LC-MS/MS Analysis of 40 Per- and Polyfluoroalkyl Substances in Solvents: A Modified EPA Method 1633A Approach

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Abstract

A modified workflow based on EPA Method 1633A was applied for the analysis of 40 per- and Polyfluoroalkyl Substances (PFAS) in a range of solvents. Solid-phase extraction (SPE) combined with LC-MS/MS was used to assess the PFAS background of 19 solvent products, including water, acetonitrile, and methanol of different grades. Ensuring solvent purity was identified as essential for achieving reliable PFAS measurements and for preventing false positives or overestimation of PFAS concentrations.

Introduction

Per- and Polyfluorinated Alkyl Substances (PFAS) are a class of synthetic compounds that have been widely used in consumer and commercial products for several decades because of their versatile physical and chemical properties (e.g., in water repellent, firefighting foams, cookware, food packaging). Due to their chemical stability arising from the strong carbon fluorine bond, their persistence, and their toxicity, these compounds have gained increasing attention with respect to contamination of water, soil, and food, along with the associated bioaccumulation in humans and animals.

Guidance for PFAS testing regulations has been issued by the United States Environmental Protection Agency (US EPA) and the European Union (EU) to support the protection of environmental and human health, including EPA methods 533, 537.1 and 1633A and FDA method C-010.03.[1-6]

In December 2024, the US EPA released the final version of EPA Method 1633A, which provides extensive guidance for environmental PFAS testing. The method was validated across multiple laboratories and includes the analysis of 40 PFAS compounds in a wide range of sample matrices, including aqueous samples such as wastewater, surface water, and groundwater, solid samples such as soil, sediment, and biosolids and biological samples such as fish and other tissues. For PFAS analysis in food, advisories were issued by the U.S. Food and Drug Administration (FDA) by releasing the method C-010.03, which employs a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure with dispersive solid phase extraction (dSPE) for clean-up prior to liquid chromatography-mass spectrometry (LC-MS) detection.

The analysis of PFAS can be performed using the analytical methods described in the guidance documents by following their established matrix-specific extraction protocols for detecting these contaminants in various sample matrices. A key requirement for the successful application of these methods is the high purity of the solvents used, such as water, acetonitrile, and methanol, which are required during both the preparative and analytical stages of the determination, such as the preparation of mobile phase, extraction reagent and calibration standards. The high sensitivity of LC-MS instruments and the need for trace level PFAS detection necessitate the use of solvents that are free of any PFAS contamination. Any PFAS present in these solvents can lead to misleading results in the form of false positives or overestimation of PFAS levels, which compromises the validity of the analytical results and the conclusions. Ensuring solvent purity is therefore essential for achieving accurate and reliable PFAS analysis.

This study describes the analysis of 40 PFAS analytes in bottled water, acetonitrile and methanol from two portfolio brands (Supelco® and Sigma-Aldrich®) across various solvent grades, including HPLC grade, HPLC plus grade, gradient grade, UHPLC grade and LC-MS grade. Solid-phase extraction (SPE) was performed using Supelclean™ ENVI-WAX™ SPE cartridges in combination with a PTFE-free Visiprep™ SPE vacuum manifold. The extracts were subsequently analyzed by LC-MS/MS using analytical and delay Fused-Core® Ascentis® Express PFAS columns.

MilliporeSigma is the U.S. and Canada
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Experimental

Solutions and Standards Preparation

40 native and 31 isotopically labeled PFAS standards were used as methanolic 50 µg/mL stock solutions. Following the recommendations of the EPA 1633A method, these native and isotopically labeled standards were then diluted to prepare seven calibration solutions (CS1 – CS7). The calibration solutions contained the native PFAS compounds at concentrations ranging from 0.2 to 5 ng/mL for CS1 and from 62.5 to 1560 ng/mL for CS7, as specified in **Table 4** of EPA Method 1633A, to establish the working range of the MS instrument.

Sample Preparation for Solvent testing

Sample collection and preparation were performed according to EPA Method 1633A with slight modifications. Three solvents, namely water, acetonitrile, and methanol (1 L bottle size), were examined for potential PFAS contamination across the grades listed in **Tables 3 to 5**. Volumes of 500 mL of water, 250 mL of acetonitrile, or 250 mL of methanol were transferred into HDPE bottles fitted with linerless polypropylene caps. To the acetonitrile and methanol samples, 500 mL or 250 mL of UHPLC grade water (**1.03728**) were added, respectively, to dilute the organic solvents and prevent poor recovery of selected PFAS compounds due to insufficient retention during the SPE loading step. The samples were fortified with 24 isotopically labeled standards (^{13}C or D), which served as extracted internal standards (EIS).

