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AN LC-Q-ORBITRAP METHOD FOR THE DETERMINATION OF THIRTY-THREE PERFLUOROALKYLATED COMPOUNDS IN LIVER

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Introduction

Perfluoroalkylated substances (PFASs) have been produced since the 1950s and they represent a wide group of highly stable synthetic compounds used in several industrial applications. They are found, for example, in food packaging, non-stick coatings, fireproof foams, paper coatings, fabrics and personal care products. Over the past decade, PFASs have proven to be ubiquitous in water, air, food, wildlife and humans thanks to their high resistance to typical environmental degradation processes. The aim of this work was the development and validation of an analytical method for the determination of a wide group of PFASs in animal liver at ppt level.

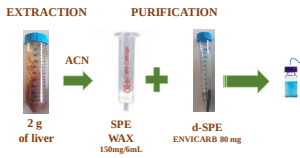

Figure 1- Sample preparation steps

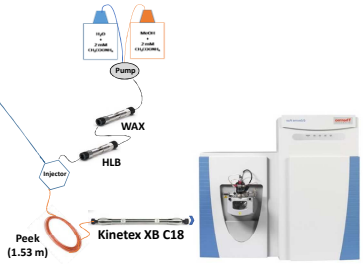

Figure 2- Instrumental settings

Experimental

Thirty-three analytes were included in the method scope together with twenty-one labelled compounds used as internal standards (Table 1). Two grams of homogenized liver were extracted and purified following the protocol suggested by Kärrman et al. [1] with slight modifications. The quantification was performed by liquid-chromatography coupled to Q-Orbitrap analyser (LC-Q Exactive, Thermo Scientific) using ESI negative ionization mode and full scan/SIM acquisitions.

Table 1- List of the 33 analytes and labelled compounds (ISs)

N	Name	Acronym	Labelled compounds
1	Perfluoro-n-butanoic acid	PFBA	$[^{13}C_4]$PFBA
2	Perfluoro-n-pentanoic acid	PFPeA	$[^{13}C_5]$PFPeA
3	Perfluoro-n-hexanoic acid	PFHxA	$[^{13}C_5]$PFHxA
4	Perfluoro-n-heptanoic acid	PFHpA	$[^{13}C_4]$PFHpA
5	Perfluoro-n-octanoic acid	PFOA	$[^{13}C_8]$PFOA
6	Perfluoro-n-nonanoic acid	PFNA	$[^{13}C_9]$PFNA
7	Perfluoro-n-decanoic acid	PFDA	$[^{13}C_6]$PFDA
8	Perfluoro-n-undecanoic acid	PFUdA	$[^{13}C_7]$PFUdA
9	Perfluoro-n-dodecanoic acid	PFDoA	$[^{13}C_2]$PFDoA
10	Perfluoro-n-tridecanoic acid	PFTrDA	$[^{13}C_2]$PFTeDA
11	Perfluoro-n-tetradecanoic acid	PFTeDA	$[^{13}C_2]$PFTeDA
12	Perfluoro-n-hexadecanoic acid	PFHxDA	$[^{13}C_2]$PFHxDA
13	Perfluoro-n-octadecanoic acid	PFODA	$[^{13}C_2]$PFHxDA
14	Potassium perfluoro-1-butanesulfonate	L-PFBS	$[^{13}C_3]$L-PFBS
15	Sodium perfluoro-1-pentanesulfonate	L-PFPeS	$[^{13}C_3]$L-PFHxS
16	Sodium perfluoro-1-hexanesulfonate	L-PFHxS	$[^{13}C_3]$L-PFHxS
17	Sodium perfluoro-1-heptanesulfonate	L-PFHpS	$[^{13}C_3]$L-PFHxS
18	Sodium perfluoro-1-octanesulfonate	L-PFOS	$[^{13}C_8]$L-PFOS
19	Sodium perfluoro-1-nonanesulfonate	L-PFNS	$[^{13}C_9]$PFDA
20	Sodium perfluoro-1-decanesulfonate	L-PFDS	$[^{13}C_7]$PFUdA
21	Sodium perfluoro-1-dodecanesulfonate	L-PFDoS	$[^{13}C_7]$PFUdA
22	Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	$[^{13}C_7]$PFUdA
23	Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	$[^{13}C_7]$PFUdA
24	Sodium 1H,1H,2H,2H-perfluorooctanesulfonate	6:2FTS	$[^{13}C_2]$-6:2FTS
25	Sodium 1H,1H,2H,2H-perfluorodecanesulfonate	8:2FTS	$[^{13}C_2]$8:2FTS
26	3-Perfluoroheptylpropanoic acid	FHpPA	d_3-N-MeFOSAA
27	2-Perfluorooctylethanoic acid	FOEA	$[^{13}C_2]$FOEA
28	2H-Perfluoro-2-decenoic acid	FOUEA	$[^{13}C_2]$FOUEA
29	2,3,3,3-tetrfluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	HFPO-DA	$[^{13}C_3]$HFPO-DA
30	Sodium dodecafluoro-3H-4,8-dioxanonanoate	NaDONA	$[^{13}C_5]$PFHxA
31	N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	d_5-N-EtFOSAA
32	N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	d_3-N-MeFOSAA
33	Potassium perfluoro-4-ethylcyclohexanesulfaonate	PFECHS	$[^{13}C_5]$PFHxA

