

**Guidelines on Validation of Non-Regulatory Chemical and Radiochemical Methods
(EPA/600/B-22/001, 2022): Method Validation Summary for SW-846 Methods 3512 and 8327**

The Guidelines provide collected information on critical areas of method performance assessment for validation studies. The Method Validation Summary Table from the Guidelines is designed to provide consistency in delivery of summary method validation results in a concise, easy-to-prepare and share format. Below is an example of the Table completed for the US EPA SW-846 Methods 3512 and 8327. Links to the complete report can be found at the end of the Table.

A	Validation Design	Description
1	Number of Laboratories	8
2	Number of Matrices	3
3	Types of Matrices Tested (water, soil, sediment, etc.)	Groundwater, surface water, wastewater

B	Method Validation Overview	Description
1	Method Title	<ul style="list-style-type: none"> • SW-846 Method 3512: Solvent Dilution of Non-Potable Waters • SW-846 Method 8327: Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS)
2	Organization	EPA/Office of Land and Emergency Management/Office of Resource Conservation and Recovery
3	Date	July 2021
4	Purpose	To validate the preparation and analysis of non-potable water samples for select PFAS by LC/MS/MS
5	Qualitative or Quantitative	Quantitative
6	Target Analytes/Parameters	Validated for 24 PFAS target analytes, including: <ul style="list-style-type: none"> • C4-C14 perfluorinated carboxylic acids • C4-C10 perfluorinated sulfonic acids, • 4:2, 6:2, and 8:2 Fluorotelomer Sulfonic Acids (FTS) <ul style="list-style-type: none"> • perfluorooctane sulfonamide • N-ethyl and N-methyl perfluorooctane sulfonamidoacetic acids Please refer to Method 8327 for more detail

C	Method Development Considerations	Description and/or Results
1	Sample Cost	Not Determined
2	Recommended Sample Holding Times	Sample collection to preparation: 14 days Sample preparation to analysis: 30 days
3	Sample Preservation	Refrigerate at 0-6°C
4	Waste Generation	These methods generate relatively small amounts of waste due to: <ul style="list-style-type: none"> • Small recommended sample volumes; • Low volumes of reagents and solvents used for sample preparation; Liquid chromatography columns with particle sizes $\leq 2 \mu\text{m}$ achieve efficient separations at low flow rates

Notes on Section C:

-C2 Holding times are published as guidelines and were based on holding time studies conducted for other PFAS methods, including EPA methods 533 and 537.1 and ASTM D7979-20.

D	Method Performance Characteristic	Description and/or Results
1	Bias/Trueness	Average (median) recovery across eight laboratories ranged from 80-118% at 95% confidence for every target analyte except 6:2 FTS in each matrix type and prepared concentration level.
2	Detection Capability and Quantification Capability	Lower limits of quantitation (LLOQs) across eight laboratories were verified at nominal concentrations of 10-20 ng/L at 95% confidence for all target analytes except for 8:2 FTS (40 ng/L) and 6:2 FTS (160 ng/L).
3	Instrument Calibration	Target analytes were calibrated by external standard using weighted regression.
4	Measurement Uncertainty	Not Applicable
5	Precision	Relative standard deviation (RSD) of measured concentrations in spiked samples was <50% in every matrix and spike level combination in each laboratory except for PFOS in one laboratory/matrix/spike level and 6:2 FTS in three laboratory/matrix/spike level combinations.
6	Range	LC/MS/MS initial calibration range was from 5 to 200 ng/L (nominal). No attempt was made to determine an upper limit for quantitative analysis.
7	Ruggedness	Formal ruggedness testing was not performed as part of the validation study.
8	Selectivity in the Presence of Interferences	No major sources of interferences were observed that impacted qualitative identification of target analytes.

Notes on Section D:

- D1 Validation study samples were tested unspiked or spiked at nominal concentrations of 60 and 200 ng/L. Each laboratory tested 5 replicate spiked samples of each matrix at each prepared concentration. Samples were prepared centrally and shipped to laboratories, which were blind to the identities of the

samples and their prepared concentrations. Half of the participating laboratories reported background contamination with 6:2 FTS.

- D2 High verified LLOQs for 6:2 FTS were attributed to background contamination in half of participating laboratories. Methods 3512 and 8327 are performance-based, and laboratories are required to establish and periodically verify LLOQs at which they can routinely meet the acceptance criteria for all categories of quality controls. Refer to Method 8000D Section 9.7 and Method 8327 Section 9.9 for more information about establishing and verifying LLOQs <https://www.epa.gov/hw-sw846/sw-846-compendium>.

- D4 Methods 3512 and 8327 are performance-based, and, like many other SW-846 methods, they recommend applying statistically-based or project-defined acceptance limits for recovery and precision in field samples and associated prepared quality control samples.

- D5 PFOS imprecision was attributed to variability in background concentrations in wastewater samples, and 6:2 FTS imprecision was attributed to laboratory contamination in half of participating laboratories.

- D7 Laboratory deviations from the method validation study protocol led to the addition cautionary measures to the methods related to ruggedness, including: 1) avoiding aqueous subsampling prior to adding sufficient organic solvent; and 2) avoiding storage of prepared samples and standards in glass containers.

- D8 Some PFAS target analytes do not make secondary product ions with sufficient relative abundance to be useful for supporting qualitative identification.

Related Links:

1. Executive summary: <https://www.regulations.gov/document/EPA-HQ-OLEM-2018-0846-0111>
2. Quality Control summary report: <https://www.regulations.gov/document/EPA-HQ-OLEM-2018-0846-0005>