



Identification of Perfluorooctanoic Acid Release from Commercial Coated Cooking Pans by Liquid Chromatography Coupled to Electrospray Ionization Tandem Mass Spectrometry

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Abstract: Salts of perfluorooctanoic acid (PFOA) can be used in the manufacture of fluoropolymers employed for coating pans; moreover, PFOA can be formed as a byproduct of thermolysis of the aforesaid fluoropolymers. This study was carried out to evaluate PFOA migration into food cooked in fluoropolymer-coated pans. The pans were purchased from a local retailer and subjected to cooking conditions. Used oil was extracted with a methanol/water solution and analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS). We found that PFOA can enter cooked food during a container's first phases of use, not only in containers already abused by kitchen tools or otherwise scratched.

Key words: PFOA, fluoropolymer, teflon, coated pans, LC/MS/MS

INTRODUCTION

Perfluorinated compounds are used in a wide variety of commercial products as surfactants and surface protectors in carpets, leather, paper, food containers, fabric, floor polishes, shampoo, telecommunications and electronic wiring insulation, chemical processing piping and vessels, nonstick cookware coatings^[1,2]. Their widespread use stems from their unique properties: Fluorochemicals can repel both water and oil and can reduce surface tension to levels much lower than other hydrocarbon surfactants^[3].

Salts of perfluorooctanoic acid (PFOA) are used to suspend and emulsify some polymers during their manufacture for use in the production of coated pans^[4].

A large number of studies in humans, animals and the environment have been conducted to examine the toxicity associated with PFOA^[5-7]. While other perfluorinated compounds are dominant in wildlife, PFOA is detected occasionally and at a lower concentration.

PFOA is generally present in human serum at higher concentrations than in wildlife, perhaps indicating additional exposure in humans through contact with commercial products containing PFOA or its derivatives. Of particular concern is the presence of PFOA in the blood of children^[5,8].

Moreover, studies have shown that thermolysis of fluorinated polymers such as teflon produces long chain

polyfluoro-carboxylic acids^[2]. PFOA is formed as a degradation product of small polymers called fluorotelomers and as an unintended byproduct of their manufacture^[9].

In light of these findings, the US Environmental Protection Agency (EPA) has mandated a 95% reduction of PFOA from emissions and product content by 2010 with efforts to eliminate PFOA from emissions and product content by 2015^[10].

Begley *et al.* used a LC/MS technique to characterize potential migrants from perfluoro coatings. Considering the amount of PFOA in cookware rather low ($\mu\text{g kg}^{-1}$) to conduce accurate migrations experiments, these authors took into account the difference in initial residual PFOA concentration between the cookware and the PTFE film and assumed that mass transfer obeys Fick's Law. These authors calculated a maximum migration of 30 ng dm^{-2} polymer in the first use, assuming that all cookware has the same initial concentration of PFOA^[11]. In the opinion of the authors of this paper it is informative to identify PFOA migration into food also under experimental cooking conditions modifying the analytical extraction conditions adopted by Powley *et al.*^[4] for measurement of PFOA migration. This work was released to object to their conclusions in which they affirm that using food simulants (water and water/ethanol) no PFOA is detected from coated cookware.

Because no legal limits are currently set for PFOA release from containers under experimentation a qualitative determination was sufficient to evidence if PTFE-coated cookware releases a detectable amount of the pollutant. Moreover no release limits have been set at a precise phase of use since the behaviour of this kind of container is not predictable.

MATERIALS AND METHODS

Reagents: Ninety six percent Pentafluorooctanoic acid (CAS # 335-67-1) was obtained from Sigma-Aldrich (Milan, Italy). Methanol (HPLC grade), 96% ethanol, acetic acid (glacial 100% anhydrous) and formic acid (98-100% GR for analysis) were obtained from Merck, (Darmstadt, Germany). Water G-Chromasolv was obtained from Sigma-Aldrich (Milan, Italy). Red wine vinegar was purchased from Acetaia Bellei and olive oil was purchased from a local outlet.

Migration tests: Two high-quality PTFE-coated aluminium pans (diameters about 16 and 20 cm respectively) and two uncoated stainless steel (same dimensions) were purchased from a local retailer.

The PTFE-coated aluminium pans were subjected to pre-washing and first domestic-like use treatments 1-4 below to avoid interference from possible PFOA release during the pans' first phases of use, followed by two quantitative cooking simulated experiences. The same pre-washing treatment was made for the stainless steel ones (blank) to evidence background levels.

The following treatments were performed:

- * Pre-washings with 96% ethanol and 3% acetic acid
- * Washing as recommended by the manufacturer
- * First domestic use: preparation of a homemade tomato sauce
- * Washing as recommended by the manufacturer
- * Simulated cooking experience 1: olive oil heat treatment (C.E.1)
- * Simulated cooking experience 2: frying of potato sticks (C.E.2)

The pans were first washed with an ethanol-moistened cotton ball and then with 15mL of 3% acetic acid. The PTFE-coated pans were washed, as recommended by the manufacturer, with kitchen paper moistened with olive oil and then with a detergent solution, rinsed with water and dried with a towel. Same treatment was made on the stainless steel ones. All pans were submitted to a first simulated domestic use: a homemade sauce was prepared using 100g of fresh tomatoes and 2 tablespoons of olive oil. The pans were washed as recommended by the manufacturer a second time. The following studies were conducted to

reproduce cooking experiences and to evidence PFOA migration.

Cooking experience (C.E.1): In each pan, 20mL of olive oil were heated at 120°-160°C for 10 min, transferred into a 250mL screw-cap Pyrex jar and cooled.

Cooking experience (C.E.2): The potato samples were peeled and cut into sticks with an average dimension of 1.0-1.3cm x 0.8-1.2cm using a manual grater. The sticks were fried in 50mL of preheated olive oil for 10min, removed from the olive oil and discarded. The oil was transferred into a 250mL screw-cap Pyrex jar and cooled.

Extraction: The oils derived from C.E.1 and C.E.2 were subjected to extraction. An aliquot of 10mL of a water/methanol 20:80 (v/v) solution was added to the oil and the sample was shaken manually for 30 min. The emulsion was transferred into two 50mL glass tubes and centrifuged at 4600rpm for 5 min; the supernatant was transferred into a beaker onto a heating plate and concentrated to a volume of approximately 2mL. The extracts were filtered through a Millipore filter (cellulose acetate, 0.2 µm pore size) and analysed to verify the presence of perfluorooctanoic acid.

To estimate the recovery of PFOA extraction from olive oil with water/methanol (20:80 v/v), various experiences have been realised spiking both 20 and 50mL of olive oil with known aliquots of PFOA (300 ng and 500 ng) using a standard solution of PFOA in water (5 mgL⁻¹). Making the extraction from 20 or 50 mL of olive oil, as before reported, the recovery values ranged between 93-95 % or 78-82 % respectively.

Equipment: The high performance liquid chromatograph was a Varian (Walnut Creek, CA, USA) composed of two Prostar pumps and a Gemini C-18 (100mm x 2mm i.d., 5µm particle size) reversed-phase column with a meta-guard cartridge Gemini C-18 (4.0L mm x 2 mm i.d.) both from Phenomenex (Torrance, CA, USA); the sample injector used was a 7725(i) type 20µl sample loop (Rheodyne, USA). The mobile phase A was water/formic acid 99.5:0.5 (v/v) and the mobile phase B was methanol/formic acid 99.5:0.5 (v/v) at a flow rate of 0.4mL/min with isocratic mode at 80% of mobile phase B.

The triple quadruple system used was a Varian 1200L quadrupole MS/MS spectrometer fitted with an electrospray ionization (ESI) interface. The ESI-MS interface was operated in the negative ion detection mode; the parent-to-daughter ion transitions at 413 → 369Da (10V collision energy) and 413 → 168Da (18V collision energy) were monitored.

Table 1: PFOA migration level (ng dm^{-2}) from two PTFE coated pans for two cooking experiences (C.E.1 C.E.2). Data derive from the mean of three determinations on each extract water/methanol (20:80 v/v). The absolute quantity of PFOA released (ng) from each pan corresponds to PFOA quantified in total concentrated extract. Comparison data (blank) derive from the experiences carried out with stainless steel pans and using the same cooking and extraction parameters

Type of pan	Pan bottom area (dm^2)	Cooking Experience 1				Cooking Experience 2			
		Extract concentration (ng L^{-1})	Extract volume (ml)	PFOA released (ng)	PFOA migration level (ng dm^{-2})	Extract concentration (ng L^{-1})	Extract volume (ml)	PFOA released (ng)	PFOA migration level (ng dm^{-2})
PTFE coated aluminium Ø 16 cm	2.01	136	2	0.27	0.13	158	2	0.32	0.15
PTFE coated aluminium Ø 20 cm	3.14	159	2	0.32	0.10	420	2	0.84	0.25
Stainless steel Ø 16 cm	2.01	< 15	2	< 0.03	< 0.02	< 15	2	< 0.03	< 0.02
Stainless steel Ø 20 cm	3.14	< 15	2	< 0.03	< 0.01	< 15	2	< 0.03	< 0.01

The LOD $15 \text{ (ng L}^{-1}\text{)}$ and LOQ $50 \text{ (ng L}^{-1}\text{)}$ of PFOA in the extracts obtained from cooked oils derive from analysis of standard solutions of PFOA in water/methanol (20:80 v/v).

The following interface parameters were used: drying gas N_2 250°C 22psi; nebulizer gas pressure (air) 40psi; capillary voltage - 40V; needle voltage - 4850V; shield voltage - 600V; argon pressure in collision cell approximately 3.0 mTorr; electron multiplier voltage, 1800V.

Calibration of the mass analyzer was performed by infusion (0.6 mL min^{-1}) of a commercial mixture of polypropylenglycol (Varian) using a $1000 \mu\text{l}$ Hamilton syringe and monitoring five mass-to-charge ratios (m/z) in the 55-1200 μm mass range. The ESI source conditions were as follows: capillary voltage 59V; needle voltage 5000V; shield voltage 600V in positive-ion (PI) mode. In negative-ion mode, the conditions were as follows: capillary voltage - 45V; needle voltage - 4500V; shield voltage - 600V. For both modes, the drying gas temperature was 250°C and nebulizer gas pressure 40psi (drying gas was high purity nitrogen and nebulizer gas high purity air); electron multiplier voltage, 1360V.

RESULTS AND DISCUSSION

The limit of detection (LOD) evaluated on PFOA standard diluted in water/methanol 20:80 (v/v) was 15 ng L^{-1} (signal-to-noise ratio 3:1); this LOD corresponds to 30 pg of PFOA migrated from a pan.

The limit of quantification (LOQ) evaluated on PFOA standard diluted in water/methanol 20:80 (v/v) was 50 ng L^{-1} (LOQ/LOD ratio 3:1); this LOQ corresponds to 100 pg of PFOA migrated from a pan.

The limits are shown by chromatographic plots A and B of PFOA standard solutions in Fig. 1.

The two PTFE-coated pans were subjected to the extraction procedures described previously. The extracts were analysed directly by LC/MS/MS. PFOA was readily detected in both samples, as shown by chromatographic plots C and D in Fig. 1. Furthermore, the solutions used for pre-washing treatments (point 1 in paragraph "Migration tests") were analysed and they gave positive results for PFOA presence. No signal of PFOA result to be detectable for the two pans of stainless steel used as blank.

To show that migration level of PFOA from PTFE-coated pans can be discriminated from the levels corresponding to LOD and LOQ detectable for the extracts produced with water/methanol 20:80 (v/v), an approximate quantification was realised. PFOA standard injection at known concentration (200 and 450 ng L^{-1}) was made before and after analysis of each extract produced from oils cooked in the coated pans and on stainless steel pans. Standards area counts were compared to extracts area counts and results were obtained by interpolation. We believe the adopted system above described is the best suited for a rather indicative evaluation of the pan behaviour. Moreover, the actual experiences show that PFOA migration is valuable (i.e. > LOQ) also in phases of use subsequent to the first one. Table 1 summarized the indicative levels of PFOA migration from two PTFE-coated pans.

From this experiment, we propose that PFOA migration into cooked food can take place in the first

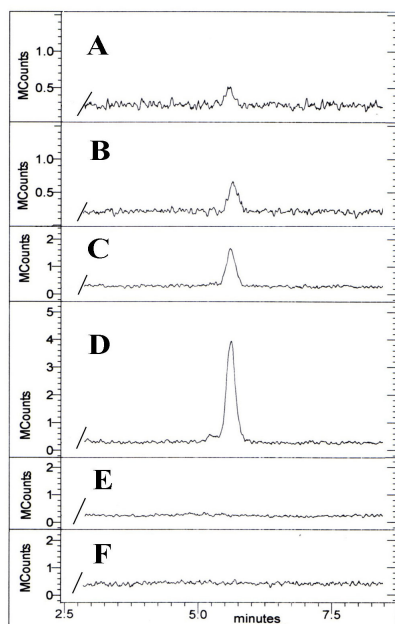


Fig. 1: Total ion current chromatogram of PFOA by LC/MS/MS (413 \rightarrow 369, 413 \rightarrow 168). (A) Limit of detection (LOD); (B) Limit of quantitation (LOQ); (C) Extract from 16 cm diam coated pan in cooking experience 2; (D) Extract from 20 cm diam coated pan in cooking experience 2; (E) and (F) Blank traces for cooking experiences with stainless steel pans

phases of container use and not only from containers abused by kitchen tools or otherwise scratched; that demonstrates both the course of migration in time and the release since the first stages of use.

Our results do not agree with the findings of Powley et al. (Powley et al. 2005); this could be due to our better extraction system and we confirm that it is possible to obtain background levels <LOD, as shown in E and F traces in Fig. 1.

Additionally, the levels of PFOA migration estimated for the samples considered in this paper, result noticeably lower than the maximum migration of 30 ngL⁻¹ calculate by Begley et al. in the first use^[11].

ACKNOWLEDGEMENTS

Thanks are due to G. Andreoli and M. Palatini for collaboration.

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