or add short section to front of column.

7.2.3 Required use of inverse weighting is good. Otherwise, low values will have a sizeable error. Section 7.2.3 implies that the correlation coefficient (CC) and coefficient of determination (COD) are the same. They are different: COD = $r^2$; CC = r; either one with an $r^2$ value of 0.920 is a poor criterion. That describes a very poor curve. Laboratories will pay a price when analyzing proficiency testing samples with a curve that poor.

Use of the RSE is appropriate, although the criteria should be <15%. Laboratories should determine the error of each individual ICAL point.

The percent relative standard deviation (% RSD) for average response factor (RF) calibration should be <20% as required in EPA Method 8270D. The CC is > 0.920. How was this derived? This is too lenient. Use 0.99 from Method 8270 and include the note from EPA Method 8000 about linearity, which states that it is not the intent to use quadratic calibration to account for the need of instrument maintenance.

7.2.2.3 This section should include the CLP requirement for first analyzing the sample in scan mode. Some instruments allow for simultaneous SCAN/SIM modes, but some do not

7.3.1 The second source calibration standard should have fixed limits. EPA 8270D utilizes ±30%. The limits in Table 6 (or calculated limits) will *not be acceptable* for some departments.

8.1.2 The option to use solid-phase extraction (SPE) is a good alternative as long as quality control (QC) criteria can be met and or program/project data quality objectives can be achieved

This section allows the use of alternate detectors. This is a mass spectrometer method. Alternate detectors should not be allowed, or the method should at least provide examples as to the intent of this statement.

8.1.2.2.1 Providing the names, titles, addresses and telephone numbers of the analyst(s) that performed the analyses and modification and QC officer who witnessed and will verify the analyses and modifications seems a bit much; contact information for the laboratory quality assurance officer or equivalent would be sufficient.

8.1.4 Clarify: Matrix spike/matrix spike duplicate (MS/MSD) at 5% and/or MS/MSD for every 20 samples analyzed and/or per batch, whichever is more frequent? Suggest: MS/MSD at 5% of all sample or per batch, whichever is more frequent.

8.2.1 Neither the laboratory control sample (LCS) nor the continuous calibration verification (CCV) should be the second source. The second source should be only the initial calibration verification standard analyzed immediately after a new calibration. This is required for consistency with EPA Method 8270 and The NELAC institute standards.

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 responsibility is that of the data user. Although other options are provided, the leading statement says “must”; assessors will see this “must” and require laboratories to comply.

If matrix effect is suspected to be an issue, then spiking the matrix using the procedure in this section is an appropriate procedure to perform per batch or 20 samples, whichever is more frequent; also note that sufficient sample volume needs to be collected.

8.3.2 For MS/MSD, this can only occur with a multi-analyte method if the client submits a sufficient volume of sample.

8.4.3 Which Section 8.4.3 is required, the first one or the second one with 8.4.4 added?

8.4.3-8.4.7 See comments in same sections of method 624A. Do any laboratories currently do this for each site being monitored?

8.5.2 This criterion is too severe for common contaminants such as phthalates.

10.1 Suggest adding a statement that SPE may be used if all method QC criteria can be met.

10.2.6 There is no mention of the use of alternate concentration technology, such as the use of a turbo-evaporator.

14.1.2 It appears that this is intended to say that the ratios of the intensities of the quantifier and qualifier ions must agree within a factor of two, but that is not really what it says. It could imply all ions, including minor ions, which would result in a good deal of false negatives, and analyst judgment needs to be applied even for major ions in cases of co-elution.

15.2.2.1 This section requires reporting to the MDL instead of reporting limits or the lowest level of the calibration. An MDL is a calculated value, and anything below the calibration curve is an estimated value. The method should not require reporting to the MDL. Certain departments have set reporting level requirements for National Pollutant Discharge Elimination System compliance sample reporting. EPA Method 625 must specify that anything reported below the calibration must be reported as estimated.

Why are this section *and* 15.2.2.2 different than the similar section (13.3.2.1-2) in Method 624a, which states that laboratories are only supposed to report results below the 3xMDL as "<3xMDL". Please also see the comments for Method 624a.

15.2.2.2 Allowing blank subtraction is troublesome. If analytes are detected in the field blank (assuming one is submitted), then that result should be reported, and the client can decide whether to subtract the blank concentrations. If this is detected at levels of concern in the reagent blank, the laboratory has a contamination issue.

This needs to be removed. This will not be acceptable for some departments.

Table 1 Replace bis(2-chloroisopropyl) ether with new compound name, 2,2'-oxybis(1-chloropropane) or Bis (2-chloro-1-methylethyl ether). [CAS # 108-60-1]

Table 3 Table 3 includes 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, and 1,4-Dichlorobenzene. These were removed from the CFR with Method Update Rule I by EPA Method 625. These should be removed from the table.

Table 4 Some of the compounds listed in the method do not have data included in Table 4. Because this is a performance-based method, the table should be populated with data for all listed extractables to the extent practical.

Table 6 The percent recovery limits are the same as in the original method, which was based on old technology and packed columns. If set limits are going to be used, they must be updated to reflect the newer technology, columns and operating conditions. In addition, the relevant percent difference limits are too high; 40% should be used as in EPA Method 8270D.

