

Human exposure to perfluorinated compounds via food



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Introduction:

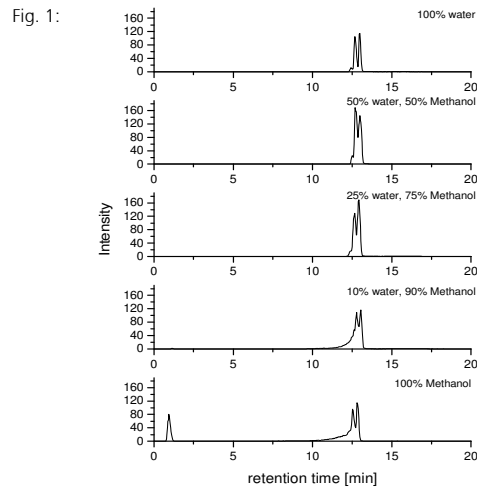
Food is an important source of human background exposure to persistent organic pollutants (POPs) and is expected to contribute human exposure to PFOS and related compounds [1,2,3]. However, little is known about levels of these substances in our food.

Thus, PFOS, PFOA, PFHxS, PFHxA and PFOSA were included in a recent German monitoring study on the dietary exposure to a number of organic contaminants. 50 volunteers were recruited from the general population and requested to collect duplicates of their daily food and beverages over a 7-day period. The sampling period started in April 2005 and still proceeds.

Basing on existing methods [4,5], an appropriate, robust and sensitive analytic method was developed and optimized. Results of this development are presented here.

Literature:

- [1] Kannan et al. (2001), Environ. Sci. Technol. 35, 1593-1598.
- [2] Kannan et al. (2002), Environ. Sci. Technol. 36, 3210-3216.
- [3] Tittlemier S, Ryan JJ, Oostdam JV. 2004. Organohalogen Compounds 66, 3959-3964.
- [4] Van de Vijver KI, Hoff PT, Das K, Van Dongen W, Esmans EL, Jauniaux T, Bouquegneau JM, Blust R, de Coen W. 2003. Environ Sci Technol 37, 5545-5550.
- [5] Guruge KS, Taniyasu S, Miyazaki S, Yamanaka, N, Yamashita N. 2004. Organohalogen Compounds 66, 3979-3984.



Abstract:

Food is expected to contribute human exposure to PFOS and related compounds but only little is known about levels of these substances in our food. Thus, PFOS, PFOA, PFHxS, PFHxA and PFOSA were included in a recent German monitoring study on the dietary exposure, basing on the duplicate concept. As a fundamental monitoring tool, an appropriate, robust and sensitive analytic method was developed and optimized.

Materials & Methods:

- Samples: Mixed food and beverage samples of a diet duplicate study.
- Daily samples are mixed, homogenized and stored at -20°C for later analysis.
- Sample fortification for determination of recovery
- MTBE extraction of the wet samples using tetrabutyl-ammonium ions as ion pairing agent
- Solvent change to an optimised MeOH/water mixture (see Fig. 1)
- HPLC: C18 phase (Hypersil gold, 100 x 2 mm, 5µm), using methanol and ammonia acetate buffer (pH 3.2) as eluents.
- Detection: Triple quadrupole mass spectrometry (Finnigan TSQ 7000, neg. ESI) in SRM mode (Details see table 1).
- Quantitation is performed by internal calibration using 7-H-dodecafluoroheptanoic acid as internal standard.

Table 1: Mass spectrometric detection parameters

Substance	Pseudo-molecular ion	SRM fragment
HI-PFHxA*	345.0	281.0
PFHxA	313.0	268.0
PFOA	413.0	368.0
PFOS	499.0	80.0
PFOSA	498.0	79.0
PFHxS	399.0	80.0

* internal Standard

Table 2: Initial concentrations [ng/g ww] of perfluorinated compounds obtained in a duplicate study.

	PFOS	PFOA	PFHxA	PFOSA
Sample 1 [ng/g ww]	8.0	8.1	4.5	< 1.0
Sample 2 [ng/g ww]	10.5	9.5	6.8	3.6
Sample 3 [ng/g ww]	4.7	< 1.0	1.8	< 1.0

Results & Discussion:

- Method allows a specific detection and quantification of perfluorinated compounds.
- Solvent change with increased water content improves peak form.
- Very first results show concentrations of PFOS, PFOA and PFHxA in the lower ppb range (Table 1).
- Limits of detection (LOD), obtained by method blank runs, were below 1-2 ng/g fresh weight.
- An initial fortification study proved a 80-120% recovery range for PFOS, PFOA and PHxA, recoveries for PFOSA were of about 50%.

Conclusions:

- First method described for mixed food samples.
- Based on very first results LOD is acceptable for quantification of perfluorinated substances in the lower ppb range.
- Method is suitable for routine application in the above mentioned diet duplicate study.
- German blood levels of PFOS are reported to exceed the reported food levels by a factor of 3-10 indicating biomagnification of PFOS and related compounds in humans

