



DIRECT MEASUREMENT OF PERFLUOROALKYLATED SURFACTANTS IN THE GREAT LAKES WATER SAMPLES

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ABSTRACT

Perfluoroalkylated surfactants were directly determined from water samples at the parts-per-trillion (ppt, ng/L) level, using a novel approach that avoids the extraction/concentration steps used in the previous studies. Internal standard and standard addition quantification methods were used. The level of 9 selected perfluorinated surfactants in Lake Ontario, Lake Erie, Lake Huron and North Channel waters was determined using this fast robust direct injection method. Perfluorooctane sulfonate (PFOS) was determined in all samples (2-8 ppt), while perfluorooctanoic acid (PFOA) was present in all samples (2-7 ppt), with the exception of the Lake Huron and North Channel samples.

INTRODUCTION

- Considerable effort has been made in the last few years to determine the level of perfluorinated surfactants contamination in the environment, particularly perfluoroalkylated acids.
- The unique physicochemical properties of the perfluorinated compounds (PFCs) contributed to their large industrial and household use over the last 50 years.
- PFCs are part of a large number of surface treatment and surfactant formulations such as fire-fighting foams, special cleaners, mining surfactants and insecticides.
- PFOS and PFOA were reported last year³ in Lake Ontario at concentrations ranging between 15 and 120 ng/L.

SAMPLE PREPARATION

- Samples collected from Lake Ontario (LO1-LO7), Lake Erie (LE1-LE3), Lake Huron (LH1) and North Channel (LS1-LS3) in 2004; one sample was collected from Lake Ontario in 2002 (LO-2002)
- Samples stored in polypropylene bottles at 4 °C
- Aliquots of 0.3 mL sample mixed 1:1 with MeOH containing the internal standards (¹³C₂-PFOA and ¹³C₂-PFDA) and filtered using Whatman Mini-UniPrepTM syringeless filter devices (0.2 µm polypropylene)



INSTRUMENTAL ANALYSIS

LIQUID CHROMATOGRAPH (LC): Agilent 1100TM LC

- LC guard and analytical columns
 - 4 mm x 2.0 mm, Phenomenex SecurityGuardTM C18
 - 50 mm x 2.1 mm, 4µm, Jones GenesisTM C18
- Mobile phase: 20:80 Water/Methanol (10 mM ammonium acetate)
- Isocratic gradient (4 min run)
- Flow rate: 250 µL/min
- Injection volume: 100 µL

MASS SPECTROMETER (MS/MS): ABS/Sciex 4000QTrapTM MS/MS

- Negative electrospray ionization (ESI)
- Q1 & Q3 Resolution : 0.7 amu FWHM
- Optimized MRM Transitions

QUANTIFICATION

- Internal Standard (¹³C₂-PFOA, ¹³C₂-PFDA) & Standard Addition
- 3 replicates with 4 injections for each sample
- 3 different standard additions (+2, +5 and +10 ppt) with 4 injections for each sample

MLOQ: 100-200 fg



RESULTS

Table 1: Concentrations (ng/L) determined using the Standard Addition Method

	PFHxS	PFOS	PFOSA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
LO-1	nd	8.1	<1	nd	6.7	<1	<1	<1	<1
LO-2	nd	3.6	<1	<2	3.3	1.0	<1	<1	1.2
LO-3	nd	6.8	<1	<2	2.5	<1	<1	<1	nd
LO-4	<1	7.1	<1	<2	2.3	<1	<1	nd	nd
LO-5	<1	8.4	<1	<2	2.9	<1	<1	nd	nd
LO-6	<1	4.9	<1	nd	5.7	<1	<1	nd	nd
LO-7	1.8	5.4	<1	nd	2.0	<1	<1	nd	nd
LO-2002	2.9	6.6	nd	nd	8.1	2.0	nd	nd	nd
LE-1	7.3	5.3	<1	nd	<2	<1	<1	nd	nd
LE-2	1.8	4.2	<1	nd	2.2	<1	<1	nd	nd
LE-3	<1	4.0	nd	<2	2.0	<1	<1	nd	nd
LH-1-A	<1	2.0	nd	<2	<2	nd	<1	nd	nd
LH-1-B	<1	3.2	<1	<2	<2	nd	<1	nd	nd
LH-1-C	1.1	2.9	nd	nd	<2	<1	<1	nd	nd
LS-1	nd	2.4	<1	<2	<2	1.7	<1	1.0	2.4
LS-2	2.1	2.3	<1	2.4	<2	1.3	1.0	<1	1.1
LS-3	<1	2.3	<1	nd	<2	1.4	<1	1.2	3.4

