

# ANALYSIS OF SELECTED PERFLUORINATED ALKYL ACIDS IN WATER AND SEDIMENT BY LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

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## Introduction

Perfluorinated compounds (PFCs), including perfluorinated carboxylated acids (PFCAs) and perfluorinated sulfonated acids (PFSAs), have been widely applied in carpet coatings, food packaging, shampoos, paper, and fire-fighting foams<sup>(1,2)</sup>. Most of these contaminants are proved persistent in the environment, they have been widely detected in indoor airs, ambient water, soils, sediments, wildlife and humans<sup>(3-6)</sup>. Within different purpose and productive technologies, the carbon chains of these compounds are varied from C4 to C14, which result to differences in physical and chemical properties of them. In another word, a proper method to analysis PFCs including C4 to C14 should be carefully chosen to match the quality control requirements. In the present study, a method was established to analysis PFCs in water and soil, and method uncertainty was also discussed.

## Materials and methods

**Chemicals.** Standards of perfluorobutanoate (PFBA, 98%), perfluoropentanoate (PFPA, 97%), perfluoroheptanoate (PFHpA, 99%), Perflorooctanoate (PFOA, 96%), perfluorononanoate (PFNA, 97%), perfluorodecanoate (PFDA, 98%), perfluoroundecanoate (PFUnA, 95%), perfluorododecanoate (PFDoA, 95%), perfluorotetradecanoate (PFTA, 97%) were purchased from Sigma Aldrich, Perfluorooctanesulfonate (PFOS, 99%) was purchased from Dr. Ehrenstorfer GmbH. Perfluoro-n-[<sup>13</sup>C<sub>8</sub>]octanoic acid (M8PFOA), perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>]octanoic acid (M2PFOA), sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]octanesulfonate (MPFOS), and sodium perfluoro-1-hexanesulfonate (L-PFHxS) were purchased from Wellington Laboratories, which were 50 µg/mL in methanol.

**Solid phase extraction columns chosen.** In this study, two types of solid phase extraction (SPE) columns were compared, one was Oasis<sup>®</sup> HLB (0.2 g, 6 cm<sup>3</sup>) in which polymer of divinyl benzene and N-vinyl pyrrole was filled, the other was Oasis<sup>®</sup> WAX (0.15 g, 6 cm<sup>3</sup>) in which weak anion exchange adsorption materials were filled. HLB was conditioned followed 4mL methanol and 4mL regent water, while WAX was conditioned by 4 mL ammonia methanol solution (w=0.5%) before methanol and water. After sample passed through, HLB was cleaned by water and methanol solutions (w=10%, followed by 20% and 30%); WAX was cleaned by water, ammonium acetate buffer solution (pH=4), and methanol, respectively. At last, analyte adsorbed in HLB column was eluted by 6mL methanol, and analyte adsorbed in WAX column was eluted by 6mL ammonia methanol solution (w=0.5%).

**Extraction solvents for soil chosen.** Generally, oscillation extraction and ultrasonic extraction are widely employed to analysis PFCs in sediment. There were several solutions to extract PFCs from sediment, and they could be grouped into three classes, pure methanol<sup>(7)</sup>, methanol solution in certain proportion<sup>(8)</sup>, and acetic acid solution<sup>(6)</sup>. Within this study, two classes, pure methanol and acetic acid

were compared. And the extraction procedure was followed, 2 g homogenized freeze-dried samples were weighted and transferred to 100 mL PP centrifuge tubes and spiked with 100  $\mu$ L of a 100 ng/mL recovery indicate standards (M8PFOA and MPFOS), to which 8 mL of methanol or acetic acid solution (w=1%) was added after 30 min aging. The 100 mL PP tubes were placed in a constant temperature oscillator rotated at the speed of 200 rpm at 25 °C for 20 min, and then were ultrasound for another 10 min. Each sample was then translated into a 15 mL PP centrifuge tubes for a 10 min centrifugation at the speed of 8000 rpm, the clarification solutions were then moved to a 500 mL PP beaker separately, whereas the soil was moved back to the 100 mL tube. Each sample was oscillated and centrifuged for another two times, and 24 mL methanol or acetic acid solution was combined for WAX enrichment and purification, while methanol extraction was diluted by 300 mL reagent water before passing through WAX.