For SPE, Supelclean™ ENVI-WAX™ SPE tubes (500 mg/6 mL, **54057-U**) were fitted with large volume SPE reservoirs (25 mL, **54258-U**) and placed on a PTFE-free Visiprep™ vacuum manifold (**57030-U**). The tubes were conditioned with 15 mL of 1.0% NH4OH in methanol and equilibrated with 5 mL of aqueous 0.3 M formic acid. The samples (500 mL of water, 500 mL of diluted methanol or 750 mL of diluted acetonitrile as described above) were then loaded and passed through the cartridges. The washing step consisted of two rinses with 5 mL of water followed by 5 mL of 0.1 M formic acid in water/methanol (1:1, v/v). The cartridges were subsequently dried for 1 min before elution of the analytes with 5 mL of 1.0% NH_4OH in methanol into collection tubes that contained seven additional isotopically labeled standards. These standards, used as non-extracted internal standards (NIS), were included to evaluate the recovery of the EIS compounds and assess the applicability of the method. Prior to LC-MS/MS analysis described below, 25 µL of concentrated acetic acid (**5.33001**) were added to the eluates.

Instrumental Analysis

LC-MS/MS analysis was performed using an Agilent 1290 Infinity II instrument coupled to an Agilent 6495C triple quadrupole mass spectrometer. Analyte separation was achieved on an Ascentis® Express PFAS 90 Å column (5 cm x 2.1 mm, 2.7 µm, **53557-U**) used as the analytical column. An Ascentis® Express PFAS Delay 160 Å column (5 cm x 3.0 mm, 2.7 µm, **53572-U**) was installed after the mixing valve and before the autosampler to offset PFAS contamination potentially originating from the LC system (e.g., pump, tubing, fittings, filters). Polypropylene snap cap vials were used instead of standard glass vials to avoid possible adsorption of PFAS to glass surface. The LC-MS employed for the analysis are summarized in **Tables 1 and 2**, including the used MRM transitions for quantification of the native PFAS by stable-isotope dilution. The allocation of extracted internal standards followed the specifications of EPA Method 1633A.

Table 1. LC-MS conditions used for analysis of 40 PFAS compounds

LC Conditions				
Instrument:	Agilent 1290 Infinity II LC system and Agilent 6495C triple quadrupole mass spectrometer			
Columns:	Analytical column: Ascentis® Express PFAS 90 Å; 2.7 µm, 5 cm x 2.1 mm (**53557-U**) Delay Column: Ascentis® Express PFAS Delay 160 Å, 2.7 µm, 5 cm x 3.0 mm (**53572-U**)			
Mobile phase:	[A] 2 mM Ammonium acetate in 95:5 water/acetonitrile (v/v); [B] Acetonitrile			
Gradient:	**Time (min)**	**A%**	**B%**	**Flow rate [mL/min]**
	0.0	98.0	2.0	0.35
	0.2	98.0	2.0	0.35
	4.0	70.0	30.0	0.40
	7.0	45.0	55.0	0.40
	9.0	25.0	75.0	0.40
	10.0	5.0	95.0	0.40
	10.4	98.0	2.0	0.40
	11.8	98.0	2.0	0.40
	12.0	98.0	2.0	0.35
Flow rate:	See gradient table			
Column temp.:	40 °C			
Detector:	MS (ESI-), MRM (see **Table 2** for details)			
Injection:	2 µL			
Sample(s):	See text			

Table 2. MRM (ESI-) transitions, chromatographic and linearity (R^2, 1/x weighting, six calibrants for FTS compounds and seven for all other compounds) data for the 40 native PFAS

