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Validation of SPE Products and Associated Procedures with EPA Method 625.1

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Validation of SPE Products and Associated Procedures with EPA Method 625.1

This document summarizes the requirements that EPA has developed in order for laboratories to utilize solid-phase extraction (SPE) as an extraction technique in EPA Method 625.1. It also provides the requirements that vendors of SPE products and equipment would have to meet in order to minimize the effort required of each individual laboratory customer as described in EPA Method 625.1, Section 8.1.2.1.1. The document is divided into two sections, based on whether the product is to be applied to analytes in Method 625.1 that have existing QC acceptance criteria, that is, those analytes listed in Tables 1 and 2 and any of the analytes listed in Table 3 for which QC acceptance criteria are specified in Table 6, or if it is to be applied to analytes in Method 625.1 without existing QC acceptance criteria.

Note: Disk-based solid-phase extraction procedures developed by the 3M Corporation and approved by EPA as an ATP are included in EPA Method 608.3 and are approved for use in measurement of the pesticide compounds in Table 1 of that method as well as the PCB Aroclors listed in Table 2 of that method. Although validation requirements for the use of SPE products and their associated procedures other than those described in Method 608.3, or for use with the additional compounds listed in Table 2 of the method, are not discussed in this document, similar concepts would apply.

For Measurement of the Analytes for which QC Acceptance Criteria are Specified in Table 6

Requirements for an Individual Laboratory

Laboratories wishing to use a vendor's SPE product and associated procedures for which a vendor has not supplied a validation package would need to generate validation data from a Tier 1, single-laboratory study on matrix type(s) (one, or additional matrix types) that represent all incoming samples at that laboratory. A nine-matrix-type study would be required for a laboratory that wishes to apply the SPE product and associated procedures to all matrix types. A laboratory wanting to use a vendor's SPE product and associated procedures on a specific discharge (matrix type) or any matrix type must perform an initial demonstration of capability (DOC) as specified in Section 8.2 of Method 625.1. The laboratory must also analyze a background sample, and MS/MSD pairs on each different matrix type that they will be analyzing up to a maximum of nine different matrix types. Note that DOC samples are also known as laboratory control (LCS) samples in Method 625.1 or as initial precision and recovery (IPR) samples for the purposes of this document.

The laboratory must fortify and analyze the IPR, and MS/MSD samples with all of the analytes that they will be measuring using the method. All samples must also be fortified with surrogates. Additionally, the laboratory must analyze a proficiency test (PT) sample containing all analytes that they will be measuring using the method (see footnote 3 to Table A).

If they are measuring only a select list of analytes from Table 1 and 2 of Method 625.1 or any of the analytes from Table 3 for which QC acceptance criteria are specified in Table 6, then they only need to demonstrate that they are able to achieve acceptable performance for those specific analytes. However, if they are running the full list of compounds in Tables 1 and 2 or any of the analytes from Table 3 for which QC acceptance criteria are specified in Table 6, they must fortify all samples with the full list of analytes in Tables 1 and 2 and any of the additional analytes from Table 3 for which QC acceptance criteria are specified in Table 6 that will be included in the analyses.

A laboratory wanting to apply a vendor's SPE product and associated procedures to samples from all matrix types (nationwide use) must prepare and analyze a background sample and MS/MSDs from nine different matrix types as described in Table C. They must demonstrate acceptable performance for all compounds on all matrix types tested. The testing of the SPE product and procedures only needs to be performed once for a specific vendor's SPE product and associated procedures to enable that product and

procedures to be used when reporting results from Method 625.1 for CWA compliance monitoring. However, the test results may not be applied to products or procedures from another vendor or to measurement of analytes that were not tested. The laboratory must continue performing the routine QC testing as described in EPA Method 625.1, Section 8 when analyzing samples on an ongoing basis.

Requirements for a SPE Vendor

Alternatively, a vendor may test their SPE product and associated procedures by performing a DOC and analyzing a background sample, and MS/MSD pairs on nine different matrix types as specified above. They must also analyze a PT sample fortified with all analytes that they are claiming that their product and associated procedures may be used to measure when performing Method 625.1. A vendor's study should focus on the analytes in Tables 1 and 2. They may also choose to include any of the additional analytes in Table 3 for which QC acceptance criteria are specified in Table 6, if desired. If the specific product and procedures being tested fail to yield acceptable performance for any of those analytes, then the product and associated procedures should be clearly labeled as applicable only to the select list of analytes for Method 625.1 for which acceptable performance was demonstrated. See Table C, "Matrix Types Recommended for Multiple Matrix Validation Studies" at the end of this document for the matrix types required for use when validating a vendor's SPE product and associated procedures for use in all matrix types. The vendor must provide a full data package, as described in Section 8.1.2.2.5 of Method 625.1, to each laboratory that will be using their product and associated procedures to report results from Method 625.1 for CWA compliance monitoring. The laboratory must have the study results (from either their own or a vendor-performed study) available for review upon request as described in EPA Method 625.1, Section 8.1.2.1.1. The laboratory must also continue to perform all routine QC testing as described in the method when analyzing samples using the SPE product and procedures with Method 625.1.