**Quality assurance and quality control (QA/QC).** Quality assurance and quality control were conducted by analyzing procedure blanks, three different levels of spiked blanks, spiked matrices and duplicate samples. At the same time, surrogate standards were added into each sample before extraction to quantify procedural recoveries. Method detection limits (MDL) and the minimum quantitative concentrations (MQC) were counted by six replicated low spiked blanks, and the equation was followed as:

$$\text{MDL}=2.57*\text{SD (when } n=6, a=0.05, t=2.57); \text{MQC}=4*\text{MDL.}$$

### Results and discussion:

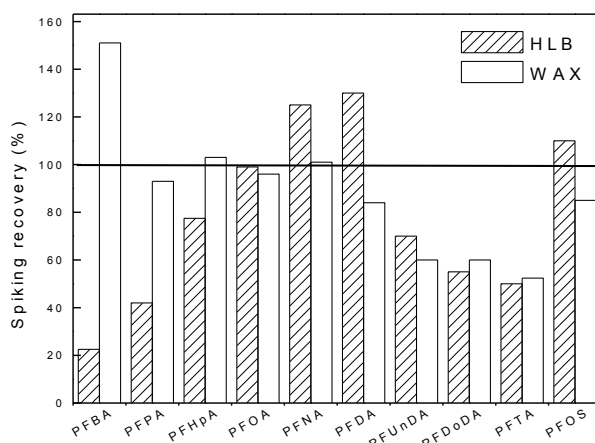


Fig.1 Spiking recoveries in fortified reagent water purified by HLB and WAX.

**Solid phase extraction columns chosen.** The spiking recoveries in fortified reagent water purified by HLB and WAX columns were shown in Fig.1. There was no significant difference in spiking recoveries for PFCAs with carbon chain ranged from C7 to C14. For PFHpA, PFOA, PFNA, PFDA, and PFOS, the recoveries purified by HLB column and WAX column were ranged from 77.5% to 130%, for C11-C14 PFCAs, the recoveries were decreased to 50% to 70%. While, for PFBA and PFPA, recoveries of HLB were much lower than that of WAX. In order to find out losses were caused in which step, water, methanol solutions was analyzed, and it was confirmed that PFBA was eluted in methanol solutions with w=10% and 20%, and PFPA was found in methanol solution with w=30%. Further study shown that when methanol was contained in sample solution (w=5%), parts of PFBA would pass through HLB column. It was suggested that, solid phase extraction column should be carefully chosen for targets.

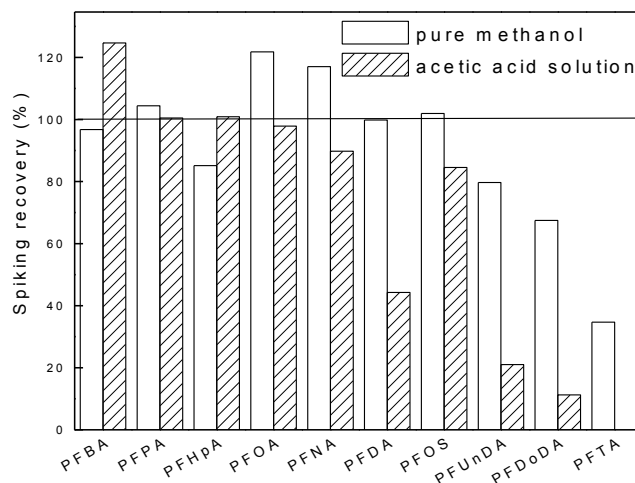


Fig. 2 Spiking recoveries in fortified sediment with methanol and acetic acid solution extraction. **Extraction solvents for sediment chosen.** Duplicate sediment samples were extracted by pure methanol and 1% acetic acid solution, respectively, and then purified by WAX column. For PFACs with C4-C9 and PFOS, the recoveries were stable and acceptable for both two extraction solution. While, the recoveries PFACs with C10 to C14 were decreased along with the carbon chain increased, and less long chain PFACs were concentrated by acetic acid solution extraction than that by pure methanol extraction.

**Measurement uncertainty.**

Table 1. Measurement uncertainties of PFOS and PFOA in water<sup>a</sup>.