Peak	Acronym	Compound	MRM Transition (Quantifier)	Collision energy (eV)	RT (min)	R2
1	PFBA	Perfluorobutanoic acid	213.0 --> 169.0	8	1.6	0.9995
2	PFMPA	Perfluoro-3-methoxypropanoic acid	229.0 --> 85.0	12	2.4	0.9994
3	3:3FTCA	3-Perfluoropropyl propanoic acid	241.0 --> 177.0	3	2.8	0.9978
4	PFPeA	Perfluoropentanoic acid	263.0 --> 219.0	4	3.3	0.9995
5	PFMBA	Perfluoro-4-methoxybutanoic acid	279.0 --> 85.0	8	3.6	0.9996
6	4:2FTS	*1H,1H, 2H, 2H*-Perfluorohexane sulfonic acid	327.0 --> 307.0	20	4.0	0.9930
7	NFDHA	Nonafluoro-3,6-dioxaheptanoic acid	295.0 --> 201.0	4	4.1	0.9990
8	PFBS	Perfluorobutanesulfonic acid	299.0 --> 80.0	48	4.2	0.9985
9	PFHxA	Perfluorohexanoic acid	313.0 --> 269.0	4	4.2	0.9993
10	HFPO-DA	Hexafluoropropylene oxide dimer acid	285.0 --> 169.0	4	4.5	0.9984
11	PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid	315.0 --> 135.0	28	4.6	0.9982
12	5:3FTCA	*2H,2H,3H,3H*-Perfluorooctanoic acid	341.0 --> 237.0	11	4.7	0.9994
13	PFHpA	Perfluoroheptanoic acid	363.0 --> 319.0	8	5.0	0.9993
14	PFPeS	Perfluoropentanesulfonic acid	349.0 --> 80.0	44	5.0	0.9988
15	ADONA	4,8-Dioxa-3H-perfluorononanoic acid	377.0 --> 251.0	8	5.2	0.9993
16	6:2FTS	*1H,1H, 2H, 2H*-Perfluorooctane sulfonic acid	427.0 --> 407.0	24	5.3	0.9932
17	PFOA	Perfluorooctanoic acid	413.0 --> 369.0	8	5.5	0.9992
18	PFHxS	Perfluoropentanesulfonic acid	399.0 --> 80.0	52	5.6	0.9991
19	7:3FTCA	3-Perfluoroheptyl propanoic acid	441.0 --> 337.0	11	6.0	0.9995
20	PFNA	Perfluorononanoic acid	463.0 --> 419.0	8	6.0	0.9991
21	PFHpS	Perfluoroheptanesulfonic acid	449.0 --> 80.0	68	6.2	0.9990
22	8:2FTS	*1H,1H, 2H, 2H*-Perfluorodecane sulfonic acid	527.0 --> 507.0	28	6.3	0.9937
23	PFDA	Perfluorodecanoic acid	513.0 --> 469.0	8	6.5	0.9987
24	NMeFOSAA	N-methyl perfluorooctanesulfonamidoacetic acid	570.0 --> 419.0	19	6.6	0.9981
25	PFOS	Perfluorooctanesulfonic acid	499.0 --> 80.0	72	6.6	0.9995
26	NEtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid	584.0 --> 419.0	19	6.7	0.9993
27	PFUnA	Perfluoroundecanoic acid	563.0 --> 519.0	8	6.9	0.9994
28	9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	531.0 --> 351.0	28	7.0	0.9989
29	PFNS	Perfluorononanesulfonic acid	549.0 --> 80.0	79	7.1	0.9992
30	PFDoA	Perfluorododecanoic acid	613.0 --> 569.0	8	7.3	0.9990
31	PFDS	Perfluorodecanesulfonic acid	599.0 --> 80.0	79	7.5	0.9985
32	PFTrDA	Perfluorotridecanoic acid	663.0 --> 619.0	11	7.7	0.9989
33	11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	630.9 --> 451.0	32	7.8	0.9985
34	PFOSA	Perfluorooctanesulfonamide	498.0 --> 78.0	35	8.1	0.9990
35	PFTeDA	Perfluorotetradecanoic acid	713.0 --> 669.0	11	8.1	0.9982
36	PFDoS	Perfluorododecanesulfonic acid	699.0 --> 80.0	80	8.3	0.9996
37	NMeFOSE	N-methyl perfluorooctanesulfonamidoethanol	616.0 --> 59.0	11	9.2	0.9985
38	NMeFOSA	N-methyl perfluorooctanesulfonamide	512.0 --> 169.0	27	9.4	0.9985
39	NEtFOSE	N-ethyl perfluorooctanesulfonamidoethanol	630.0 --> 59.0	15	9.6	0.9988
40	NEtFOSA	N-ethyl perfluorooctanesulfonamide	526.0 --> 169.0	27	9.7	0.9991

Results and Discussion

A representative chromatogram of the calibration solution 5 (CS5) containing the 40 native compounds is shown in **Figure 1**. As indicated in **Table 2**, linear calibration curves with R^2 ≥0.99 were obtained for all PFAS analytes.

