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Simultaneous determination of per- and polyfluoroalkyl substances in fish: method development, matrix effect evaluation and quantitation methods comparison

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) have been recognized as important environmental contaminants.[1] Perfluorooctanesulfonate (PFOS) have been listed in the Stockholm Convention as persistent organic pollutants (POPs). Perfluorooctanoic acid (PFOA) and perfluorohexanesulfonate (PFHxS) have been listed as POPs candidates.

LC-MS/MS was the most common detection technique for PFASs analysis in fish. However, the results were strongly matrix dependent and varied for different target PFASs. The objectives of this work were to develop sensitive and accurate methods for PFASs detection in fish, to evaluate the matrix effect, and to compare different quantitation methods.

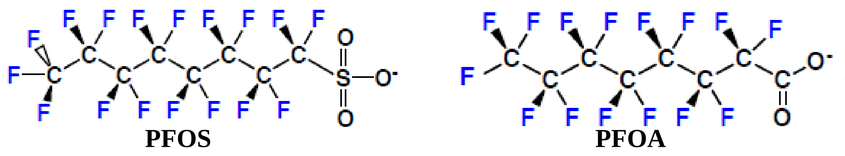


Fig. 1 Molecular structures of PFOS and PFOA

METHODS

Basic methanol (10 mM KOH) extraction and acetonitrile extraction were optimized for PFASs extraction[2]. SPE and QuEChERS methods were developed[2,3]. The analysis of PFASs was performed using a UHPLC-ESI-MS/MS system. PFASs were separated on a Waters ACQUITY UPLC BEH C18 column (1.7 μm, 2.1 mm×100 mm). Acetonitrile and 2 mM ammonium acetate aqueous solution were used as mobile phases.

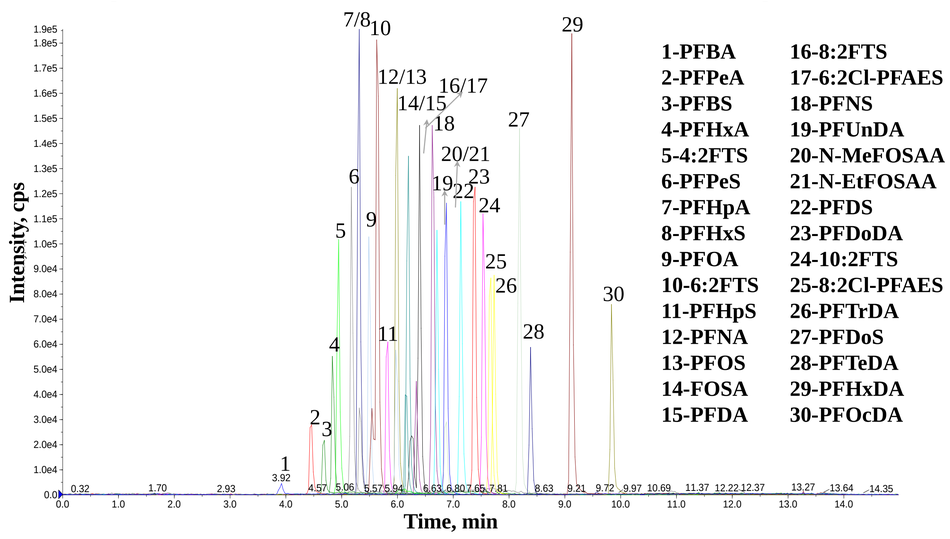


Fig. 2 PFASs chromatogram

RESULTS AND DISCUSSION

PFASs matrix spiked recoveries ranged from 83.75% to 112.99% and 87.09% to 104.10% for basic methanol extraction (alkaline digestion) and acetonitrile extraction respectively. However, more interference peaks were detected by alkaline digestion extraction because of the hydrolysis. Acetonitrile extraction was applied in this study.

For SPE method, OASIS WAX and Envi-carb SPE cartridges were compared. The recoveries of shorter chain PFCAs got better recoveries than longer chain PFCAs for WAX cartridges and the opposite results were found for the Envi-carb cartridges. The longer chain PFCAs got stronger hydrophobicity and weaker acidity than shorter chain PFCAs, which can lead to the relatively weaker stay in the WAX cartridges and the stronger binding capacity in the carbon cartridge. In general, recoveries of WAX cartridges were better than Envi-carb cartridges for shorter chain PFASs. No obvious difference was found for other PFASs (Fig. 3). Therefore, WAX cartridge was selected for PFASs cleanup in this study.

For QuEChERS method, a 4-factor at 3-level Taguchi Orthogonal Arrays experiment was applied in this study (Fig. 4). Experiment 6 exhibited best recoveries and relatively low RSDs for the 30 PFASs (Fig. 4). Recoveries of 30 PFASs in experiment 6 ranged from 83.7% to 116%. The RSDs were all below 9.62%.

