EFFECT OF SOLVENT ON ELUTION OF PERFLUORINATED COMPOUNDS FROM WATER AND INDUSTRIAL WASTEWATER SAMPLES

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Introduction

The method development of PFCs analysis in environmental samples has been a major focus for many years[1]. In general, Solid Phase Extraction (SPE) coupled with LC-MS/MS is used to analyze PFCs in environmental matrices. SPE is used for concentrating analyte and removing matrix and inorganic compounds. PresepC-Agri (C_{18}) and Oasis®HLB plus was generally used in SPE process for analyzing PFOS and PFOA in environmental samples[2, 3]. The difficulty in analysis of industrial wastewater was noted from our previous survey [4]. The ineffective SPE procedure and matrix interferences were the two major difficulties for analyzing environmental water and industrial wastewater samples. Literature also reported the difficulty of determination of PFCs in environmental and human samples due to the matrix interferences[5]. To overcome ineffective in analytical procedure, the optimizing SPE process and matrix removal procedure were needed. There are many pretreatment options that can be optimized in SPE procedure. Solvent elution step is one of the major steps in SPE procedure. To identify the proper solvent in elution of PFCs is essential. The purposes of the study were to identify the proper solvent type and percentage for surface water and industrial wastewater samples.

Materials and methods

Conventional PFCs Analysis Method

A sample was filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The filter was then further analyzed by using Accelerated Solvent Extraction (ASE-200) from Dionex, Japan. SPE process was used for concentrating PFCs. The filtrate (500 mL) was passed through a PresepC-Agri (C_{18}) cartridge (Wako, Japan) preconditioned by 10 mL of LC/MS-grade methanol followed by 20 mL Milli-Q water manually. PFCs internal standards were spiked (10 ng/L) into a duplicated sample before loading to find their recoveries. A flow rate of 10 mL/min was maintained through the cartridge. Each cartridge was dried completely under vacuum. Then, the target compounds were eluted with 2×2 mL LC/MS-grade methanol into a polypropylene tube, evaporated to dryness with nitrogen gas, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetronitrile) to final volume 2 mL [4].

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ion was monitored by using multiple reactions monitoring (MRM) mode.

Samples

1. Ultrapure water samples were prepared by using ultrapure water (LC/MS grade) from Wako, Japan and PFCs standards. 1 L PP bottles were used as sample containers.

2. Industrial wastewater samples were collected from two industrial zones from Eastern Thailand in 2008/6. Influent, Aeration tank, and Effluent samples were collected from central wastewater treatment plant of each industrial zone. Effluents from different types of industry (air condition, glass, and electronics) inside industrial zones were also collected.

Optimizing Options

Eight target PFCs were PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS and PFOS. From the difficulties in PFCs analysis, the expected problems in the elution step were listed as (A) Solvent methanol could not eluted eight target PFCs and (B) Eluted too much matrix interferences. The suggested modification for (A) was changing solvent or using combination and for (B) was identifying the specific proper solvent percentage to elute target PFCs. The experimental conditions of each experiment were listed in Table 1.

Table 1. SPE modification experiments

Step	Experiment	Sample	Standard	Cartridge	Solvent
Elution	A. Solvent type	Ultrapure water	PFCs: 10 ng/L *(n=4)*	PresepC-Agri (C18) and Oasis®HLB	methanol, acetronitrile, aceton, isopropanol
	B1. Solvent % (ultrapure water)	Ultrapure water	PFCs: 10 ng/L *(n=4)*	PresepC-Agri (C18) and Oasis®HLB	methanol (10% - 100%), acetronitrile (10% - 100%)
	B2. Solvent % (industrial wastewater)	Industrial wastewater	PFCs: 10 ng/L *(n=10)*	PresepC-Agri (C18) and Oasis®HLB	methanol (10% - 100%), acetronitrile (10% - 100%)

Results and discussion:

(A) Solvent type

Elution experiment was performed to evaluate the suitable solvent for cartridge elution for eight target PFCs. Methanol 2×2 mL was used in conventional process. Other stronger strength solvents: acetronitrile, acetone, and isopropanol were tested in this experiment [6]. The experiment was done by loading PresepC-Agri (C$_{18}$) and Oasis$^{®}$HLB cartridges separately with spiked PFCs standards 10 ng/L in ultrapure water *(n=4)* at the flow rate 5 mL/min. Then, cartridges were dried and separately eluted by methanol, acetronitrile, acetone, and isopropanol (all LC/MS grade) by 2×2 mL. The effect of elution solvent to recovery rates was shown in Figure 1.