Analytes

- Perfluorohexane sulfonate PFHxS
- Perfluorooctane sulfonate PFOS
- Perfluorooctane sulfonamide PFOSA
- Perfluoroheptanoic acid PFHpA
- Perfluorooctanoic acid PFOA
- Perfluorononanoic acid PFNA
- Perfluorodecanoic acid PFDA
- Perfluoroundecanoic acid PFUnA
- Perfluorododecanoic acid PFDoA



Internal Standards

- C13-Perfluorooctanoic acid ¹³C₂-PFOA
- C13-Perfluorodecanoic acid ¹³C₂-PFDA

LC-MS-MS Chromatograms for 10 ppt standard

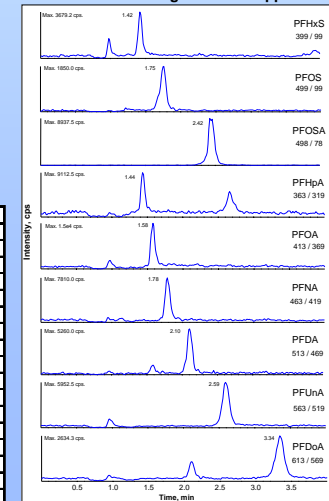


Table 2: Comparison between the values determined for the concentration of PFOS with the standard addition and internal standard methods (¹³C₂-PFOA)

	Standard Addition			Internal Standard		
	Conc (ng/L)	RSD (%)	R2	Conc (ng/L)	RSD (%)	R2
LO-1	8.1	6.98	0.9976	9.5	20.27	0.9988
LO-2	3.6	17.72	0.9953	5.3	27.65	0.9988
LO-3	6.8	9.38	0.9937	9.3	19.38	0.9988
LO-4	7.1	5.98	0.9935	8.7	23.69	0.9988
LO-5	8.4	3.43	0.9995	8.5	23.36	0.9988
LO-6	4.9	25.50	0.9959	6.7	30.65	0.9988
LO-7	5.4	14.85	0.9943	6.5	30.30	0.9988
LE-1	5.3	28.11	0.9818	8.4	45.37	0.9988
LE-2	4.2	14.96	0.9838	5.2	38.38	0.9988
LE-3	4.0	5.76	0.9995	6.2	35.55	0.9988
LH-1-A	2.0	41.32	0.9874	2.9	101.60	0.9988
LH-1-B	3.2	17.43	0.9872	3.1	67.64	0.9988
LH-1-C	2.9	21.08	0.9782	3.6	36.72	0.9988
LS-1	2.4	10.84	0.9949	4.9	12.48	0.9988
LS-2	2.3	6.48	0.9951	4.3	18.83	0.9988
LS-3	2.3	5.27	0.9976	4.1	17.84	0.9988

CONCLUSIONS

- PFCs were determined in all Great Lakes samples after 1:1 dilution with MeOH
- Ion suppression effects were observed and accounts for the relatively small differences between the values obtained using the two quantification methods
- The standard addition method is the preferred quantification method since it is less prone to matrix effects than the internal standard method
- Mass labeled internal standards are required for each analyte to minimize possible quantification errors
- Concentrations of PFOS and PFOA are one order of magnitude lower than the concentrations reported earlier for Lake Ontario³

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