Perfluorinated Compounds: Occurrence of Emerging Food Contaminants in Canned Fish and Seafood Products

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Abstract

Hrádková P., Poustka J., Hloušková V., Pulkrabová J., Tomaniová M., Hajšlová J. (2010): **Perfluorinated compounds: occurrence of emerging food contaminants in canned fish and seafood products**. Czech J. Food Sci., **28**: 333–342.

The contamination levels of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (FOSA), which represent an important subgroup of the environmental contaminants known as perfluorinated compounds (PFCs), were examined in 35 imported canned fish and seafood products (tuna, sardine, cod liver) obtained from the Czech retail market in 2009. An analytical procedure was employed based on a fast and simplified sample preparation using activated charcoal clean-up followed by a LC-MS/MS determinative step. The content of PFOS, which was the dominating pollutant, ranged from 0.7 μg/kg to 12.8 μg/kg, PFOA levels were in the range of 1.2 μg/kg to 5.1 μg/kg, FOSA was detected only at trace levels in two samples. Several products originated in the Baltic Sea were the most contaminated within the sample set.

Keywords: perfluorinated compounds; contamination; fish; seafood; canned products; charcoal; liquid chromatography; tandem mass spectrometry

Perfluorinated compounds (PFCs) belonging to the emerging class of persistent organohalogenated contaminants comprise a diverse group of chemicals including perfluorinated alkylated substances. The common characteristics of PFCs are the fully fluorinated alkyl chain of varying length, typically C4 to C16, and a hydrophilic end group, $F(CF_2)_n$-R (Voogt & Sáez 2006). The most studied compounds within PFCs group are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (Figure 1), and their derivatives such as perfluorinated sulfonates (PFSAs), perfluorocarboxylic acids (PFCAs) and further perfluorinated telomer alcohols (FTOH), perfluorinated sulfonamides (FOSA) or perfluorinated phosphonic acids (PFPAs) (Table 1) (Jogsten *et al.* 2009). The unique physico-chemical properties of PFCs make it difficult to replace them in a number of industries. PFCs have been used as emulsifiers, lubricants, fire-fighting foams, water-, grease-

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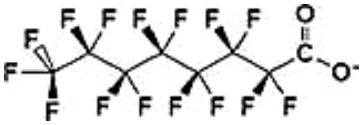
PFOS



PFOA

Figure 1. Structure of PFOS and PFOA

and dirt-repellents, coating materials in the textile industry (e.g. Gore-Tex, upholstery, carpet, leather protection) and as processing aids in food paper containers, cooking tools, medical aids and plastics, products for personal and domestic hygiene, electronics, photographic industry, inert components in pesticides and cement additives (Nania *et al.* 2009).

After five decades of their production, the 3M Company, the major PFOS producer phased out PFOS and some of its derivatives in 2002 due to their persistence, toxicity, bioaccumulation and global distribution. Also, the European Union (EU) banned most uses of PFOS and related compounds as from the summer 2008 (EU directive 2006/122/EC, 2008). The European Food Safety Authority (EFSA), based on CONTAM (Scientific Panel on Contaminants in the Food Chain) recommendation, established the tolerable daily intake (TDI) 150 ng/kg b.w. for PFOS and 1500 ng/kg b.w. for PFOA, from July 2008 (Anonymous 2008). In May 2009, PFOS, together with other 8 halogenated POPs, was addedd on the Stockholm convention on persistent organic pollutants (http://chm.pops.int/default.aspx). DuPont, the major producer of PFOA and related products such as polytetrafluoroethylene (PTFE) mostly well-known by the brand name Teflon, achieved a voluntary total reduction in PFOA manufacturing emissions of approximately 95%. Despite the restriction of PFOS and PFOA production as already mentioned, hundreds of related chemicals (such as homologues with shorter or longer alkyl chains, PFOA and telomers) which potentially may degrade to PFCAs or PFSAs, have not been regulated yet (Del Gobbo *et al.* 2008; Jogsten *et al.* 2009).