Table A. Summary of Validation Approaches for SPE Products and Associated Procedures with EPA Method 625.1 for Measurement of Analytes for which QC Acceptance Criteria are Specified in Table 6 (1)

	Number of		Number of Analyses					
Method Application	**Labs**	**Matrix types**	**Back-ground Analysis**	**IPR-Reagent Water** (2)	**PT Sample** (3)	**MS / MSD** (4)	**MDL**(5)	**Total**
Tier 1: Single-lab First matrix type	1	1	1	4	1	2	7	15
Each additional matrix type (8 max.)	1	1-8	1-8	0 (6)	0	2 (7) (16 max)	0 (6)	3 (24 max)
Vendor-Performed Study: All labs, all matrix types	1	9	9	4	1	18 (7)	7	39

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc. Nine is the maximum number of matrix types needed to validate the use of SPE products and associated procedures with Method 625.1.for measurement of the analytes in for which QC acceptance criteria are specified in Table 6 in wastewater. Additional matrix types will be required if the method is to be applied to analysis of sewage sludge or ocean water.

(2) Initial precision and recovery (IPR) reagent water analyses are used to demonstrate that the SPE product and associated procedures can achieve acceptable method performance in reagent water.

(3) The proficiency testing (PT) sample should be obtained from a third party vendor and must contain all analytes in Tables 1 and 2 and may include any of the additional analytes in Table 3 for which QC acceptance criteria are specified in Table 6, if desired. If either sewage sludge or ocean water are matrices of interest, PT samples for those matrices are required as well.

(4) The matrix spike/matrix spike duplicate (MS/MSD) test would demonstrate that the EPA-approved method MS/MSD QC acceptance criteria have been met when using the SPE product and associated procedures.

(5) A method detection limit (MDL) test would be performed by the laboratory performing the study, using the SPE product and associated procedures. 40 CFR Part 136 Appendix B requires a minimum of seven analyses per laboratory to determine an MDL. If Appendix B is modified at a later date, then the validation study must conform to the most recent MDL requirements.

(6) The MDL and reagent water IPR tests do not have to be repeated after the first matrix type is validated.

(7) The MS/MSD analyses would demonstrate that MS/MSD recovery and precision criteria associated with the EPA-approved reference method have been met. The number of MS/MSD analyses is two times the number of matrix types tested (*i.e.*, one MS/MSD pair per laboratory).

For Measurement of Additional Analytes without QC Acceptance Criteria (Analytes in Table 3 for which no QC Acceptance Criteria are Specified in Table 6)

Requirements for an Individual Laboratory

Laboratories wishing to use a vendor's SPE product and associated procedures for which a vendor has not supplied a validation package for measurement of the additional analytes for which no QC acceptance criteria have been developed by EPA (those analytes listed in Table 3) must generate QC acceptance criteria for those compounds by performing a Tier 1, single-laboratory study, on matrix types (one, or additional matrix types) that represent all incoming samples at that laboratory. A nine-matrix-type study would be required for the laboratory that wishes to apply the SPE product and associated procedures to all matrix types for measurement of these additional analytes. A laboratory wanting to use a vendor's SPE product and associated procedures for measurement of these additional analytes in a specific discharge (matrix type) or in any matrix type, must perform an initial demonstration of capability (DOC) as specified in Section 8.2 of Method 625.1. The laboratory must also analyze a background sample, and MS/MSD pairs on each different matrix type that they will be analyzing up to a maximum of nine different matrix types.

The laboratory must fortify and analyze the IPR, and MS/MSD samples with all of the analytes that they will be measuring using the method, including any of the additional analytes listed in Table 3. All samples must also be fortified with surrogates. Additionally, the laboratory must analyze a PT sample containing all analytes that they will be measuring using the method, including any of the analytes in Table 3. If they are measuring only a select list of analytes from Table 3, then they only need to demonstrate that they are able to achieve acceptable performance on those specific analytes.

If the laboratory wants to apply the use of a vendor's SPE product and associated procedures to all samples from all matrix types (nationwide use), they must prepare and analyze MS/MSDs from nine different matrix types as described in Table C. They must demonstrate acceptable performance for all compounds for which QC acceptance criteria exist (the analytes in Tables 1 & 2) on all matrix types that will be analyzed, up to a maximum of nine different matrix types. They must also use the results of the validation study to develop QC acceptance criteria for any of the additional analytes in Table 3 using the procedures in Section 3.1 of Appendix G to "Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program" (EPA 821-B-16-001, February 2016). This document is available at: www.epa.gov/cwa-methods/alternate-test-procedure-documents . The testing of the SPE product and procedures only needs to be performed once for a specific vendor's SPE product and associated procedures to enable that product and procedures to be used when reporting results from Method 625.1 for CWA compliance

monitoring. However, the test results may not be applied to products or procedures from another vendor or to measurement of analytes that were not tested. The laboratory must continue performing the routine QC testing required by the method when analyzing samples on an ongoing basis.