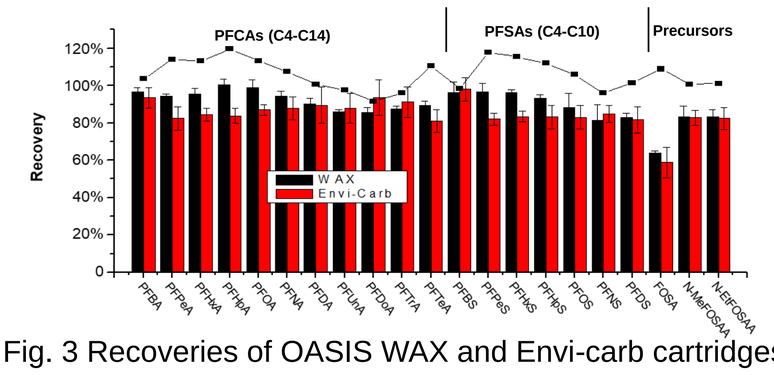
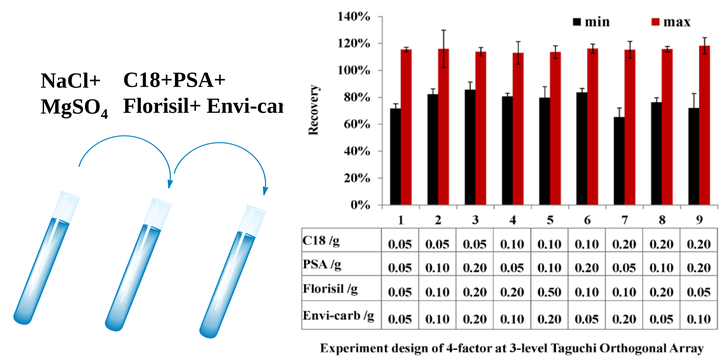


Fig. 3 Recoveries of OASIS WAX and Envi-carb cartridges



	1	2	3	4	5	6	7	8	9
C18 /g	0.05	0.05	0.05	0.10	0.10	0.10	0.20	0.20	0.20
PSA /g	0.05	0.10	0.20	0.05	0.10	0.20	0.05	0.10	0.20
Florisil /g	0.05	0.10	0.20	0.20	0.50	0.10	0.10	0.20	0.05
Envi-carb /g	0.05	0.10	0.20	0.10	0.20	0.05	0.20	0.05	0.10

Experiment design of 4-factor at 3-level Taguchi Orthogonal Array

Fig. 4 Results of Taguchi Orthogonal Array experiment for QuEChERS method

Matrix effect (ME) factors of SPE and QuEChERS methods were in the range of 0.68 to 1.88 and 0.79 to 1.31, respectively. QuEChERS method exhibited higher cleanup efficiency. Matrix effects occurred when the target compounds competed with the co-eluting components from the matrix during the ionization process. The ME factors increased with the increasing of acetonitrile phase proportions in mobile phase at the elution time of individual PFASs (Fig. 5). After correction by isotope labeled internal standards, the ME factors of most PFASs were in the range of 0.96 to 1.07. The results indicated that the matrix effect could be partly compensated by efficient cleanup procedure and the correction of isotope labeled internal standards.

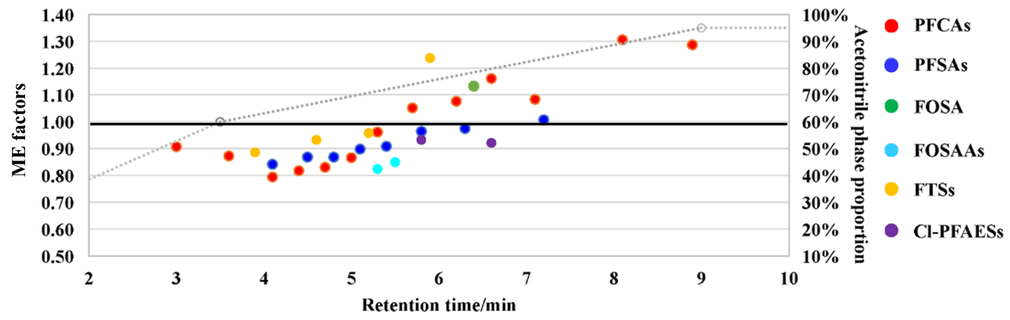


Fig. 5 Relationship between ME factors and mobile phase composition

Quantitation methods of isotope dilution mass spectrometry (IDMS) and standard addition (SA) - IDMS were also compared. The similar quantitative results of IDMS and SA-IDMS also indicate that matrix effect was not obvious on PFASs quantitation by IDMS in this work.

In conclusion, efficient cleanup strategy and IDMS method can compensate the matrix effect to a large extent. The developed methods were efficient, sensitive and accurate for simultaneous determination of PFASs.

REFERENCES

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3. Y. Gao, Q. Zhang, X. Li, X. Li, H. Li. Anal. Meth., 10: 5715-5722 (2018)