Designation: D8535 – 23

Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Soil/Biosolid Matrices by Solvent Extraction, Filtering, and Followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D8535; 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 (PFAS) in soil/biosolid matrices by solvent extraction, filtering, separation using liquid chromatography (LC), and detection with tandem mass spectrometry (MS/MS). These analytes are extracted from soil/biosolids with basic water and methanol then qualitatively and quantitatively determined by this test method. Quantitation is by selected reaction monitoring (SRM), sometimes referred to as multiple reaction monitoring (MRM).

1.2 The reporting limit (RL) and reporting range (see Note 2) for the target analytes are listed in Table 1. The reporting limit is calculated from the concentration of the Level 1 calibration standard as shown in Table 5 for the PFAS after taking into account a 2 g sample weight and a final extract volume of 10 mL, 50 % water/50 % MeOH with 0.1 % acetic acid. The final extract volume is assumed to be 10 mL because 10 mL of 50 % water/50 % MeOH with 0.1 % acetic acid was added to each soil sample and only the liquid layer after extraction is filtered, leaving the solid and any residual solvent behind. Sporadic PFAS hits due to PFAS contamination in consumables/collection tools used during sample collection and preparation is possible while executing this standard and must be monitored. All samples should be taken at a minimum as duplicates in order to compare the precision between the two prepared samples to help ensure the concentration/positive result is reliable.

NOTE 1—This standard only includes the determination of the analytes listed in Table 1 and is only applicable to soil and biosolid matrices; any added compost or soil additives may contain PFAS that may be bound and not able to be determined by this method. Analysis of packaging materials and polymeric PFAS moieties are not amenable to this standard.

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 revalidate the modified test.

1.2.3 Analyte detections under the reporting limit are estimated concentrations. If results are to be reported below the RL using this standard and following the method detection limit procedure in 40 CFR Part 136 Appendix B, data shall be qualified estimated and extra caution must be taken to evaluate and identify false positives.

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*

[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

Current edition approved Nov. 1, 2023. Published November 2023. DOI: 10.1520/D8535-23.

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
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
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 Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit
EPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

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

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

3.2.7 *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.

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

3.2.9 *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 solid 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 For PFAS analysis, samples are shipped to the lab on ice and analyzed within 28 days of collection. A sample (2 g) is transferred to a polypropylene tube, spiked with surrogates (all samples) and target PFAS compounds (laboratory control and matrix spike samples). The analytes are tumbled for an hour with 10 mL of methanol:water (50:50) under basic condition (pH ~9 to 10 adjusted with ~20 µL ammonium hydroxide). The samples are centrifuged and the extract, leaving the solid behind, is filtered through a polypropylene filter unit. Acetic acid (~50 µL) is added to all the filtered samples to adjust the pH ~3 to 4 and then analyzed by LC/MS/MS.

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 transition. As an additional quality control measure, isotopically labeled surrogate (Table 1, 13.3) recoveries are monitored. With external standard calibrations, there is no correction to the data based upon surrogate recoveries. Alternatively, extract an isotopically labeled analog of each analyte (isotope dilution), if available, and correct for recovery. Only exact isotopes of the native analytes may be used for isotope dilution correction. If a structurally different isotope is used to correct a native analyte, this is called surrogate correction and either

[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.

[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