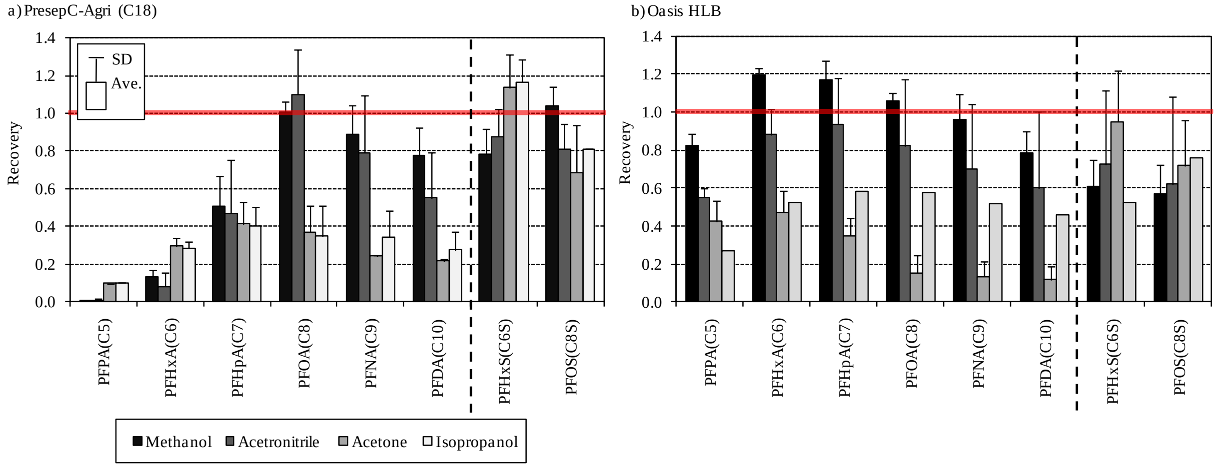


Figure 1. Recovery of a) PresepC-Agri and b) Oasis®HLB eluted by methanol, acetronitrile, acetone and isopropanol

Recoveries of the samples by using methanol and acetronitrile as elution solvents were relatively higher than acetone and isopropanol for all carboxylic acids. Methanol was the better solvent for all carboxylic acids, except PFHxA and PFHpA, which were better by eluting by acetronitrile. Comparing between methanol and acetronitrile, the recovery rate of acetronitrile was slightly better than methanol for eluting perfluorinated sulfonates. As a result, methanol and acetronitrile were both selected as the elution solvent. The suggested elution step was 2 mL methanol followed by 2 mL acetronitrile.

(B1) Solvent Percentage (ultrapure water)

The objective of the experiment was to find suitable solvent percentages to elute each PFC. Conventional process was using 100% solvent. Matrix interferences in LC-MS/MS analysis might be decreased by changing solvent percentages. The experiment was done by loading ultrapure water (1 L) spiked with 10 ng/L PFCs standard passing through PresepC-Agri (C$_{18}$), *(n=8)* and Oasis$^{®}$HLB, *(n=8)* cartridges separately. The cartridges were dried after loading of samples. Half of the samples (*n=4* for each cartridge) were eluted by varying methanol percentages (in ultrapure water) from 10 - 100% (2×2 mL). Another half of the sample (*n=4* for each cartridge) were eluted with 10 - 100% acetronitrile (in ultrapure water), (2×2 mL). Totally, each cartridge was eluted ten times. The extracts were separately collected in PP tubes, then dried by N_2, reconstituted with 40% acetronitrile and analyzed by HPLC-ESI-MS/MS.