A performance-based method must provide QC acceptance criteria for all compounds listed in the method.

Table 7 Table 7 is based on a reference from 1984. This table should either be removed or, preferably, updated with newer technology

Figure 2 Chromatogram should be updated with modern chromatography to better reflect current technology and chromatogram output.

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## Specific Comments – EPA Method 624A_Draft 6-10-12

**Please note** that these comments are *by section* within EPA Method 624A_Draft 6-10-12

1.4 The MDL values in Table 3 are from 1980 (reference 6). The MDLs have not been updated from the previous revision. These MDL values will not meet permit limits and are based on outdated technology. These either need to be removed completely or new MDLs used that were performed using updated technology, columns and operating conditions should be provided. The table must also list how the MDLs were derived (e.g. purging conditions, instrument operating conditions).

5.1.1 Add "…or purchase precleaned".

5.3.3 A scan rate of up to a maximum of 5/second can produce poor identifications; with high-resolution columns, a 5/second scan can miss a peak completely. A scan rate of no more than 2/second, like Method 625A, is much better.

6.5.5 & 6.6 Suggest making the standard holding time requirements equivalent to EPA Method 8260.

7.3.2.1 Same comment as for Method 625A: 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. The low point of the calibration should be at the quantitation limit

This section states the low-calibration level should be at or near the MDL. Certain states do not require reporting to the MDL, so this should not be a requirement. It says "should" in the language, but this should not to be a requirement.

7.3.4 The % RSD for average RF calibration should be <20% as required in EPA Method 8260C. The CC is > 0.920. How was this derived? This is too lenient. Use 0.99 from Method 8260 and include the note from EPA Method 8000 about linearity that states it is not the intent to use quadratic calibration to account for the need of instrument maintenance.

7.4 This section states that the LCS is also the ICAL verification; however, the note in Section 8.4.3 encourages the laboratory to run back-to-back LCSs in case one fails. This is counter to the position

taken by the laboratory accreditation community; why introduce a concept that has already been rejected by this community?

8.1.2 Changing the detector for a determinative technique certainly allows for flexibility. Mass spectrometry (MS) and fragmentation ion pattern recognition is *key* for the selectivity of this method. Suggest this section read as follows: …and changes in columns and MS detector configurations or operating conditions. Alternate mass spectrometric detector configurations and operating conditions may be used as long as the selectivity associated with this technique is retained.

8.1.4 & 8.3 Same comment as for Method 625A except that this method does not give the laboratory options: the requirement to analyze an MS/MSD for each sample site places a burden on the laboratory to track the different sample sites. This is the responsibility of the data user. Although other options are provided, the leading statement says "must"; assessors will see this "must" and require laboratories to comply. Suggest: MS/MSD 5% of all sample or per batch, whichever is more frequent.

This tracking is virtually impossible for the laboratory. The section should state that MS/MSD per batch is required, and whoever is submitting the sample should identify samples that they want to have an MS/MSD. Similar language also needs to be fixed in Section 8.3.

8.3.2 The second sentence covers preparation of new spiking solutions depending on the concentration of the analytes in samples, which is unreasonable, especially for a multi-analyte method. Suggest removing this sentence.

8.4 Should a CCV be added at the end of the 12-hour period? This seems to be counter to the section that states a CCV is needed only at the start if an internal standard is used. Can the CCV at the start of a run serve as the end-of-run CCV for the previous batch even if it is analyzed the next day?

The requirement to bracket the samples is a major change and should not be adopted without a significant investigation of current data to determine whether it is reasonably possible to use the same criteria for an ending standard.

8.4.3 Suggest removing the note in this section.

9 This whole section needs to be rewritten to be consistent with current practice. Preservation should be by adding the sample to 0.5 mL 1:1 HCl in a VOA vial. The section is written as if it is standard practice to analyze each sample twice, once acidified and once not acidified, but that is not normal practice. Section 9.6 is particularly problematical; if followed, most of the more volatile analytes would be lost.

11.2-11.7 These sections should be rewritten to reflect modern laboratory practices.

12.1.3 Co-eluting standards with overlapping mass-to-charge ratios should be taken into consideration.

This section should be clarified to take into account co-eluting compounds; note that co-eluting compounds may result in relative intensities not agreeing with the calibration standard.

13.3.2.1 Suggest changing this requirement to “report down to the lowest laboratory reporting limit confirmed with the calibration standard at that concentration.”

13.3.2.2 This section allows for blank subtraction. This needs to be removed. This will not be acceptable for some departments.

14.1 This section refers to data from 1984; please update or remove these references.

17.3.1 The section number should be 13.3.1.

17.3.2 The section number should be 13.3.2.

Table 7 This table is based on a reference from 1984. This table should either be removed or, preferably, updated with newer technology

General In regard to collection comments on whether or not to use CLP DMCs and associated acceptance criteria, the samples analyzed under these programs are typically solid and hazardous waste samples, and the acceptance criteria would not necessarily be applicable to a wastewater matrix. EPA should develop revised criteria for this table using current technology. The laboratory should calculate its own acceptance limits for internal control based on historical data.

Diagrams Suggest updating the diagrams to reflect current technologies.