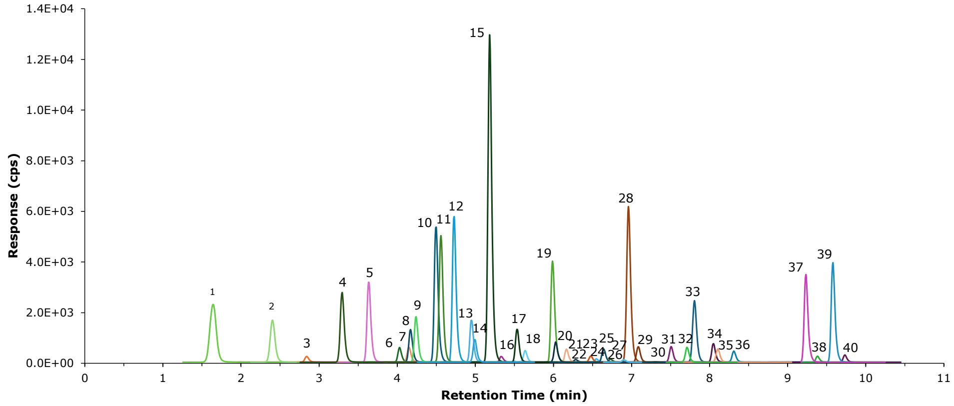

Figure 1. LC-MS/MS chromatogram of 40 PFAS compounds obtained for CS5 in methanol containing 4% water, 1% ammonium hydroxide, and 0.6% acetic acid (Peak IDs see **Table 2**).

Potential PFAS contamination in the solvents was quantified by stable-isotope dilution using extracted internal standards (EIS) that were added to the sample (*n* = 2) prior to SPE. Recovery of the EIS surrogates was assessed using the non-extracted internal standards (NIS), which were spiked into the concentrated extract after the SPE step. The PFAS evaluation of the three solvents across the various grades revealed negligible levels of all investigated PFAS compounds, as all measured values were below the respective lower limits of quantification (LOQ) specified in EPA method 1633A (**Table 3**) for each of the compounds. To account for the varying analyzed sample volumes (500 mL of water, 250 mL of pure methanol, and 250 mL of pure acetonitrile) which result in different LOQs for each solvent, the LOQ for each PFAS compound was additionally calculated for a 1 L bottle size and expressed in parts per trillion (ppt) to improve comparability of the data (**Table 4**).

Tables 5 and 6 present the recoveries determined for the 24 EIS surrogates in the investigated solvents, calculated using the seven NIS compounds that were spiked after extraction. The EPA requirements for acceptable recoveries were met for all analytes examined, as outlined in Table 6 of EPA Method 1633A[1], with most compounds exhibiting recoveries between 73.4% and 109.8%. Lower recoveries between 20.7% and 39.0% were observed for d$_7$-NMeFOSE and d$_9$-NEtFOSE in acetonitrile, which may be attributed to insufficient retention during the SPE loading step caused by the higher eluotropic strength of the acetonitrile samples despite prior dilution.

Table 3. Overview of the investigated solvent grades and the corresponding results for the PFAS compounds

Solvent (Brand)	Grade	Cat. No.	Results for each of the 40 PFAS analytes following EPA method 1633A
Acetonitrile (Supelco®)	HPLC grade	**1.14291**	< LOQ
	Gradient grade	**1.00030**	< LOQ
	UHPLC grade	**1.03725**	< LOQ
	LC-MS grade	**1.00029**	< LOQ
Acetonitrile (Sigma-Aldrich®)	Gradient grade	**34851**	< LOQ
	UHPLC grade	**900667**	< LOQ
Methanol (Supelco®)	HPLC grade	**MX0475**	< LOQ
	Gradient grade	**MX0488**	< LOQ
	UHPLC grade	**1.03726**	< LOQ
	LC-MS grade	**1.06035**	< LOQ
Methanol (Sigma-Aldrich®)	HPLC grade	**34860**	< LOQ
	HPLC plus grade	**646377**	< LOQ
	Gradient grade	**34885**	< LOQ
	UHPLC grade	**900688**	< LOQ
Water (Supelco®)	UHPLC grade	**1.03728**	< LOQ
	LC-MS grade	**1.15333**	< LOQ
Water (Sigma-Aldrich®)	HPLC grade	**270733**	< LOQ
	Gradient grade	**34877**	< LOQ
	UHPLC grade	**900682**	< LOQ

