US EPA SW-846 Validated Method 8327

Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

Executive Summary

EPA has validated SW-846 Method 8327: *Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)* in a two-phase study for 24 PFAS analytes and 19 isotopically-labeled PFAS surrogates in four aqueous matrices of reagent water, surface water, groundwater, and wastewater effluent, three of which were intended to represent non-potable water matrices. The PFAS targets included sulfonic acids (e.g., PFOS), carboxylic acids (e.g., PFOA), fluorotelomer sulfonic acids (e.g., 6:2 fluorotelomer sulfonate, or FTS), and sulfonamides and sulfonamidoacetic acids (e.g., N-MeFOSAA).

The **Statistical Analysis Report for SW-846 Method 8327 Multi-Lab Validation Study (June 2019)** (Statistical Report) analyzes the study results for bias using percent (%) recovery and for precision using the relative standard deviation (RSD) of target analyte concentrations, which the study measured in the four aqueous matrices prepared at 60 and 200 nanograms/liter (ng/L) (parts per trillion) spiking levels. The Statistical Report contains additional analyses of study results for performance per media, per concentration level, and per laboratory.

The **US EPA SW-846 Method 8327 Multi-Laboratory Validation Study Quality Control Summary Report (June 2019)** (Data Validation Summary) summarizes the quality control (QC) results from the multi-laboratory validation of Method 8327 using the dilution preparation method in Appendix B of Method 8327. EPA evaluated data from 12 laboratories for compliance with the study instructions, method, and overall usability (i.e., for instrument calibration and for study sample preparation and analysis). EPA excluded data from four laboratories for not following the specified protocols (more detail about the basis used for exclusion of each laboratory's data is provided in Appendix E of the Statistical Report). For the remaining eight laboratories, EPA reviewed data for completeness and validated data using criteria provided in the method and study instructions.

The Statistical Report and Data Validation Summary showed more bias and/or less robust measurement precision for the longer-chain carboxylic acids, the amidoacetic acids, the fluorotelomer sulfonic acids, and perfluorobutanoic acid. The performance for 6:2 fluorotelomer sulfonate (6:2 FTS) was erratic, with high average recovery and high RSDs in some matrices and spike levels. Multiple laboratories reported high or variable background levels of this chemical, including in method blanks and calibration standards. A summary of study sample results is provided below for the 24 PFAS analytes and two spiking levels across all four aqueous matrices (Table 1).

With the exception of 6:2 FTS, the target analytes in the study generally met the precision and bias criteria defined in the method and study instructions. The principal problems laboratories encountered with preparation and analysis of study samples were retention of the target analytes

and surrogates in solution (particularly when stored in glass containers), background contamination, and instrument sensitivity.

EPA revised draft Method 8327 to address the precision and bias problems observed in the study data by adding several cautions, particularly for the longer chain PFAS carboxylic acids and amidoacetic acids, including:

- ensuring that the composition of the stock and intermediate standards contain enough organic cosolvent ($\geq 95\%$);
- avoiding storage in glass containers; and
- avoiding subsampling prior to adding a sufficient proportion of organic cosolvent.

Considering the issues observed with multiple QC failures in the validation study as described above, EPA also added a general caution for 6:2 FTS.

Based on the Statistical Report and Data Validation Summary, EPA deems draft SW-46 Method 8327 generally acceptable. According to the SW-846 method publication process, EPA is posting the draft validated method and supporting materials for a 30-day public comment period. After the public comment period closes, EPA will adjudicate comments and revise the method accordingly before finalizing it and incorporating it into the Test Methods for Evaluating Solid Waste: Physical/Chemical Methods compendium.

Table 1. Summary of bias (as % recovery)[1] and precision (as % RSD) of target analyte concentrations in study samples, across four matrices and eight laboratories

Target Analyte	Prepared concentration: 60 ng/L (nom.; n=159)				Prepared concentration: 200 ng/L (nom.; n=160)			
	Average (Mean) % Recovery	Median % Recovery	% RSD	% measured within 70-130% of prepared conc.	Average (Mean) % recovery	Median % Recovery	% RSD	% measured within 70-130% of prepared conc.
PFTeDA	89.5	90.1	27.3	73.6	95.0	93.1	18.3	90.0
PFTrDA	95.7	93.9	25.2	79.9	99.8	99.0	18.2	87.5
PFDoA	95.8	91.7	25.2	81.1	102	98.5	18.0	89.4
PFUdA	97.3	94.4	18.9	90.6	104	101	16.1	91.3
PFDA	99.4	97.0	18.8	92.5	104	102	12.7	96.9
PFNA	96.8	96.1	14.3	96.9	102	102.2	11.4	99.4
PFOA	99.9	99.4	13.9	97.5	103	103	10.6	98.8
PFHpA	97.9	95.9	13.3	98.7	100	99.2	9.2	99.4
PFHxA	97.2	94.9	18.4	91.2	98.5	97.0	11.2	98.8
PFPeA	107	103	24.7	91.2	100	98.8	12.6	100
PFBA	93.6	91.3	24.1	80.5	94.8	93.7	17.5	90.0
PFDS	95.7	93.2	20.4	86.8	100	98.5	17.6	91.3
PFNS	100	99.7	17.8	89.3	106	103	13.9	93.8
PFOS	104	100	17.8	89.3	108	104	27.9	96.9
PFHpS	98.9	97.7	14.2	96.9	102	102	10.2	98.8
PFHxS	97.2	97.5	15.9	93.1	102	99.8	10.5	98.8
PFPeS	96.0	95.1	10.8	98.1	99.3	97.8	8.8	99.4
PFBS	96.7	94.7	14.4	96.2	99.8	98.4	11.1	98.8
FOSA	88.7	88.1	14.1	92.5	95.5	94.2	10.6	99.4
8:2 FTS	103	99.9	20.1	87.4	110	108	16.1	87.5
6:2 FTS	95.0	84.7	191.7	61.0	92.4	94.6	51.8	66.9
4:2 FTS	95.1	91.8	19.7	86.8	102	99.9	14.4	96.3
NEtFOSAA	99.3	96.0	26.4	83.6	107	99.1	20.1	85.6
NMeFOSAA	98.2	94.9	22.7	89.3	102	98.5	16.6	91.9

[1] Note: Recoveries were calculated from concentrations in field samples after correcting for background, which was accomplished by subtracting the average unspiked matrix concentration reported by the same laboratory (n=5). Correction for background was not performed for average unspiked matrix concentrations < 5 ng/L. Refer to the Statistical Report, Data Validation Summary, or Method 8327 for definitions of analyte abbreviations.