Requirements for a SPE Vendor

Alternatively, a vendor may conduct a Tier 3, nine-laboratory, nine-matrix type (multi-lab, all matrix types) validation study using their SPE product and associated procedures. The IPR samples used in the DOC tests, and the MS/MSD samples analyzed in each of the nine laboratories must be fortified with all of the analytes that the vendor is claiming that their product and associated procedures may be used to measure when performing Method 625.1, including any additional analytes from Table 3. Additionally, each laboratory in the vendor's study must analyze a PT sample fortified with all analytes that they are claiming that their product and associated procedures may be used to measure when performing Method 625.1 including any additional analytes from Table 3 (see footnote 4 to Table B). The vendor must use the results from the study to develop QC acceptance criteria for any of the additional analytes in Table 3 using the procedures in Section 3.3 of Appendix G to "Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program" (EPA 821-B-16-001, February 2016). This document is available at: www.epa.gov/cwa-methods/alternate-test-procedure-documents. See Table C, "Matrix Types Recommended for Multiple Matrix Validation Studies" for matrix types required for use when validating a vendor's SPE product and associated procedures for use in all matrix types. The vendor must provide a full data package, as described in the method, to each laboratory that will be using their product and associated procedures to report results from Method 625.1 for CWA compliance monitoring. The laboratory must have the study results (from either their own or a vendor-performed study) available for review upon request as described in EPA Method 625.1, Section 8.1.2.1.1. The laboratory must also continue to perform all routine QC testing as described in the method when analyzing samples using the SPE product and procedures with Method 625.1.

Table B. Summary of Validation Approaches for SPE Products and Associated Procedures with EPA Method 625.1 for Measurement of Analytes in Table 3 for which no QC Acceptance Criteria are Specified in Table 6 (1)

Method Application	Number of		Number of Analyses						
	Labs	Matrix types	Back-ground Analysis	IPR-reagent water (2)	IPR-sample matrix (3)	PT Sample (4)	MS / MSD	MDL (5)	Total
Tier 1: Single-lab First matrix type	1	1	1	4	4	1	0	7	17
Each additional matrix type (8 max.)	1	1-8	1-8	0 (6)	0	0	2 (7) (16 max)	0 (6)	3 (24 max)
Tier 3: Multi-lab, all matrix types	9	9	9	36	0	9	18 (7)	63	135

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc. Nine is the maximum number of matrix types required for validation of use of SPE with Method 625.1 at Tier 1 or Tier 3.

(2) Initial precision and recovery (IPR) reagent water analyses are used to validate a method modification. The number of IPR analyses is four times the number of laboratories used to validate the use of SPE because each laboratory performs a four-replicate IPR test.

(3) IPR sample matrix analyses are used to establish QC acceptance criteria for matrix spike/matrix spike duplicate (MS/MSD) recovery and precision for a Tier 1 new method only. IPR sample matrix analyses are not needed for validation of the use of SPE with Method 625.1 by vendors at Tier 3 because this variability data would be obtained from MS/MSD tests in multiple labs.

(4) The proficiency testing (PT) sample should be obtained from a third-party vendor and should be analyzed by each laboratory participating in the study. If sewage sludge or ocean water are matrices of interest, PT samples for those matrices are required as well. The PT samples must contain all analytes to which use of SPE will be applied when performing Method 625.1 including any additional analytes from Table 3.

(5) A method detection limit (MDL) test would be performed in each laboratory, using the SPE product and associated procedures. 40 CFR Part 136 Appendix B requires a minimum of seven analyses per laboratory to determine an MDL. If Appendix B is modified at a later date, then the validation study must conform to the most recent MDL requirements.

(6) The MDL and reagent water IPR tests do not have to be repeated after the first matrix type is validated.

(7) The MS/MSD analyses would be used to establish MS/MSD acceptance criteria for recovery and precision for the additional analytes in Table 3 to which the use of the SPE product and associated procedures with Method 625.1 will be applied. The number of MS/MSD analyses is two times the number of matrix types tested (*i.e.*, one MS/MSD pair per laboratory).

Table C. Matrix Types Recommended for Multiple Matrix Type (Nationwide Use) Validation Studies

1. Effluent from a POTW
2. ASTM D 5905 - 98 (Reapproved 2013), *Standard Specification for Substitute Wastewater*
3. Sewage sludge, if sludge will be in the permit
4. ASTM D 1141 - 98 (Reapproved 2013), *Standard Specification for Substitute Ocean Water*, if ocean water will be in the permit
5. Untreated and treated wastewaters up to a total of nine matrix types (See www.epa.gov/eg/industrial-effluent-guidelines for a list of industrial categories with existing Effluent Guideline regulations)
At least one of the above wastewater matrix types should have at least one of the following characteristics: • Total suspended solids (TSS) greater than 40 mg/L • Total dissolved solids (TDS) greater than 100 mg/L • Oil and grease greater than 20 mg/L • NaCl greater than 120 mg/L • $CaCO_3$ greater than 140 mg/L