Table 4. Compound-specific LOQ values of EPA method 1633A expressed in ng/mL and corresponding LOQ values for the analyzed solvent samples expressed in ppt

Native PFAS compounds	Water Samples LOQ (ppt)	Methanol Samples LOQ (ppt)	Acetonitrile Samples LOQ (ppt)
Perfluoroalkyl carboxylic acids (LOQ: 0.2 – 0.8 ng/mL)			
PFBA	8	16	16
PFPeA	4	8	8
PFHxA	2	4	4
PFHpA			
PFOA			
PFNA			
PFDA			
PFUnA			
PFDoA			
PFTrDA			
PFTeDA			

Native PFAS compounds	Water Samples LOQ (ppt)	Methanol Samples LOQ (ppt)	Acetonitrile Samples LOQ (ppt)
Perfluoroalkyl sulfonic acids (LOQ: 0.2 ng/mL)			
PFBS	2	4	4
PFPeS			
PFHxS			
PFHpS			
PFOS			
PFNS			
PFDS			
PFDoS			
Fluorotelomer sulfonic acids (LOQ: 0.8 ng/mL)			
4:2FTS	8	16	16
6:2FTS			
8:2FTS			
Perfluorooctane sulfonamides (LOQ: 0.2 ng/mL)			
PFOSA	2	4	4
NMeFOSA			
NEtFOSA			
Perfluorooctane sulfonamidoacetic acids (LOQ: 0.2 ng/mL)			
NMeFOSAA	20	40	40
NEtFOSAA			
Perfluorooctane sulfonamide ethanols (LOQ: 2 ng/mL)			
NMeFOSE			
NEtFOSE			
Per- and Polyfluoroether carboxylic acids (LOQ: 0.4 - 0.8 ng/mL)			
HFPO-DA	8	16	16
ADONA			
PFMPA	4	8	8
PFMBA			
NFDHA			
Ether sulfonic acids (LOQ: 0.4 - 0.8 ng/mL)			
9Cl-PF3ONS	8	16	16
11Cl-PF3OUdS			
PFEESA	4	8	8
Ether sulfonic acids (LOQ: 0.4 - 0.8 ng/mL)			
3:3FTCA	10	20	20
5:3FTCA	50	100	100
7:3FTCA			

Table 5. Recoveries (*n* = 2) of extracted internal standards (EIS) for the tested water and acetonitrile solvents, together with the acceptance criteria specified for aqueous matrices in EPA method 1633A

EIS compounds	Recovery in %										
	Water (Supelco®)		Water (Sigma-Aldrich®)			Acetonitrile (Supelco®)				Acetonitrile (Sigma-Aldrich®)		Acceptance criteria of EPA method 1633A (aqueous matrices)
	UHPLC grade	LC-MS grade	HPLC grade	Gradient grade	UHPLC grade	HPLC grade	Gradient grade	UHPLC grade	LC-MS grade	Gradient grade	UHPLC grade	
$^{13}C_4$-PFBA	98.0	100.4	99.1	101.2	92.0	99.0	100.9	100.3	99.4	99.3	101.1	5 – 130
$^{13}C_5$-PFPeA	97.2	103.6	102.1	104.2	102.1	102.0	103.6	103.3	102.2	102.5	104.1	40 – 130
$^{13}C_5$-PFHxA	94.4	99.9	98.9	100.2	99.4	99.4	100.8	98.6	97.6	96.8	99.1	40 – 130
$^{13}C_4$-PFHpA	94.9	102.6	99.2	102.7	99.2	99.3	99.7	101.3	100.4	98.4	99.6	40 – 130
$^{13}C_8$-PFOA	95.9	100.0	96.8	98.8	97.2	96.4	97.5	97.7	97.2	97.0	99.2	40 – 130
$^{13}C_9$-PFNA	96.0	102.5	100.8	99.9	98.9	99.0	101.1	100.9	101.3	99.6	103.1	40 – 130
$^{13}C_6$-PFDA	95.8	101.0	97.7	99.8	95.6	95.8	101.4	103.1	97.2	96.3	97.3	40 – 130
$^{13}C_7$-PFUnA	98.7	101.1	100.4	99.7	97.1	99.4	104.9	102.8	100.3	98.5	102.0	30 – 130
$^{13}C_2$-PFDoA	92.1	95.8	95.1	98.1	92.3	94.2	97.9	98.6	95.9	97.6	98.5	10 – 130
$^{13}C_2$-PFTeDA	89.2	93.3	92.5	92.5	88.4	96.3	99.0	100.1	97.9	98.3	98.6	10 – 130
$^{13}C_3$-PFBS	102.3	109.8	106.7	105.8	104.9	101.4	101.2	106.2	101.7	100.8	104.9	40 – 135