Method					Low level fortified					High level fortified					
	D. E. <sup>b</sup>	S. C. <sup>c</sup>	Conc.	Mean	Bias	RSD	n	U	Conc.	Mean	Bias	RSD	n	U	
	%	%	ng/L	ng/L	%	%		%	ng/L	ng/L	%	%		%	
ISO 25101	PFOS	±25	8	2.1	2.6	19	3.3	28	42	43.2	47.8	4.4	4.4	38	27
	PFOA	±25	8	21	17	20	7.3	39	45	374	359	5	5.0	36	21
EPA 537	PFOS	±30	8	9.6	11	17	6.5	7	40	46.0	47.8	3.6	3.6	7	19
	PFOA	±30	8	9.1	11	14	4.1	7	33	96.0	97.0	3.8	3.8	7	18
Present Study	PFOS	±30	8	2.0	1.9	5.7	15	6	36	20.0	19.2	4.2	4.2	6	20
	PFOA	±30	8	2.0	2.1	4.2	9.5	6	26	20.0	20.6	2.9	10	6	26

a: measurement uncertainties were calculated based on fortified reagent water, and the calculation basis was referred to NT Techn Report 537(11).

b: D.E. is demand expanded uncertainty by extraction, purification, and instrument analysis, when recoveries did not lie between D.E., results were rejected as outliers and not counted.

c: S.C. is standard control, because uncertainties introduced by standards were unknown for ISO 25101 and EPA 537, 8%<sup>(11)</sup> were used.

The measurement uncertainties were shown in Table 1, Bias and RSD of duplicated samples contributed more than 50% proportion of the uncertainty. And the uncertainties for low level fortified samples were significantly higher than that of high level fortified samples. It's suggested that uncertainties for analyte with low recoveries or method with poor reproducibility would result to high uncertainty.

**Conclusion.** A method was developed for determining PFCAs and PFSA in water and sediments. In order to meet the requirement of QA/QC, solid phase column should be carefully chosen. Because the losses during washing procedure, HLB column was not suited for short carbon chain compounds (PFBA, PFPA), and WAX column was suited for all analyte except PFTA (C<sub>14</sub>). The measurement

uncertainty of present study had a compared result with EPA method 537 and ISO 25101, which suggested that this method was accurate and reliable. And the uncertainty's calculation procedure also showed that the improvement of analyte recovery and method reproducibility would raise the accuracy and reliability of the method.

### Acknowledgements

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### References:

1. Giesy, JP., Kannan, K., 2001. *Environ. Sci. Technol.* 35, 1339–1342.
2. Paul, AG., Jones, KC., Sweetman, AJ., 2009. *Environ. Sci. Technol.* 43, 386–392.
3. Houde M., Silva AOD., Muir DCG., Letcher RJ., 2011. *Environ. Sci. Technol.*, 45, 7962–7973.
4. Vestergren R., and Cousins IT., 2009. *Environ. Sci. Technol.*, 45, 5565–5575.
5. Harrad S., Wit CA, Abdallah MAE., Bergh C., Björklund JA., Covaci A, Darnerud PO., Boer J., Diamond M., Huber S., Leonards P., Mandalakis M., Ostman C., Haug LS., Thomsen C., Webster TF., 2010. *Environ. Sci. Technol.*, 44, 3221–3231.
6. Naile JE, Khim JS., Wang T., Chen C., Luo W., Kwon BO., Park J., Koh CH., Jones DP., L Y., Giesy JP., 2010. *Environ. Pollu.*, 158, 1237-1244.
7. Sakurai T., Shigeo S., Tomohiko I., Jun K., Keita K., Gen K., Lee JH., Hideaki M., Yoshitaka I., Noriyuki S., Toshihiro H., Masatoshi M., Hiroaki S., 2010. *Environ. Sci. Technol.*, 44, 4110-4115.
8. Lutz A., Nobuyoshi Y., Yeung LWY., Taniyasu S., Yuichi H., Lam PKS., Evinghaus R., 2009. *Environ. Sci. Technol.*, 43, 6969-6975.
9. EPA Method 537. Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS), 2009.
10. ISO 25101. Water quality-Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA)-Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry, 2009.
11. NT Techn Report 537, Handbook for calculation of measurement uncertainty in environmental laboratories, Edition 2, 2004.