

Automated, Low Background, Solid Phase Extraction of Perfluorinated Compounds, Pharmaceuticals, and Personal Care Products in Water Samples

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Introduction

Perfluoralkylated substances is a general term used to describe substances which are largely comprised of or contain a perfluorinated or polyfluorinated carbon chain moiety such as $F(CF_2)_n-$ or $F(CF_2)_n-(C_2H_4)_n$. They are widely used in carpets, coatings, fire fighting foams, industrial applications and non-stick cookware. Potential health risks posed by PFCs to humans may have been underestimated.¹

Over the last decade the use of Pharmaceuticals and Personal Care Products (PPCPs) has doubled in the United States. As a result, PPCPs have entered the environment through both human activity and as byproducts from manufacturing, agricultural activities, medical use and veterinarian facilities. This has led in some cases to ppm level concentrations of these compounds in some of the Great Lakes and significant risks for the ecosystem.²

Solid Phase Extraction (SPE) can be used for measuring any of these compound classes in water samples. Automation of the sample prep process can result in faster turnaround time of samples, lower costs, and improved quality of the data generated.

Materials and methods

SPE Procedure for PFCs

The SPE system was loaded with DVB 225 mg cartridges that were then each conditioned with 15 mL methanol and 40 mL water. Five hundred mL water samples were spiked with 25 uL of 1 ug/mL PFC standard solution. Samples were loaded onto the SPE system and passed across the cartridge under -12 psi vacuum. After loading, the bottle was rinsed with 25 mL of water and loaded onto the cartridge under negative pressure. The cartridges were dried using nitrogen until no residual water was present (typically 20 min). The cartridges were then eluted with 15 mL methanol.

SPE Procedure for PPCPs

1. Condition the cartridge with 10 mL of methanol and 10 mL of water 2. Load the 1 liter water sample at 100 mL/min 3. Rinse the cartridge 4. Dry the cartridge with nitrogen and vacuum for 20 minutes 5. Elute the cartridge with 15 mL of methanol base fraction 6. Elute the cartridge with 15 mL of 2% formic acid in methanol 7. The fractions are directly eluted to the SuperVap Concentrator system.

Concentration

The collection tubes with sample were pre-heated in the SuperVap® concentrator to 50 °C for 20 min, followed by heating in the sensor mode under 9 psi of nitrogen which assured automatic shut-off at 0.5 mL. The extracts were concentrated to 500 uL, after which internal standard was added (PFCs). The samples were diluted to a final volume of 1 mL of water for LC/MS analysis.

Analysis

Samples were analyzed with a Waters Acquity® H-class LC and Waters Xevo® TQ MS.



Figure 1. Automated Solid Phase Extraction System for Perfluorinated Compounds and PPCPs.

Results and discussion

Recoveries of spiked standards for PFCs varied between ~ 75-125% (Figure 2) with low background contributions coming from the SPE system. The automated SPE system with PEEK tubing for PFCs produces reliable, reproducible results for perfluorinated compounds in water. The system, by design, has very low background of PFC allowing for analysis of samples without any significant interference.

Figure 3 shows recoveries for a group of PPCPs using automated Solid Phase Extraction. Excellent recoveries are seen between 80-100%. Efficiency of the extraction was increased by the use of nitrogen and vacuum to dry the cartridge and a water free extract that enables a fast concentration step with no loss of analytes. Direct-to-vial connections eliminate the necessity of sample transfer. After concentration into a vial the samples are ready for LC/MS analysis. This eliminates human error, saves time and increases efficiency while producing reproducible, consistent recoveries.

References:

1. Grandjean, P, Clapp, R (2014), *Public Health Rep*, **129** (6), 482-485.
2. Blair, BD, Crago, JP, Hedman, CJ, Klaper, RD (2013), *Chemosphere*, **93** (9), 2116-2123.