EIS compounds	Recovery in %											
	Water (Supelco®)		Water (Sigma-Aldrich®)			Acetonitrile (Supelco®)				Acetonitrile (Sigma-Aldrich®)		Acceptance criteria of EPA method 1633A (aqueous matrices)
	UHPLC grade	LC-MS grade	HPLC grade	Gradient grade	UHPLC grade	HPLC grade	Gradient grade	UHPLC grade	LC-MS grade	Gradient grade	UHPLC grade	
$^{13}C_3$-PFHxS	95.6	105.6	98.8	103.4	100.4	96.4	96.9	96.7	94.6	93.2	93.6	40 – 130
$^{13}C_8$-PFOS	97.4	106.4	100.1	102.1	100.6	95.6	100.4	96.6	96.1	98.0	99.6	40 – 130
$^{13}C_2$-4:2FTS	95.5	104.2	98.8	93.7	97.2	100.7	99.8	101.1	97.7	96.9	100.4	40 – 200
$^{13}C_2$-6:2FTS	92.3	101.4	94.6	98.7	93.3	95.4	94.6	95.4	94.1	92.8	97.4	40 – 200
$^{13}C_2$-8:2FTS	88.2	97.1	95.2	91.4	91.4	85.3	94.3	94.5	92.0	90.7	94.0	40 – 300
$^{13}C_8$-PFOSA	88.7	97.9	97.1	96.9	90.7	76.8	82.7	73.4	76.7	77.6	77.9	40 – 130
D_3-NMeFOSA	75.5	83.3	95.2	91.7	80.3	96.2	105.2	99.2	96.2	96.8	99.2	10 – 130
D_5-NEtFOSA	76.0	85.7	96.2	93.3	79.5	95.5	105.7	98.5	98.2	99.5	98.2	10 – 130
D_3-NMeFOSAA	92.8	103.1	102.3	101.3	95.6	99.4	104.6	99.6	101.7	103.2	105.4	40 – 170
D_5-NEtFOSAA	87.5	100.7	94.7	95.7	91.6	96.5	100.8	96.3	96.5	99.6	101.1	25 – 135
D_7-NMeFOSE	85.0	93.4	92.6	91.7	90.4	21.5	23.5	24.9	20.7	24.5	22.0	10 – 130
D_9-NEtFOSE	83.3	91.8	89.7	89.3	87.4	33.6	36.6	39.0	32.1	38.2	34.5	10 – 130
$^{13}C_3$-HFPO-DA	99.3	105.7	105.7	105.3	105.5	104.2	105.4	105.4	104.2	103.6	106.4	40 – 130

Table 6. Recovery (n = 2) of Extracted Internal Standards (EIS) for tested methanol solvents, together with the acceptance criteria specified for aqueous matrices in EPA method 1633A

