# DEVELOPMENT AND VALIDATION OF A PRESSURIZED LIQUID EXTRACTION METHOD TO DETERMINE PERFLUORINATED COMPOUNDS IN FISH

**Y. Picó[1], M. Llorca[2], M. Farré[2], and D. Barceló[2,3]**

[1]Laboratori de Nutrició i Bromatologia, Facultat de Farmàcia, Universitat de València, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain. Tel. +34963543092; Fax: +34 96 3544954; E-mail: Yolanda.Pico@uv.es

[2]Department of Environmental Chemistry, IDAEA-CSIC c/ Jordi Girona, 18-26, 08034 Barcelona, Spain.

[3]Catalan Institute of Water Research, ICRA c/ Pic de Peguera, 15, 17003 Girona, Spain

Bioaccumulation in fish has been shown to be the main influence of perfluorinated compounds (PFCs) in dietary exposure[1,2]. Some reports have also found a positive correlation between PFCs concentrations in plasma and consumption of fish, corroborating the importance of this route[1]. Accordingly, these compounds have been widely analyzed in blood, bile and liver but not so often in the edible part (muscle) of fish. Only levels of PFOS and PFOA have been reported in suitable for eating parts of mussels, oysters, shrimp and fish from different countries. Indeed, it is often impossible to give details of the other PFCs homologues present in this matrix.

This paper describes the development of an analytical methodology to determine eight PFCs in edible fish using pressurized liquid extraction (PLE) with water and solid-phase extraction (SPE) with a ion-exchanger as extraction and pre-concentration procedures, followed by liquid chromatography–triple quadrupole-mass spectrometry (LC–QqQ-MS). The rapidity and effectiveness of the proposed extraction procedure were compared with those most commonly used to isolate PFCs from fish (ion-pairing and alkaline digestion). The average recoveries of the different fish samples, spiked with the eight PFCs at three levels ( at LOQ, 10 and 100 μg kg−1 of each PFC), were always higher than 85 % with relative standard deviation (RSD) lower than 17 %. A good linearity was established for the eight PFCs in the range from 0.1-0.25 to 100 μg kg−1, with r > 0.9994. The limits of quantification (LOQs) were between 0.1 and 0.25 μg kg−1, which improve those previously reported for this type of samples. The method demonstrated its successful application for the analysis of different parts of several fish species. Most of the samples tested positive, mainly for perfluoropentanoic acid (PFPA), perfluorobutane sulfonate (PFBS) and perfluoroctanoic acid (PFOA) but other of the eight studied PFCs were also present.

Table 5. Mean PFCs concentrations (μg $kg^{-1}$) detected in the fish samples analyzed.

| Compound | Hake Roe | Swordfish | Stripped Mullet | | Young Hake | | Anchovy | |
|---|---|---|---|---|---|---|---|---|
| | | | Muscle | Liver | Muscle | Liver | Muscle | Liver |
| PFPA | 50.00 | 12.84 | 42.03 | 12.32 | 0.52 | 0.71 | 0.09 | 0.12 |
| PFBS | 10.00 | 13.45 | < LOQ | 2.04 | < LOQ | 1.24 | 0.83 | 2.23 |
| PFOA | 2.50 | 1.25 | 2.43 | 2.83 | 3.25 | 5.21 | 0.21 | 1.03 |
| i,p-PFNA | 0.44 | 3.24 | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| PFNA | 0.58 | 1.02 | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| PFOS | 23.04 | 8.24 | <LOQ | <LOQ | 1.25 | 3.54 | 0.25 | 0.94 |
| PFDA | <LOQ | 0.24 | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| PFDS | <LOQ | 1.02 | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |

The present study demonstrates that LC–MS/MS using a QqQ mass analyzer was applicable to the simultaneous analysis of 8 PFCs in liver, roe and muscle fish samples. PLE extraction was chosen for the pre-treatment because its being more suitable than par ionic and alkaline digestion for liver and fish samples. It is more rapid, automatic and achieves the simultaneous process of up to 24 samples. The main advantage of this new method over earlier methods is that it provides higher absolute recoveries PFCs, lower LOQs and higher precision.

[1] M. Villagrasa, M.L. de Alda, D. Barcelo, Anal. Bioanal. Chem. 386 (2006) 953.
[2] P. de Voogt, M. Saez, Trac-Trends Anal. Chem. 25 (2006) 326.