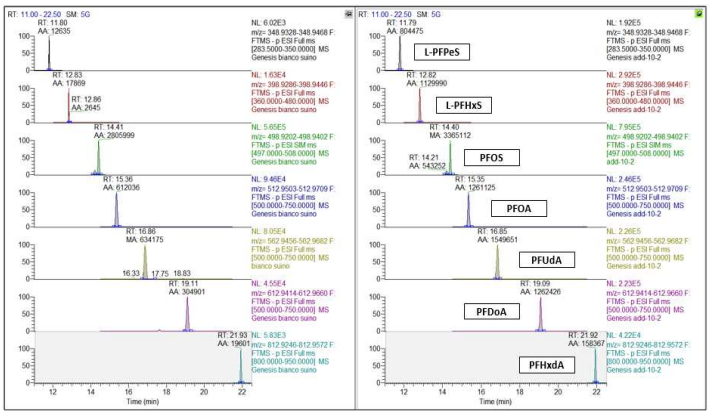

Figure 3- LC-Q-Orbitrap chromatograms of a blank pig liver (left) and pig liver fortified at 10 ng/kg (right). The incurred levels (left side) of PFOS, PFOA, PFUdA, PFDoA were 90, 12, 5 and 4 ng/kg, respectively.

Results and Discussion

One of the major drawback of PFAS analysis is laboratory contamination due to the extensive use of these substances in industrial products and also in labware and equipments. For example, during the preliminary experiments, it was noticed that the LC system released some PFASs (mainly PFOA, PFNA and 6:2FTS). Two cartridges (2.1 x 20 mm) packed with a weak anion exchange (WAX) and hydrophilic-lipophilic balance (HLB) stationary phase, respectively, were therefore installed between the pumping system and the injector device to minimize PFAS emission (Figure 2). With regard to the optimization of chromatographic conditions, to dilute the high percentage of "strong" phase (80% MeOH) contained in the dissolution mixture of the final liver extracts, a peek tube was installed between the injector and the analytical column, improving peak symmetry and reducing broadening. The validation study was performed spiking liver samples (bovine, pig and poultry) at eight concentrations from 2 to 1000 ng/kg on wet weight basis. The intra-laboratory reproducibility CVs were lower than 20% and trueness in the range 80-110%. Detection and quantification limits were from 2 to 50 ng/kg, except HFPO-DA. Method validation was concluded by the analysis of the certified reference material IRMM-427 (pike fish tissue) with results within the ranges indicated by the producer. In Figure 3, the LC-Q-Orbitrap chromatograms of a pig liver are shown. Some PFASs were found, confirming the ubiquity of perfluoroalkylated substances also in farm animals [2].

Conclusions

The measures put in place during the method development allowed to minimize the laboratory contamination. One of the consequences was the possibility of reaching limits of detection and quantification lower than 100 ng/kg. The achievement of satisfactory performances in PFAS analysis does not only depends on the available instrumentation, but also on the implementation of rigorous quality assurance practices including the availability of a wide set of labelled compounds to quantify PFASs.

References

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