EIS compounds	Recovery in %								
	Methanol (Supelco®)				Methanol (Sigma-Aldrich®)				Acceptance criteria of EPA method 1633A (aqueous matrices)
	HPLC grade	Gradient grade	UHPLC grade	LC-MS grade	HPLC grade	HPLC grade plus	Gradient grade	UHPLC grade	
$^{13}C_4$-PFBA	98.3	99.0	99.7	99.9	102.4	99.7	100.7	99.8	5 – 130
$^{13}C_5$-PFPeA	100.1	102.9	103.0	103.4	103.2	100.1	103.6	102.8	40 – 130
$^{13}C_5$-PFHxA	96.6	98.7	98.7	98.4	103.5	98.2	101.5	100.0	40 – 130
$^{13}C_4$-PFHpA	98.7	100.2	100.5	100.1	101.7	100.9	102.3	102.2	40 – 130
$^{13}C_8$-PFOA	94.3	95.4	98.4	97.5	99.1	96.1	97.9	97.8	40 – 130
$^{13}C_9$-PFNA	99.0	98.8	98.6	100.9	101.9	100.2	100.5	100.5	40 – 130
$^{13}C_6$-PFDA	98.4	101.5	99.8	102.6	99.7	99.9	99.9	100.2	40 – 130
$^{13}C_7$-PFUnA	98.9	99.9	102.1	103.4	103.3	102.5	100.0	100.8	30 – 130
$^{13}C_2$-PFDoA	96.7	97.7	98.9	99.1	99.1	102.0	96.0	99.3	10 – 130
$^{13}C_2$-PFTeDA	97.1	99.2	100.7	99.3	98.1	99.8	94.7	97.1	10 – 130
$^{13}C_3$-PFBS	101.3	104.4	107.9	101.7	108.3	103.3	106.5	101.4	40 – 135
$^{13}C_3$-PFHxS	95.2	97.2	97.9	97.4	103.8	95.5	100.9	99.3	40 – 130
$^{13}C_8$-PFOS	94.2	101.1	97.6	99.6	103.0	99.7	106.2	96.1	40 – 130
$^{13}C_2$-4:2FTS	96.8	100.7	103.0	98.3	103.4	98.3	100.8	98.1	40 – 200
$^{13}C_2$-6:2FTS	92.7	97.2	100.2	95.8	99.8	95.1	98.5	93.7	40 – 200
$^{13}C_2$-8:2FTS	92.5	104.7	100.2	92.8	95.4	91.6	98.5	94.6	40 – 300
$^{13}C_8$-PFOSA	95.6	98.2	97.2	98.2	102.0	99.4	102.3	94.9	40 – 130
D_3-NMeFOSA	90.7	96.1	96.8	97.8	101.5	95.4	99.3	94.8	10 – 130
D_5-NEtFOSA	95.3	98.8	98.8	99.0	101.9	99.6	96.8	96.7	10 – 130
D_3-NMeFOSAA	102.5	105.5	104.8	104.2	108.6	106.5	109.4	100.3	40 – 170
D_5-NEtFOSAA	98.6	102.5	101.4	101.1	104.2	100.8	109.1	100.2	25 – 135
D_7-NMeFOSE	96.7	104.7	100.3	100.0	104.9	101.3	104.0	97.0	10 – 130
D_9-NEtFOSE	95.4	100.2	99.5	98.7	104.3	98.8	101.4	96.4	10 – 130
$^{13}C_3$-HFPO-DA	102.3	105.6	106.1	104.9	106.3	104.1	107.1	105.2	40 – 130

Conclusion

An adjusted workflow based on EPA method 1633A was applied for the analysis of 40 PFAS compounds in water, methanol, and acetonitrile of various grades using SPE with a Supelclean™ ENVI-WAX™ cartridge followed by LC-MS/MS quantification with Ascentis® Express PFAS analytical and delay columns. Robust method performance was demonstrated by satisfactory recovery values for all 24 EIS surrogates, which fell within the acceptance range of EPA method 1633A. None of the investigated solvents showed PFAS contamination at levels exceeding the respective LOQs defined in EPA Method 1633A, indicating their suitability for trace-level PFAS analysis according to the relevant analytical methods issued by regulatory agencies. Laboratories operating under the EPA 1633 guideline remain responsible for independent verification of each reagent lot to avoid issues with method blanks and other quality control samples. When available, certification of PFAS levels in additives and solvents provided by the supplier is sufficient for meeting this requirement. As a consequence we introduced the "tested for PFAS Methods LiChrosolv®" solvents which are tested according to three EPA method incl. EPA 1633 as documented in their certificate of analysis (CoA).