Chemicals containing the fluorinated chain are commercially manufactured by two major production processes – electrochemical fluorination (ECF) and telomerisation. ECF is a relatively cheap way of production yielding substances with sulfonate group. Unfortunately, the ECF produces up to 30% of impurities as branched chains in addition to the final linear chain product (Hekster *et al.* 2002; Sandford 2003; Voogt & Sáez 2006; Fromme *et al.* 2009). Telomerisation, as mentioned above, provides fluorinated substances with CH_2CH_2 moiety, which are produced by a two-steps radical reaction. Unlike the cheaper ECF, telomerisation provides only linear chain products of higher purity (Hekster *et al.* 2002; Sandford 2003; Voogt & Sáez 2006; Fromme *et al.* 2009).

As a result of human manufacture and use, PFCs are released to the environment by various ways (*i*) during synthesis, (*ii*) incorporation into final products, (*iii*) distribution of the products to consumers, (*iv*) using the product by the consumers and (*v*) during disposal. Fluorinated surfactants usually reach the aquatic environment either through their release into rivers or via wastewater discharge into receiving waters (Figure 2). Predominantly, however, they are adsorbed onto sewage sludge. The use of sludge for the land treatment or its disposal on dump sites leads to the remobilisation of these compounds. Their polarity and mobility in water and soil allow them to reach the sea or ground water in unaffected or undegraded conditions. As a consequence, these compounds have been shown to be distributed globally (Villagrasa *et al.* 2006; Kärrman *et al.* 2009).

The persistence and bioaccumulation of PFCs can be explained by their resistance to hydrolysis, photolysis, biodegradation and metabolism (Del Gobbo *et al.* 2008). The C-F bond confers thermal and chemical stability (attack by acids or bases, reducing and oxidising agents) to PFCs. Thus, the perfluorinated carbon chain is in practice non-degradable in nature. On the other hand, a bulky functional end group will be more readily transformed in the environment and in organisms, and therefore the compounds will be eventually degraded to the ultimate, perfluorinated sulfonates (e.g. PFOS) and carboxylates (e.g. PFOA) finally, which under normal circumstances seem to persist in the environment for foreseeable time (Hekster *et al.* 2002; Del Gobbo *et al.* 2008; Jahnke & Berger 2009). Although the accumulation and trends of PFCs are still largely unknown, it is well established that in contrast to the classical more lipophilic persistent organic pollutants (POPs) such as dioxins, polychlorinated biphenyls (PCBs),

Table 1. Full names, abbreviations, and chemical formulas of a selection of PFCs

Analyte	Molecular Formula	Abbreviation
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluro-*n*-butanoic acid	$C_4HF_7O_2$	PFBA
Perfluoro-*n*-pentanoic acid	$C_5HF_9O_2$	PFPeA
Perfluoro-*n*-hexanoic acid	$C_6HF_{11}O_2$	PFHxA
Perfluoro-*n*-heptanoic acid	$C_7HF_{13}O_2$	PFHpA
Perfluoro-*n*-octanoic acid	$C_8HF_{15}O_2$	PFOA
Perfluoro-*n*-nonanoic acid	$C_9HF_{17}O_2$	PFNA
Perfluoro-*n*-decanoic acid	$C_{10}HF_{19}O_2$	PFDA
Perfluoro-*n*-undecanoic acid	$C_{11}HF_{21}O_2$	PFUdA
Perfluoro-*n*-dodecanoic acid	$C_{12}HF_{23}O_2$	PFDoA
Perfluoro-*n*-tridecanoic acid	$C_{13}HF_{25}O_2$	PFTrDA
Perfluoro-*n*-tetradecanoic acid	$C_{14}HF_{27}O_2$	PFTeDA
Perfluoro-*n*-pentadecanoic acid	$C_{15}HF_{29}O_2$	PFPeDA
Perfluorinated sulfonates (PFSAs)		
Potassium perfluoro-1-butanesulfonate	$C_4F_9SO_3Na$	L-PFBS
Sodium perfluoro-1-hexanesulfonate	$C_6F_{13}SO_3Na$	L-PFHxS
Sodium perfluoro-1-octanesulfonate	$C_8F_{17}SO_3Na$	L-PFOS
Sodium perfluoro-1-decanesulfonate	$C_{10}F_{21}SO_3Na$	PFDS
Non-ionic PFCs		
Perfluorinated sulfonamides (FOSA)		
N-Methyl fluorobutane sulfonamide	$C_5H_4F_9NO_2S$	N-MeFBSA
Perfluoro-1-octansulfonamide	$C_8H_2F_{17}NO_2S$	FOSA
N-Methylperfluoro-1-octanesulfonamide	$C_9H_4F_{17}NO_2S$	N-MeFOSA
N-Ethylperfluoro-1-octanesulfonamide	$C_{10}H_6F_{17}NO_2S$	N-EtFOSA
Perfluorooctanesulfonamidoacetic acid	$C_{10}H_4F_{17}NO_4S$	FOSAA
Perfluorinated sulfonamidoethanols (FOSE)		
N-Methyl perfluorobutane sulfonamidoethanol	$C_7H_8F_9NO_3S$	N-EtFBSE
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	$C_{11}H_8F_{17}NO_3S$	N-MeFOSE
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	$C_{12}H_{10}F_{17}NO_3S$	N-EtFOSE
Fluorinated Telomer Alcohols (FTOHs)		
2-Perfluorohexylethanol	$C_8H_5F_{13}O$	6:2 FTOH
2-Perfluorooctylethanol	$C_{10}H_5F_{17}O$	8:2 FTOH
2-Perfluorodecylethanol	$C_{12}H_5F_{21}O$	10:2 FTOH
2-Perfluorododecylethanol	$C_{14}H_5F_{25}O$	12:2 FTOH
Perfluoroalkylphosphonic acids (PFPAs)		
Perfluorohexylphosphonic acid	$C_6H_2F_{13}PO_3$	PFHxPA
Perfluorooctylphosphonic acid	$C_8H_2F_{17}PO_3$	PFOPA
Perfluorodecylphosphonic acid	$C_{10}H_2F_{21}PO_3$	PFDPA

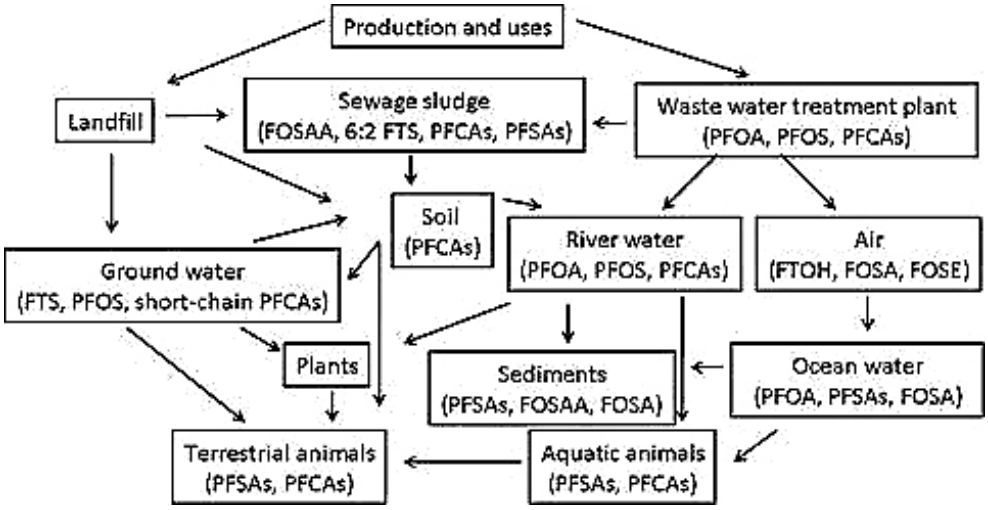


Figure 2. Circulation of PFCs in the environment (all abbreviations of analytes are summarised in Table 1)

or brominated flame retardants (BFRs), PFCs do not typically accumulate in lipid-rich tissues, but they bind to blood proteins and accumulate in liver and gall bladder (Ericson *et al.* 2008; Del Gobbo *et al.* 2008; Berger *et al.* 2009).

Human exposure to PFCs, mainly PFOS and PFOA, is due to a variety of environmental and product-related sources. Direct skin exposure from impregnated products (all-weather-clothes, textiles, tents, footwear, furniture, and carpets) is one way. The inhalation of aerosols originated from impregnation sprays may be another route of exposure. Recent investigations have indicated PFCs in indoor air and dust at high concentrations which could be an important source of these compounds (Shoeib *et al.* 2005; Björklund *et al.* 2009). The consumption of contaminated food, including water, has been suggested as the greatest source and the main pathway of human exposure to PFCs. Not only the food but also food wrappers may be an important source of perfluorinated chemicals in humans (e.g. in microwave popcorn bags, from which the chemicals can be released gradually during microwave heating and leak into the food or the vapours) (Sinclair & Kannan 2007). Despite the growing numbers of studies focused on the examination of the presence of PFCs in commercially available food items, only a limited amount of papers have reported PFCs levels in the canned fish products (Tittlemier *et al.* 2007; Ericson *et al.* 2008; Ostertag *et al.* 2009,) and also in fish fillets (Berger *et al.* 2009; Delinsky *et al.* 2009; Nania *et al.* 2009). The majority of publications is focused on the examination of protein-rich tissues such as liver, kidney, blood, or whole fish homogenate. Ericson *et al. (*2008*)* examined food items from the Catalan (Spain) market and found PFOS at the level of 0.27 µg/kg in tinned products. Ostertag *et al.* (2009) reported PFOS concentration in canned fish and fish products like fish burger from Canadian market to be below the detection limit. In a similar study conducted by Tittlemier *et al.* (2007), no PFCs were determined either in the canned fish contrary to the marine and freshwater fishes. PFCs levels determined in the whole contents of fish cans are usually lower in comparison with freshwater or marine fishes. Not only the fish species but also the specified type of tissue must be taken into consideration because usually the PFCs concentrations in the fish livers are usually higher than those in the muscles. Berger *et al.* (2009) investigated six muscles of freshwater and marine fish subspecies such as salmon, perch, brown trout, burbot, and whitefish from the Baltic Sea and Lake Vättern in Sweden. PFOS was typically the most abundant analyte and out of all species examined, higher levels were found in fishes originating from the lake Vättern ranging from 0.97 µg/kg (brown trout) up to 23.1 µg/kg (perch). PFOS was followed by PFHxS, FOSA and carboxylic acids (PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, and PFTeDA) which were detected only at trace levels, not exceeding the concentration of 1 µg/kg. Other study, published by Nania *et al.* (2009), was focused on the examination of PFOS

and PFOA in the samples of livers and muscles from two groups: (*i*) benthonic fish (*Conger conger*, *Scyliorhinus canicula*, *Mullus surmuletus*, *Pagellus erythrinus* and *Scorpaena scrofa*), (*ii*) pelagic fish (*Mugil cephalus*, *Dentex dentex*, *Trachurus mediterraneus*, *Lamna nasus*, *Mustelus mustelus*, *Xiphias gladius*, and *Thunnus thynnus*) originated in the Mediterranean Sea. Thus the results obtained were not specified by the individual species but, on an average, by the tissues of each group. The target analytes concentrations were comparable in the case of the muscle samples – PFOS/PFOA levels reached up to 14/12 μg/kg and 43/40 μg/kg in pelagic and benthonic groups, respectively. Unlike, with the muscle samples, higher PFOS levels in the livers of those – 40 μg/kg and 83 μg/kg were found, respectively. PFOA followed PFOS also in the liver samples at lower concentration levels – 13 μg/kg and 37 μg/kg in pelagic and benthonic groups, respectively. The results of the researches realised within Europe show the same or slightly higher levels in fish depending on the localities. Voogt *et al.* (2008) detected perfluorocarboxylated acids (PFNA, PFDA, PFUnA, PFDoA and PFTrDA) in cod which had been bought in the local supermarket in Flanders, the concentrations did not exceed 0.5 μg/kg. PFOS was found in this sample at the level of 2.6 μg/kg, PFOA was not detected. Llorca *et al.* (2009) investigated the livers and muscles of swordfish, stripped mullet, young hake, including hake roe, and anchovy obtained from retail fish markets and supermarkets in Spain. The highest concentration of PFOS, 23 μg/kg, was determined in the hake rRoe, but in term of fillets, a high content, 8.2 μg/kg, was found in the swordfish. Surprisingly, the measured levels of PFOS in the other samples were lower than those of PFOA and did not exceed levels of 1.3 μg/kg in the muscles and of 3.5 μg/kg in the livers (young hake), PFOA was found at maximum levels of 3.3 μg/kg and 5.2 μg/kg (young hake). In the sample of the stripped mullet, PFOS was not detected (Llorca *et al.* 2009).

Very high concentrations were found in the livers of carps and eels collected in the localities adjacent to a fluoro-chemical factory in Belgium, where the values reached up to 1822 μg/kg in the carp livers and to 9030 μg/kg in the eel livers (Hoff *et al.* 2005). Very high levels were also found in the localities of North Germany where the PFOS concentration ranged (median residue) from 11 μg/kg up to 163 μg/kg (Schuetze *et al.* 2010). The objectives of this study were: (*i*) to measure the concentrations of the selected PFCs (perfluorooctane sulfonate, perfluorooctanoic acid, and perfluorooctane sulfonamide) in fish and seafood tinned products imported to the Czech Republic from various countries and (*ii*) to evaluate the levels of PFCs in canned fish products with respect to the fish species and origins (country/region). Unlike in the seaside countries, the canned fish and seafood products contribute to diet on the average more than freshwater and marine fishes. The common kinds of cans such as tunas, sardines, mackerels, or cod livers were collected in August and September 2009 from local retail markets. The additional aim of the present study was to enlarge the limited information concerning the contamination levels of PFCs in the canned fish and seafood products worldwide.

MATERIALS AND METHODS

Chemicals. Stock standard solutions of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (FOSA), sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate ($^{13}C_4$-PFOS), perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid ($^{13}C_4$-PFOA), were purchased from Wellington Laboratories (Canada) in the concentration of 50 μg/ml methanol (purity > 98%) each. The working standard solutions in the concentration range of 0.01–500 ng/ml methanol were prepared by the appropriate dilution of the stock solutions. The working solution of $^{13}C_4$-PFOS and $^{13}C_4$-PFOA, used as internal standards, at the concentration level of 500 ng/ml, was also prepared in methanol. All solutions were stored at –18°C. Methanol for liquid chromatography LiChroSOLV was supplied by Merck (Darmstadt, Germany). Deionised water was prepared using of a MilliQ system (Millipore, Billerica, USA). The activated charcoal untreated powder (100–400 mesh) and ammonium acetate (99.999%) were purchased from Sigma-Aldrich (Hamburg, Germany).

Samples. For the assessment as a source of human exposure of the contamination of fish and seafood products imported to the Czech Republic, with PFCs, the fish products were bought at the Czech retail market during the sampling period of August and September 2009 within Czech-Norwegian project EMERCON. Altogether 35 canned products, very often consumed kinds of fish – tuna,

Table 2. Levels (μg/kg) of PFOS, FOSA, and PFOA in examined samples

Sample code	Sample type	Country of origin	Net/drained weight (g)	PFOS	FOSA	PFOA
1	calamari	Spain	110/72	< 0.3	< 0.2	< 0.2
2	cod liver in oil	Poland	120/118	8.3	< 0.2	1.2
3	cod liver in oil	Iceland	120/-	1.0	< 0.2	1.9
4	cod liver in oil	Poland	115/105	3.6	< 0.2	1.7
5	herring in vegetable oil	Poland	170/119	< 0.3	< 0.2	< 0.2
6	herring in vegetable oil	Poland	170/102	< 0.3	< 0.2	2.0
7	mackerel in vegetable oil	Morocco	115/81	0.7	< 0.2	< 0.2
8	mackerel in brine	Latvia	240/168	1.3	< 0.2	< 0.2
9	mackerel in vegetable oil	Poland	170/102	< 0.3	< 0.2	< 0.2
10	mackerel in vegetable oil	Poland	170/119	< 0.3	< 0.2	< 0.2
11	mackerel in vegetable oil	Poland	170/119	< 0.3	< 0.2	< 0.2
12	mussels in vegetable oil	Spain	111/69	< 0.3	< 0.2	< 0.2
13	mussels in vegetable oil	Thailand	103/80	< 0.3	< 0.2	2.3
14	octopod in vegetable oil	Indonesia	170/119	7.5	< 0.2	1.8
15	octopod in vegetable oil	Spain	111/72	< 0.3	< 0.2	3.3
16	saira in oil	Latvia	250/175	< 0.3	< 0.2	< 0.2
17	salmon in olive oil	Italy	150/120	< 0.3	< 0.2	< 0.2
18	sardine in olive oil	Morocco	120/84	< 0.3	< 0.2	3.1
19	sardine in olive oil	Portugal	120/90	< 0.3	< 0.2	< 0.2
20	sardine in vegetable oil	Latvia	160/120	12.8	1.7	5.1
21	sardine in vegetable oil	Thailand	125/90	< 0.3	< 0.2	< 0.2
22	sardine in brine	Morocco	125/90	< 0.3	< 0.2	< 0.2
23	sardine in vegetable oil	Morocco	125/90	< 0.3	< 0.2	2.7
24	sardine in vegetable oil	Latvia	240/168	< 0.3	< 0.2	< 0.2
25	sprat in vegetable oil	Latvia	160/112	6.9	1.1	3.5
26	sprat in vegetable oil	Estonia	100/70	< 0.3	< 0.2	< 0.2
27	tuna in brine	Philippines	185/140	< 0.3	< 0.2	< 0.2
28	tuna in vegetable oil	Philippines	185/130	< 0.3	< 0.2	< 0.2
29	tuna in brine	Italy	80/56	< 0.3	< 0.2	< 0.2
30	tuna in vegetable oil	Philippines	170/120	< 0.3	< 0.2	< 0.2
31	tuna in brine	Philippines	185/130	< 0.3	< 0.2	< 0.2
32	tuna in brine	Spain	160/106	< 0.3	< 0.2	< 0.2
33	tuna in brine	Thailand	185/130	< 0.3	< 0.2	< 0.2
34	tuna in vegetable oil	Spain	80/52	< 0.3	< 0.2	< 0.2
35	tuna in vegetable oil	Spain	80/52	< 0.3	< 0.2	< 0.2

LOQ – 0.3 μg/kg for PFOS and 0.2 μg/kg for PFOA and FOSA

salmon, sardine, cod liver, sprat, herring, and mackerel and less usual canned products – octopus and mussels originated from different countries, are summarised in Table 2.

Analysis. The whole can content delivered to the laboratory was thoroughly mixed with UltraTurrax before the extraction. The extraction method development was carried out within the EU project Confidence. 2 g of the representative fish sample were transferred to 50 ml disposable polypropylene centrifuge tube and mixed with 6 ml of methanol using UltraTurrax homogeniser (IKA, Staufen, Germany). The isotopically labelled standards $^{13}C_4$-PFOS, $^{13}C_4$-PFOA were applied as

internal standards. Subsequently, 340 mg of activated charcoal were added to the suspension to purify the crude extract. After 1 min shaking with a minishaker (vortex), the sample was centrifuged (10 000 rpm, 5 min). The supernatant was centrifuged (5000 rpm, 2 min) and filtered at the same time through 0.2 µm PVDF filter (National Scientific Company, Arlington, USA), and ca 500 µl were transferred into a LC-vial prior to instrumental analysis.

The target analytes were separated by means of high performance liquid chromatography realised with a Alliance 2695 HPLC instrument (Waters, Milford Massachusetts, USA) comprising a quaternary pump, autosampler, degasser, and thermostated column compartment. The separation was carried out using Atlantis T3 (100 mm × 2.1 mm, 3 µm particle) analytical column from Waters (USA) maintained at 30°C. The injection volume was 10 µl. The mobile phase was (A) water containing 2 mmol/l ammonium acetate and (B) methanol; at a flow rate of 0.3 ml/min. The gradient was employed at the starting composition of 10% B, rising linearly to 100% B over 8 min, with helding for 2 min before the equilibration to the original conditions. The total analysis time was 19 minutes.

The identification/quantification was performed with tandem-quadrupole mass spectrometer equipped with a Z-spray electrospray interface. The instrument was operated in negative electrospray ionisation multiple reaction monitoring (MRM) mode. Nitrogen was used as a drying and nebulising gas (supplied by nitrogen generator Peak Scientific, Inchinnan, UK); argon (5.0, Siad, Braňany u Mostu, Czech Republic) was used as the collision gas. The capillary potential was held at 0.5 kV; cone potential between 15 V and 50 V was optimised for each analyte. The source block and desolvation temperatures were maintained at 120°C and 350°C, respectively. The desolvation gas and cone gas flows were 850 l/h and 70 l/h, respectively. The identification of the analytes was confirmed by comparison of chromatographic retention times and by mass spectral daughter characterisation. The retention times, monitored transitions together with MS-settings are listed in Table 3.

Quality control. Procedural blanks (two parallels) were prepared by the extraction procedure described above, no occurrence of contamination with PFCs investigated was observed. The matrix spiked experiments (trout muscles) at the level of 1 µg/kg resulted in the individual analyte recoveries between 104–116% (n = 6). The precision of the analytical method expressed as relative SD ranged from 6% to 8%. The compound specific limits of detection, limits of quantification are given in Table 4.

RESULTS AND DISCUSSION

The results obtained by a rapid convenient LC-MS/MS method implemented for the purpose of this study are summarised in Table 2. Since some partition of the target analytes between the oil/brine and solid portion (fish tissue, cod liver etc), might have taken place, the whole content of the can was analysed. An example of the analysis of sardine in oil (Latvia) containing all target PFCs is shown in Figure 3.

PFOS, in accordance with our expectation of is being the dominantly occurring compound, was found

Table 3. MS/MS multiple reaction monitoring parameters

Analyte	t_R (min)	Transition	Cone (V)	Collision energy (eV)
PFOA	10.11	413 → 369	15	9
		413 → 169	15	16
$^{13}C_4$ – PFOA	10.11	417 → 372	50	10
		417 → 169	50	45
PFOS	10.34	499 → 99	50	35
		499 → 80	50	45
$^{13}C_4$ – PFOS	10.34	503 → 99	50	10
		503 → 80	50	45
FOSA	10.69	498 → 78	40	10
		498 → 498	40	30

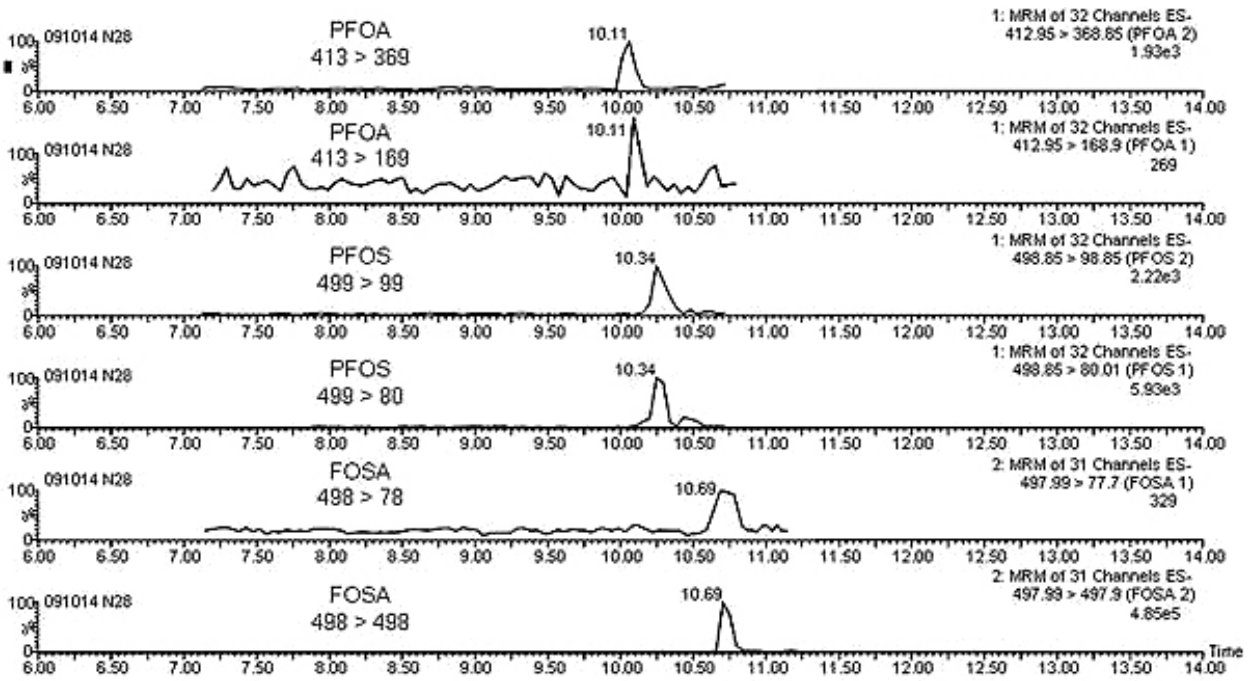


Figure 3. LC-MS/MS record of sardine in oil (sample No. 20)

in eight samples at the maximum concentration of 12.8 μg/kg in sardine in oil (sample No. 20). For this sample the calculation is demonstrated of the intake of PFOS based on the whole can content (including complete amount of contaminating PFOS). The consumption of 160 g results in the intake of 2 μg of PFOS. TDI for a consumer weighing 60 kg is 9 μg, which means that one can of this product provides 22.7% of TDI. The contribution including all positively detected fish canned products to TDI of PFOS ranged from 0.9% (sample No. 7 – cod liver) to 22.7% (sample No. 20 – sardine in oil).

PFOA was found in eleven samples, but at lower levels comparing to PFOS. The highest concentration (5.1 μg/kg) was again determined in sardine in oil from Latvia (sample No. 20). The levels in other contaminated samples, representing different regions and products – mussels in oil (Thailand), herring in oil (Poland), sardines in oil (Morocco, Latvia), octopod in oil (Spain, Indonesia), sprat in oil (Latvia), cod livers (Poland, Iceland), ranged from 1.2 μg/kg to 3.5 μg/kg. The contribution to TDI was negligible, the most contaminated sample (sample No. 20) would provide only 1% of TDI. FOSA was detected in two samples only at low levels – sardine in oil and sprat in oil (Latvia) as an accompanying compound in the samples highly contaminated with PFOS and PFOA.

Based on the results obtained in this study, it is possible to speculate on a higher incidence of PFOS in the products containing some of fish species coming from the Baltic region like cod livers, sardines, and sprats, which can reasonably contribute to TDI. But it is not the case of PFOA, with which this trend was not observed. Comparing our data with the studies published worldwide, the levels found in tins imported to the Czech Republic are significantly higher. In several works, no PFOS, PFOA or FOSA were detected, only a low level was found in a composite sample of canned products (tuna, sardine, and mussel) – 0.27 μg/kg as published by Ericson *et al.* (2008). The trends

Table 4. Method performance characteristics

Analyte	Recovery (%)	RSD (%)	LOD (μg/kg)	LOQ (μg/kg)
PFOS	104	8	0.1	0.3
PFOA	111	6	0.1	0.2
FOSA	116	7	0.05	0.2

and levels determined in our study correspond rather to the reported PFOS levels in freshwater and marine fish samples discussed at the beginning of this paper. Therefore, further investigation is necessary to evaluate the possible trends based on e.g. regional and/or fish and seafood species differences. Also an analytical procedure improvements on the detection capabilities can facilitate new achievements.

CONCLUSIONS

In summary, this study provides the primary information on the contamination of the canned fish and seafood products by imported to the Czech Republic with perfluorinated compounds. In the 35 examined samples PFOS and PFOA were found in 23% and 31% of the samples at the levels ranged from 0.7 μg/kg to 12.8 μg/kg and from 1.2 μg/kg to 5.1 μg/kg, respectively. FOSA was detected only in two samples below LOQ. The most contaminated were the samples of cod livers, sardines and sprats originated in the Baltic region, in the majority of the samples the targeted perfluorinated compounds were not detected.

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