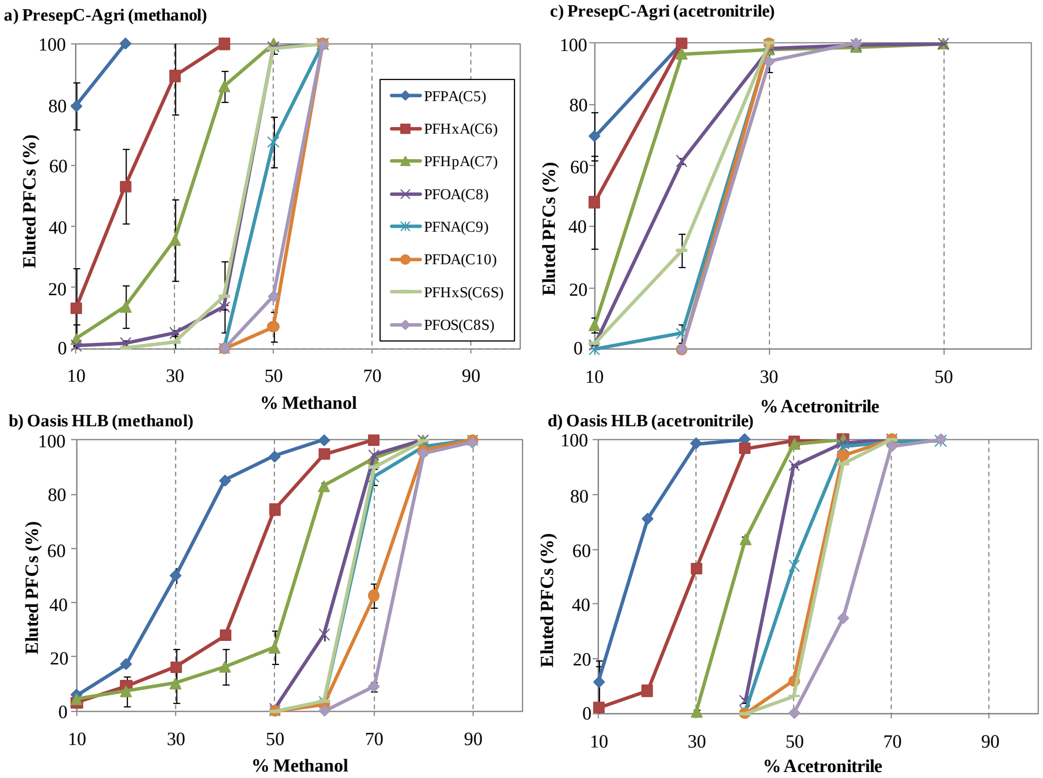


Figure 2. Effect of methanol and acetronitrile percentage on elution of PFCs in ultrapure water