Related Products

Description	Cat. No.
Sample Prep	
Supelclean™ ENVI-WAX™ SPE Tube, 500 mg, volume 6 mL, Pk.30	**54057-U**
Visiprep™ SPE Manifold, PTFE Free, standard, 12-port model	**57030-U**
Large Volume SPE Reservoir, volume 25 mL, Pk. 30	**54258-U**
HPLC	
Ascentis® Express PFAS 90 Å, 2.7 µm, 5 cm x 2.1 mm I.D.	**53557-U**
Ascentis® Express PFAS Delay 160 Å, 2.7 µm, 5 cm x 3.0 mm I.D.	**53572-U**
Solvents	
Acetonitrile tested for PFAS Methods LiChrosolv® (Supelco®)	**1.04726**
Methanol tested for PFAS Methods LiChrosolv® (Supelco®)	**1.04732**
Water tested for PFAS Methods LiChrosolv® (Supelco®)	**1.04735**
Acetonitrile, HPLC grade, LiChrosolv® (Supelco®)	**1.14291**
Acetonitrile, Gradient grade, LiChrosolv® (Supelco®)	**1.00030**
Acetonitrile, LC-MS grade, LiChrosolv® (Supelco®)	**1.00029**
Acetonitrile, UHPLC grade, LiChrosolv® (Supelco®)	**1.03725**
Acetonitrile, Gradient grade (Sigma-Aldrich®)	**34851**
Acetonitrile, UHPLC grade (Sigma-Aldrich®)	**900667**
Methanol, HPLC grade (Supelco®)	**MX0475**
Methanol, Gradient grade (Supelco®)	**MX0488**
Methanol, LC-MS grade, LiChrosolv® (Supelco®)	**1.06035**
Methanol, UHPLC grade, LiChrosolv® (Supelco®)	**1.03726**
Methanol, HPLC grade (Sigma-Aldrich®)	**34860**
Methanol, HPLC plus grade (Sigma-Aldrich®)	**646377**
Methanol, Gradient grade (Sigma-Aldrich®)	**34885**
Methanol, UHPLC grade (Sigma-Aldrich®)	**900688**
Water, LC-MS grade, LiChrosolv® (Supelco®)	**1.15333**
Water, UHPLC grade, LiChrosolv® (Supelco®)	**1.03728**
Water, HPLC grade (Sigma-Aldrich®)	**270733**
Water, Gradient grade (Sigma-Aldrich®)	**34877**
Water, UHPLC grade (Sigma-Aldrich®)	**900682**
Reagents	
Ammonium acetate LiChropur™, eluent additive for LC-MS	**73594**
Formic acid for LC-MS LiChropur™	**5.33002**
Ammonium hydroxide for LC-MS LiChropur™	**5.33003**
Acetic acid for LC-MS LiChropur™	**5.33001**
Accessories	
BRAND® PP graduated centrifuge tube, screw cap, volume 15 mL, without base, non-sterile, Pk. 750	**BR114817**
Nalgene Polypropylene bottles, style 2104, Pk.12	**B9282**
Certified Reference Materials TraceCERT®	
Perfluorobutanoic acid (PFBA), 10 mg	**75930**
Perfluoropentanoic acid (PFPeA), 10 mg	**73551**
Perfluorohexanoic acid (PFHxA), 25 mg	**93899**
Perfluoroheptanoic acid (PFHpA), 25 mg	**93983**
Perfluorooctanoic acid (PFOA), 25 mg	**93973**
Perfluorononanoic acid (PFNA), 10 mg	**05167**
Perfluorodecanoic acid (PFDA), 10 mg	**91367**
Perfluoroundecanoic acid (PFUnA), 10 mg	**89988**
Perfluorododecanoic acid (PFDoA), 10 mg	**76467**
Perfluorotridecanoic acid (PFTrDA), 10 mg	**76705**
Perfluorotetradecanoic acid (PFTeDA), 10 mg	**38400**
Perfluorobutanesulfonic acid (PFBS), 25 mg	**93634**
Perfluoroheptanesulfonic acid (PFHpS), 10 mg	**78049**

Description	Cat. No.
Certified Reference Materials TraceCERT®	
Perfluorooctane sulfonic acid, (PFOS), 25 mg	**95181**
Hexafluoropropylene oxide dimer acid (HFPO-DA), 25 mg	**94275**
1H, 1H, 2H, 2H-Perfluorooctane sulfonic acid (6:2FTS), 25 mg	**93497**
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid (8:2FTS), 25 mg	**93587**
Perfluorooctane sulphonamide (PFOSA/FOSA), 25 mg	**95179**
N-Methylperfluorooctanesulfonamide (NMeFOSA), 10 mg	**89868**
N-Ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA), 25 mg	**94707**
N-Methylperfluorooctanesulfonamidoethanol (NMeFOSE), 10 mg	**89348**
Perfluoro-3-methoxypropanoic acid (PFMPA), 25 mg	**73014**
Nonafluoro-3,6-dioxaheptanoic acid (NFDHA), 50 mg	**04292**
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS), 25 mg	**04453**
Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA), 25 mg	**95201**
2H,2H,3H,3H-Perfluorooctanoic acid, 10 mg	**94743**

Find more on PFAS testing at **SigmaAldrich.com/PFAS**

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