Designation: D8421 – 22

Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Co-solvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D8421; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of per- and polyfluoroalkyl substances (PFASs) in aqueous matrices using liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). These analytes are co-solvated by a 1+1 ratio of sample and methanol then qualitatively and quantitatively determined by this test method. Quantitation is by selected reaction monitoring (SRM) or sometimes referred to as multiple reaction monitoring (MRM).

1.2 The method detection limit (MDL) (see Note 1) and reporting range (see Note 2) for the target analytes are listed in Table 1. The target concentration for the reporting limit for this test method is an integer value that is calculated from the concentration from the lowest standard from the final volume of the prepared sample. This value may be lower than the calculated MDL due to sporadic PFAS hits due to PFAS contamination in consumables/collection tools used during sample collection and preparation. All samples should be taken at a minimal as duplicates in order to compare the precision between the two prepared samples to help ensure the concentration/positive result is reliable.

NOTE 1—The MDL is determined following the Code of Federal Regulations (CFR), 40 CFR Part 136, Appendix B utilizing dilution and filtration. A detailed process determining the MDL is explained in the reference and is beyond the scope of this test method.

NOTE 2—Injection volume variations, and sensitivity of the instrument used will change the reporting limit and ranges.

1.2.1 Recognizing continual advancements in the sensitivity of instrumentation, advancements in column chromatography and other processes not recognized here, the reporting limit may be lowered assuming the minimum performance requirements of this test method at the lower concentrations are met.

1.2.2 Depending on data usage, you may modify this test method but limit to modifications that improve performance while still meeting or exceeding the method quality acceptance criteria. Modifications to the solvents, ratio of solvent to sample, or shortening the chromatographic run simply to save time are not allowed. Use Practice E2935 or similar statistical tests to confirm that modifications produce equivalent results on non-interfering samples. In addition, use Guide E2857 or equivalent statistics to re-validate the modified test.

1.2.3 Analyte detections between the method detection limit and the reporting limit are estimated concentrations. The reporting limit is based upon the concentration of the Level 1 calibration standard as shown in Table 5.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D8272 Guide for Development and Optimization of D19 Chemical Analysis Methods Intended for EPA Compliance Reporting
E694 Specification for Laboratory Glass Volumetric Apparatus
E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
E2857 Guide for Validating Analytical Methods
E2935 Practice for Evaluating Equivalence of Two Testing Processes

2.2 *Other Standards:*[3]

Code of Federal Regulations 40 CFR Part 136, Appendix B

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *collision cell, n*—chamber in the ion path between m/z separation elements, or between ion source and the first analyzer, in tandem mass spectrometry in space configurations.

3.2.2 *continuing calibration verification (CCV), n*—a mid-range calibration standard which checks the continued validity of the initial calibration of the instrument.

3.2.3 *mass spectrometry/mass spectrometry (MS/MS), n*—acquisition and study of the spectra of the product ions or precursor ions of m/z selected ions, or of precursor ions of a selected neutral mass loss.

3.2.3.1 *Discussion*—MS/MS can be accomplished using instruments incorporating more than one analyzer (tandem mass spectrometry in space) or in trap instruments (tandem mass spectrometry in time).

3.2.4 *multiple reaction monitoring (MRM), n*—application of selected reaction monitoring to multiple product ions from one or more precursor ions.

3.2.5 *per- and polyfluoroalkyl substances (PFAS), n*—synthetic organofluorine chemical compounds with multiple fluorine atoms that includes PFOA, PFOS, GenX, and many other chemicals.

3.2.5.1 *Discussion*—PFAS have a hydrophobic and oleophobic fluorinated "tail" and a hydrophilic "head" making them surfactants. They include the perfluoro sulfonic acids such as the perfluorooctanesulfonic acid (PFOS) and the perfluoro carboxylic acids, such as the perfluorooctanoic acid (PFOA). PFOS and PFOA are persistent organic pollutants. The definition does not include the mass labeled surrogates or internal standards.

3.2.6 *precursor ion, n*—ion that reacts to form product ions or undergoes specified neutral losses.

3.2.7 *product ion, n*—ion formed as the product of a reaction involving a precursor ion.

3.2.8 *single (or selected) reaction monitoring (SRM), n*—data acquired from one or more specific product ions corresponding to m/z selected precursor ions recorded via two or more stages of mass spectrometry.

3.2.9 *tandem mass spectrometer, n*—mass spectrometer designed for mass spectrometry/mass spectrometry.

3.2.10 *triple quadrupole mass spectrometer (triple quad or QQQ), n*—tandem mass spectrometer comprising two transmission quadrupole mass spectrometers in series, with a (non-selecting) RF-only quadrupole (or other multipole) between them to act as a collision cell.

4. Summary of Test Method

4.1 The operating conditions presented in this test method have been validated for use in the determination of PFASs in aqueous samples. Alternative instrument operating conditions may be used provided data quality objectives are met. Follow the manufacturer's instructions. The preparation process, as summarized in 4.2 and described in Section 14 may be automated, but cannot be modified.

4.2 Samples are shipped to the lab at a temperature between 0 °C and 6 °C and analyzed within 28 days of collection. A sample (5 mL) is collected and processed in the same collection tube in order to limit analyte loss; extra samples must be collected for duplicates/triplicates and matrix spikes. All samples and associated QC samples are spiked with labeled surrogates (QC samples such as laboratory control and matrix spike samples are additionally spiked with target PFASs) and shaken for 2 minutes after adding 5 mL of methanol. The samples are then filtered through a polypropylene filter. Acetic acid (~10 µL) is added to all the samples to adjust to pH ~4 and analyzed by LC/MS/MS. If samples contain more than about 1.0 g/L suspended or settled solids, (for example, sludge, pretreatment, or wastewater influent) adjust to pH ~9 (adding ~20 µL of ammonium hydroxide), shake for 2 minutes, filter, acidify to pH ~4 (~50 µL acetic acid), and then analyze by LC/MS/MS.

NOTE 3—Sludge in this test method is defined as sewage sample containing between 0.1 and 2 % solids based upon a sample by weight.

NOTE 4—Since contact with surfaces may bias data, collect a 5.0-mL sample in a graduated 15-mL polypropylene tube in the field so that the whole sample is processed in the lab. Once this 5.0-mL sample is spiked according to this test method and methanol is added, the sample is filtered into another 15 mL polypropylene tube without analyte loss.

NOTE 5—For accurate volume, the weight of the 15-mL polypropylene tube may be taken before and after sampling. The density of water is assumed to be 1.0 g/mL unless the exact density of the water sample is known, then that conversion should be used.

4.3 Most analytes are identified by comparing the SRM transition and its confirmatory SRM transition correlated to the known standard SRM transition (Table 3) and quantitated utilizing an external calibration. The retention times and ion ratios are shown in Table 4 for each native analyte and isotope. The surrogates and some analytes only have one SRM transition due to a less sensitive or non-existent secondary SRM

[3] Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm