AWRA 2007 SUMMER SPECIALTY CONFERENCE
Vail, Colorado
June 25-27, 2007

DEVELOPMENT OF AN EPA METHOD FOR PERFLUOROALKYL COMPOUNDS IN DRINKING WATER

Jody A. Shoemaker, Brenda K. Boutin, Paul E. Grimmett*

ABSTRACT:

Over the past five years, perfluoroalkyl compounds (PFCs) in water have become an emerging environmental issue. This research focuses on the development of an analytical method for the determination of perfluoroalkyl compounds in drinking water to be used by EPA's Office of Ground Water and Drinking Water for the potential future collection of nationwide occurrence data. Drinking water samples are concentrated by solid phase extraction and analyzed using liquid chromatography/tandem mass spectrometry. For reagent water fortified with 14 target PFCs at 4-34 ng/L, recoveries ranged from 93 to 118% with a relative standard deviation of 2-14%.

KEY TERMS: perfluoroalkyl compounds, solid phase extraction, LC/MS/MS, PFOA, drinking water

INTRODUCTION

PFCs have been manufactured for over a half century and their use has dramatically increased over the years. Due to their unique properties of repelling both water and oil, PFCs have been used in a wide variety of applications, such as carpets, leather, fabric, upholstery, paper, food containers, fire-fighting foams, and pesticides. These compounds received world-wide attention when the presence of perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluorooctane-sulfonamide (PFOSA) were reported in blood and liver samples of marine mammals, birds and fish in both urban and remote locations (Giesy, 2001). Since this finding, a number of researchers have confirmed the global distribution of PFCs in wildlife (Hansen, 2001; Giesy, 2001; Kannan, 2002; Martin, 2004; Kannan, 2001).

PFCs have also been detected globally in ground and surface waters that can be potential sources of drinking water. For example, PFOS and PFOA have been found in surface waters in Japan at concentrations typically below 20 ng/L, with the exception of a few locations where the PFOA concentrations were in the range of 100 to 500 ng/L (Harada, 2003; Saito, 2003; Saito, 2004). Similar PFOS and PFOA concentrations were found in the Great Lakes, the Tennessee River, and ocean water (Boulanger, 2004; So, 2004; Hansen, 2002; Yamashita, 2004).

The 1996 amendments to the Safe Drinking Water Act (SDWA) required the U.S. Environmental Protection Agency (EPA) to establish a Drinking Water Contaminant Candidate List (CCL) that contains a list of drinking water contaminants that the Agency will consider for future regulation. The first CCL was published in 1998 (EPA, 1998) and is updated every five years. Because of the recent interest in PFCs, it is likely that they will be included on a future CCL. One of the key pieces of information that must be available in order to make a regulatory determination is nationwide occurrence data for the chemical contaminants under consideration. Historically, EPA's Office of Ground Water and Drinking Water has collected the necessary occurrence data under its Unregulated Contaminant Monitoring Regulations. To gather the occurrence data, a rugged analytical method, suitable for determination of PFCs in drinking water, is needed. The success of this method development task is expected to result in more accurate monitoring for these contaminants in drinking water.

While several methods for PFCs in water have been reported in the literature, these methods do not adequately address issues specific to analyzing compounds in drinking water for regulatory purposes, such as sample preservatives, internal and surrogate standards, and establishing acceptable background levels. In the method described here, the target analyte list of 14 PFCs (Table 1) included the C6 through C14 perfluorinated carboxylic and C4, C6, and C8 perfluorinated sulfonic acids, as well as two perfluorooctane-sulfonamidoacetates. Drinking water samples were concentrated by solid phase extraction (SPE)

* Respectively, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, 513-569-7298, shoemaker.jody@epa.gov

National Council on the Aging, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, 513-569-7125, boutin.brenda@epa.gov

National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, 513-569-7663, grimmett.paul@epa.gov

and analyzed using liquid chromatography/tandem mass spectrometry (LC/MS/MS). Recovery and precision data for the 14 target PFCs in water are presented. Although a number of health effect studies have been initiated on PFOS and PFOA over the past few years, screening levels and health effects for the PFCs are still being evaluated. Thus, the goal of this method development effort was to obtain detection limits as low as reasonably possible using cost-effective, but sensitive and selective analytical methodology.

MATERIALS AND METHODS

Reagents/Standards

The target analytes were obtained from a variety of sources as shown in Table 1. Ammonium acetate was purchased from Sigma-Aldrich (St. Louis, MO), Trizma® (preset crystals, pH 7.0) from Sigma, cupric sulfate from Fisher, and Absolv grade methanol from Tedia (Fairfield, OH). All spiking mixes and calibration mixes were prepared with 4% water in methanol. Five or six calibration standards were prepared spanning 20-fold in concentration. The calibration standards were spiked with three isotopically labeled internal standards (ISs) and three surrogates (SURs) (See Table 1 for compound identifications). All standards were prepared and stored in 15 mL capped polypropylene centrifuge tubes.

Table 1. List of PFCs evaluated, their acronyms, their sources and IS used for quantitation.

Analyte	Acronym	Source	IS Used
Perfluorobutanesulfonic acid	PFBS	Aldrich	IS-2
Perfluorohexanoic acid	PFHxA	Fluka	IS-1
Perfluoroheptanoic acid	PFHpA	Aldrich	IS-1
Perfluorohexanesulfonic acid	PFHxS	Fluka	IS-2
Perfluorooctanoic acid	PFOA	Aldrich	IS-1
Perfluorononanoic acid	PFNA	Aldrich	IS-1
Perfluorooctanesulfonic acid	PFOS	Fluka	IS-2
Perfluorodecanoic acid	PFDA	Aldrich	IS-2
N-methylperfluorooctanesulfonamidoacetate	NMeFOSAA	3M Environmental Lab	IS-3
N-ethylperfluorooctanesulfonamidoacetate	NEtFOSAA	3M Environmental Lab	IS-3
Perfluoroundecanoic acid	PFUnA	Aldrich	IS-1
Perfluorododecanoic acid	PFDoA	Aldrich	IS-1
Perfluorotridecanoic acid	PFTrA	Exfluor	IS-1
Perfluorotetradecanoic acid	PFTA	Aldrich	IS-1
Internal Standards			
^{13}C-perfluorooctanoic acid	IS-1	PerkinElmer	
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonic acid	IS-2	Wellington Labs	
d_3-N-methylperfluoro-1-octanesulfonamidoacetic acid	IS-3	Wellington Labs	
Surrogate Standards			
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	SUR-1	Wellington Labs	IS-1
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	SUR-2	Wellington Labs	IS-1
d_5-N-ethylperfluoro-1-octanesulfonamidoacetic acid	SUR-3	Wellington Labs	IS-3

Solid Phase Extraction

All 250 mL water samples in polypropylene bottles were preserved with 0.5 mg/L cupric sulfate and 5 g/L trizma to prevent microbial growth and bind the free chlorine. Samples were extracted using a Zymark AutoTrace SPE WorkStation (Hopkinton, MA) and Varian (Palo Alto, CA) styrene divinyl benzene (SDVB) polymer cartridges (6 mL, 500 mg). The cartridges were conditioned with 15 mL of methanol followed by 18 mL of deionized water. Water samples, fortified with method analytes and surrogates, were passed through the cartridges. Polypropylene tubing was used to transfer the samples from the bottles to the cartridges. The cartridges and sample bottles were rinsed with two 7.5 mL aliquots of deionized water. The target analytes were eluted from the SDVB cartridges by rinsing the sample bottles with two 4 mL aliquots of methanol and pulling the solvent through the sample transfer lines and the cartridges in a dropwise fashion. Extracts were evaporated to dryness with nitrogen in a 65ºC water bath, spiked with the internal standards and reconstituted to 1 mL with methanol containing 4% deionized water. Small aliquots of the extracts were transferred with polyethylene pipettes to polypropylene 0.7 mL autosampler vials with molded polypropylene caps.

LC/MS/MS

Extracts were analyzed on a Waters Micromass (Manchester, U.K.) Premier triple quadrupole mass spectrometer equipped with an atmospheric pressure ionization source and a Waters (Milford, MA) Acquity LC. The target analytes were ionized by negative ion electrospray. Quantitation was performed using selected reaction monitoring (SRM) MS/MS where the $[M-H]^-$ was selected with the first quadrupole mass analyzer and the third quadrupole mass analyzer scanned the predominant product ion with a mass width of 0.5 daltons. A Waters Atlantis dC18 (2.1 x 150 mm, 5 µm) analytical column was used to separate the target analytes at a flow rate of 0.3 mL/min. The injection volume was 10 µL. The binary mobile phase gradient composition was (A) 20 mM ammonium acetate (ammonium acetate in deionized water) and (B) methanol. The gradient was held at initial conditions of 60:40 A:B for 1 min, then stepped to 10:90 A:B in 24 minutes and held for 7 min. The post equilibration time was minimized to 5 min.

RESULTS/DISCUSSION

During the course of method development, a number of important issues were identified that affect the determination of PFCs in drinking water. Not surprisingly, many of these target PFCs are in many laboratory supplies and instrumentation. It was discovered that while idle for more than one day, PFCs built up in the Teflon® solvent transfer lines. To prevent long delays in purging high levels of PFCs from the LC solvent lines, they were replaced with PEEK™ tubing and the Teflon® solvent frits replaced with stainless steel frits. In addition, LC system components, as well as the mobile phase constituents, were found to contain many of the target analytes in this method. Thus, these PFCs will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFC peaks and to keep background levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). While it is not possible to remove all PFC background contamination, these measures help to minimize their levels.

The data presented in Table 2 demonstrate that all 14 target PFCs are well retained on SDVB cartridges in deionized water and chlorinated surface water. The mean recoveries were 93-118% with % relative standard deviations (%RSDs) ≤ 14% in deionized water spiked at approximately ≤ 10 times the detection limit (DL). Chlorinated surface water spiked with the PFCs near the mid-level calibration point yielded mean recoveries of 92-104% with %RSDs ≤ 11%. These recoveries meet the drinking water method development data quality objectives of 70-130% and %RSDs of <30%. The detection limits obtained by this method are also shown in Table 2 and range from 1.1 to 9.7 ng/L.

Table 2. Detection limits, recovery and precision data for spiked deionized water and chlorinated surface water.

		Spiked Deionized Water (n=7)			Spiked Chlorinated Surface Water (n=7)		
Analyte	**DL[a] ng/L**	**Spike Level ng/L**	**Mean Recovery %**	**RSD %**	**Spike Level ng/L**	**Mean Recovery %**	**RSD %**
PFBS	2.1	9.1	98	7.5	91	92	6.8
PFHxA	1.2	5.0	106	7.4	50	103	5.5
PFHpA	1.4	12	108	4.1	41	101	3.4
PFHxS	4.2	34	108	2.9	113	95	2.8
PFOA	2.6	14	110	3.0	46	104	6.2
PFNA	1.1	14	106	3.3	48	93	3.1
PFOS	1.7	9.6	118	4.8	96	92	11
PFDA	1.6	11	103	5.5	37	95	2.7
NMeFOSAA	9.7	20	108	14	202	95	5.5
NEtFOSAA	7.9	21	116	10	214	94	5.5
PFUnA	1.5	11	116	6.6	54	95	3.6
PFDoA	1.2	3.7	112	9.3	37	100	5.6
PFTrDA	1.9	11	107	4.0	55	102	4.6
PFTA	2.2	8.7	113	4.8	44	97	4.1
SUR-1		40	94	2.2	40	95	6.4
SUR-1		40	98	3.8	40	102	6.5
SUR-3		160	93	5.1	160	95	7.6

[a] DL=Detection Limit = $St_{(n-1,\ 1-alpha\ =\ 0.99)}$, where S is the standard deviation of replicate analyses and $t_{(n\ 1,1\ alpha\ =\ 0.99)}$ is the Student's t value for the 99% confidence level with n-1 degrees of freedom, n is number of replicates (Glaser, 1981).

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

Boulanger, B.; J. Vargo, J. L. Schnoor and K. C. Hornbuckle, 2004. Detection of perfluorooctane surfactants in Great Lakes water. Environ Sci Technol 38:4064-70.

EPA, 1998. Announcement of the Drinking Water Contaminant Candidate List., Fed. Regist. 63, pp. 10274-10287.

Giesy, J.P. and K. Kannan, 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 35:1339-42.

Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, 1981. Trace analyses for wastewaters. Environ. Sci. Technol 15:1426-1435.

Hansen, K.J.; H. O. Johnson, J. S. Eldridge, J. L. Butenhoff and L. A. Dick, 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. Environ Sci Technol 36:1681-5 (2002).

Harada, K.; N. Saito, K. Sasaki, K. Inoue and A. Koizumi, 2003. Perfluorooctane sulfonate contamination of drinking water in the Tama River, Japan: estimated effects on resident serum levels. Bull Environ Contam Toxicol 71:31-6.

Kannan, K., J. C. Franson, W. W. Bowerman, K. J. Hansen, P. D. Jones and J. P. Giesy, 2001. Perfluorooctane sulfonate in fish-eating water birds including bald eagles and albatrosses. Environ Sci Technol 35:3065-70.

Kannan, K., K. J. Hansen, T. L. Wade and J. P. Giesy, 2002. Perfluorooctane sulfonate in oysters, Crassostrea virginica, from the Gulf of Mexico and the Chesapeake Bay. USA, Arch Environ Contam Toxicol 42:313-8.

Martin, J.W., M. M. Smithwick, B. M. Braune, P. F. Hoekstra, D. C. Muir and S. A. Mabury, 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ Sci Technol 38:373-80.

Saito, N.; K. Harada, K. Inoue, K. Sasaki, T. Yoshinaga and A. Koizumi, 2004. Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan. J Occup Health 46:49-59.

Saito, N.; K. Sasaki, K. Nakatome, K. Harada, T. Yoshinaga and A. Koizumi, 2003. Perfluorooctane sulfonate concentrations in surface water in Japan. Arch Environ Contam Toxicol 45:149-58.

So, M.K.; S. Taniyasu, N. Yamashita, J. P. Giesy, J. Zheng, Z. Fang, S. H. Im and P. K. Lam, 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. Environ Sci Technol 38:4056-63.

Taniyasu, S., K. Kannan, Y. Horii, N. Hanari and N. Yamashita, 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ Sci Technol 37:2634-9.

Yamashita, N.; K. Kannan, S. Taniyasu, U. Horii, T. Okazawa, G. Petrick and T. Gamo, 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ. Sci. Technol. 38:5522-28.