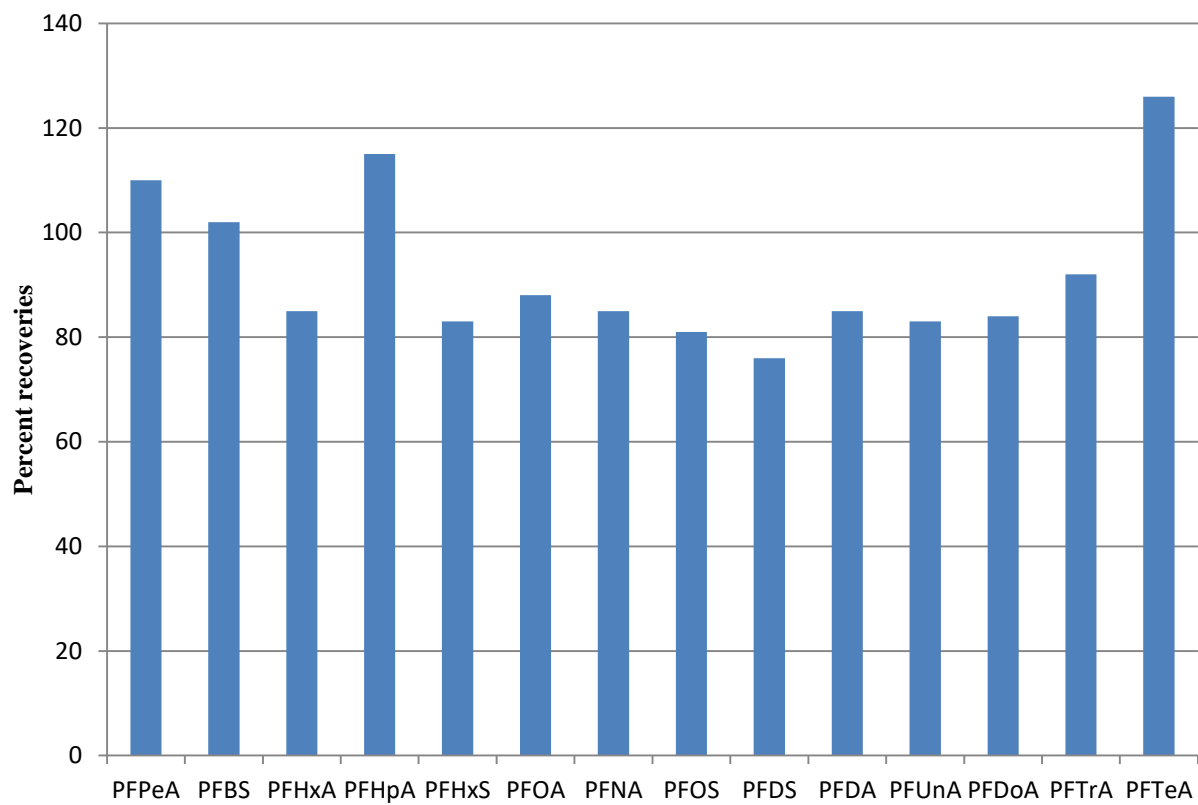


Figure 2. Recoveries for a number of Perfluorinated Compounds.

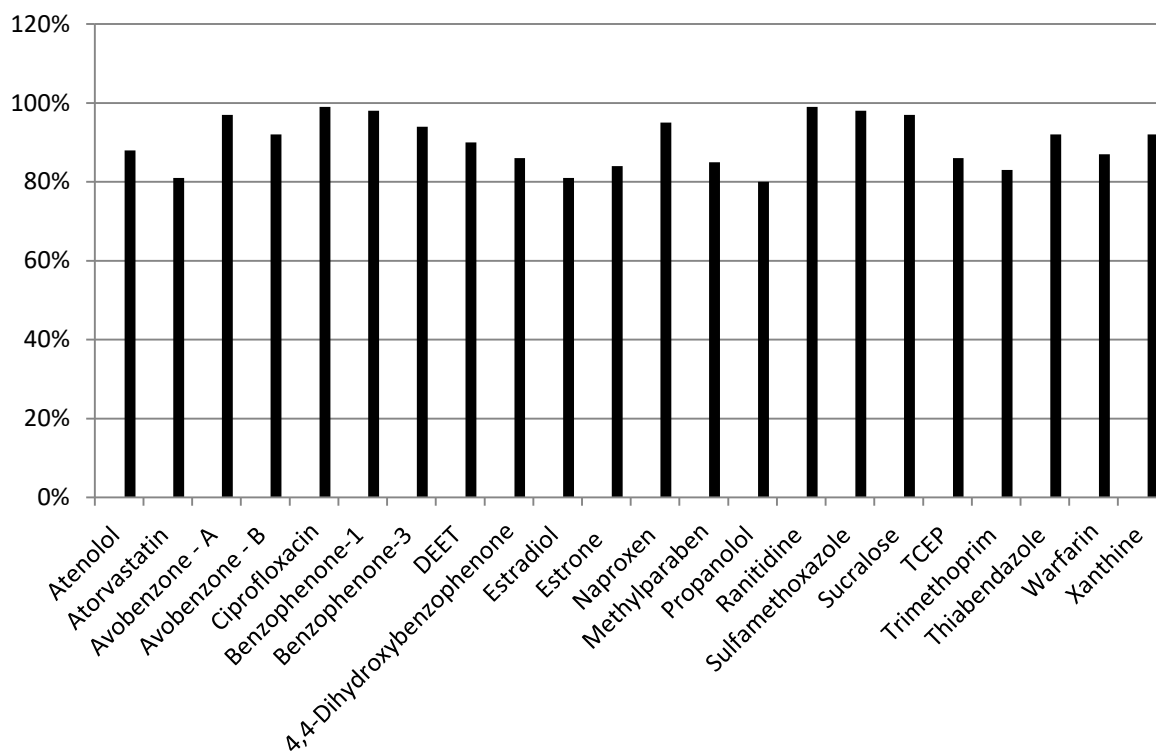


Figure 3. Recoveries for a number of Pharmaceuticals and Personal Care Products..