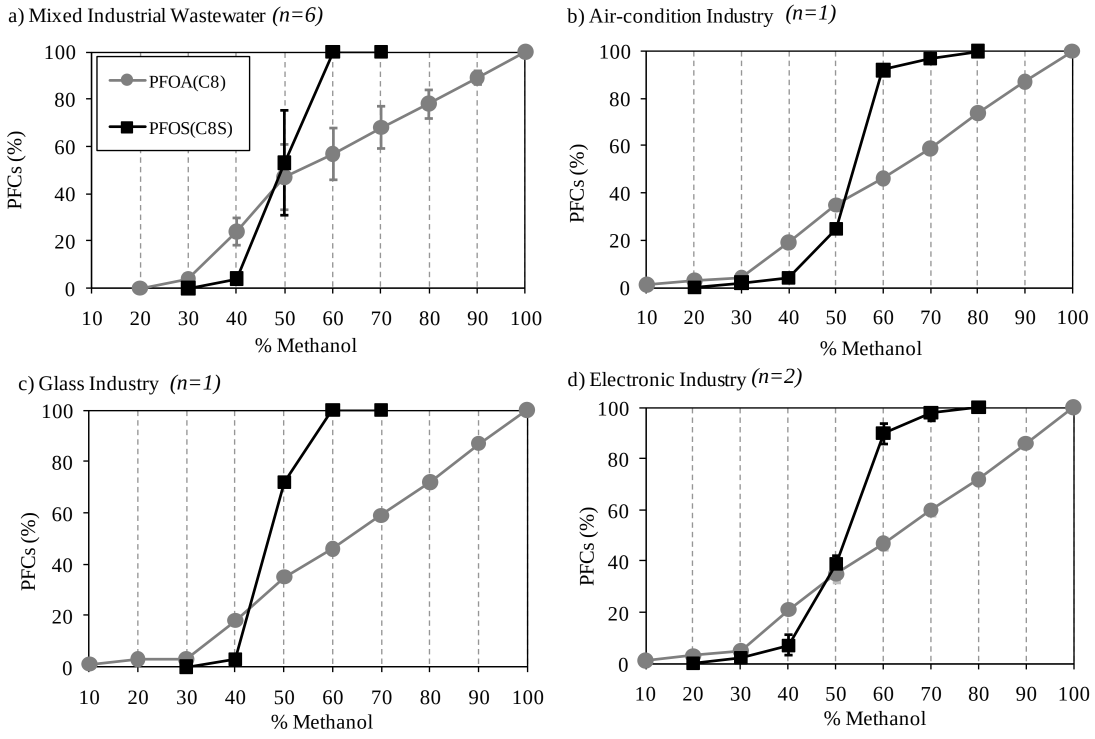
Figure 2a and 2b show the percentages of PFCs eluted by different methanol percentage from PresepC-Agri and Oasis®HLB. All PFCs could elute by 80% methanol from PresepC-Agri and 100% methanol from Oasis®HLB. Methanol percentage for elution of each PFC was varied according to hydrophobic properties. Longer chain PFCs has higher hydrophobic value. Shorter chain PFCs such as PFPA and PFHxA were eluted by lower methanol percentage, while longer chain PFCs such as PFNA and PFDA eluted by higher methanol percentage. PFOS and PFOA, were eluted by 60% methanol from PresepC-Agri cartridge, while eluted by 90% and 80% from Oasis®HLB, respectively. From the results, washing step before eluting each PFC could be performed by using low methanol percentage. For example, when PFOS is only the target compound and PresepC-Agri is used as the cartridge, 40% methanol can use as washing step to eliminate other compound in the extract. In addition, this washing step can be performed together with the elution step, for instance, 60% methanol is used for elution. Thus, the specific target PFC can be eluted with less matrix interferences in the extract.

Figure 2c and 2d show the percentage of PFCs eluted by different percentage of acetronitrile from PresepC-Agri and Oasis®HLB. As acetronitrile is a stronger solvent, lower percentage of solvent was needed to elute all PFCs. All PFCs could eluted by 50% acetronitrile from PresepC-Agri and 80% acetronitrile from Oasis®HLB cartridge. The action of percentage of acetronitrile on PFCs elution was similar to methanol.

(B1) Solvent Percentage (industrial wastewater)

Unlike the environmental water, industrial wastewater contains many chemicals and compounds which interfere the LC-MS/MS detection. Not only the matrix interference but also PFCs might attach to a bigger molecule and cannot elute with the same solvent percentages as performed in the last experiment. The similar solvent percentage experiment was performed to industrial wastewater samples to purpose the technique to reduce matrix interferences in the extracts.

The filtrates (500 mL) were spiked with 10 ng/L PFCs standards and loading through PresepC-Agri (C_{18}) connected with Oasis®HLB cartridges. The cartridges were dried. Samples were eluted by varying methanol percentages (in ultrapure water) of 10 - 100% (2×2 mL). Duplicated samples were eluted with 10 - 100% acetronitrile (in ultrapure water), (2×2 mL). The extracts were separately collected in PP tubes. The extracts were dried by N_2, reconstituted with 40% acetronitrile and analyzed by HPLC-ESI-MS/MS.



Note: Mixed industrial wastewater = samples from WWTP (influent, aeration tank and effluent)

Figure 3. Effect of methanol percentage on elution of PFCs in industrial wastewater samples

Figure 3 shows results of varied methanol percentage for elution from a) mixed industrial wastewater, b) air-condition industry, c) glass industry, and d) electronics industry. Only PFOS, PFOA were shown in the diagram. PFOS could elute by 70 – 80% methanol, which is similar to ultrapure water experiment, while 100% methanol was required for eluting PFOA and other carboxylic acids. The reason might be the perfluorinated acids can easily attached to the matrix and needed higher solvent strength to elute. Significant differences of percentage for elution were not shown in all types of wastewater. For acetronitrile, all PFCs could be eluted by 50% acetronitrile in all samples. Results were not shown much difference in all types of samples. Consequently, 50% acetronitrile could be used for all PFCs elution to reduce the matrix interference in industrial wastewater samples.

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