



Analysis of Fluorinated Alkyl Compounds in Air Samples from England



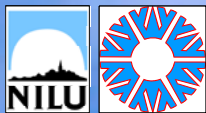
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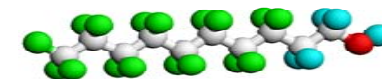
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Introduction

In recent years, perfluorooctane sulfonate (PFOS) and perfluorinated carboxylic acids (PFCAs) have been detected in high-trophic biota from as remote places as the Arctic [1]. These compounds are ionic and possess very low volatility. The question arose, how they were transported from densely populated application areas to remote places. Ellis et al. [2] proposed that neutral precursor compounds could undergo atmospheric long-range transport and finally be degraded to persistent products in the Arctic. Possible precursor compounds for PFCAs and PFOS are fluorotelomer alcohols (FTOHs, figure 1) and fluoro-octane sulfonamides/sulfonamido ethanols (FOSAs/FOSEs), respectively. The aim of this study was to provide first evidence for the presence of FTOHs, FOSAs and FOSEs in European air samples.



Structure of 8:2 FTOH

Colour code: Carbon, fluorine, oxygen, hydrogen

Experimental

- Method based on literature [3]
- High-volume sampling (1000 – 1400 m³ air)
- Particles on glass fibre filter (GFF), air phase on PUF/XAD-2/PUF (figure 2)
- Cold-column extraction with ethyl acetate (neutral compounds) or methanol (ionic compounds from particles) (see figures 3 and 4)
- GC/PCI-MS (quant.) and GC/NCI-MS (confirm.) for neutral compounds
- HPLC/ESI(neg)-TOF-MS for ionic compounds [4]
- Quantification: Internal standard method (7:1 FTOH and 3,7-di-Me-PFOA)



Figure 2. Sampling tube with GFF and PUF/XAD/PUF sandwich

Method validation

Table 1. Extraction recoveries and whole method recoveries (%).

	10:2 FTOlefin	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	N-Me-FOSA	N-Et-FOSA	N-Me-FOSE	N-Et-FOSE
Extraction	23	51	65	102	88	83	76	127	141
Whole method	12	6	37	80	73	76	79	133	143

Table 2. Relative recoveries (%) on front PUF/XAD/PUF and back XAD/PUF from breakthrough experiments (PUF/XAD/PUF/XAD/PUF sandwich, 1000 m³ of air pumped through).

	10:2 FTOlefin	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	N-Me-FOSA	N-Et-FOSA	N-Me-FOSE	N-Et-FOSE
Front PUF/XAD/PUF	96	60	87	99	99	99	98	99	99
Back XAD/PUF	4	40	13	1	1	1	2	1	1

Table 3. Interlab comparison of GC/MS methods using a standard solution. Values in pg/μl.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	N-Me-FOSA	N-Et-FOSA	N-Me-FOSE	N-Et-FOSE
Theoretical values	67	-	100	20	233	167	33	-
GKSS results	67	<LOD	86	20	205	142	29	<LOD
NILU results	70	5*	96	33	288	67	33	27*

* Calibration curve was not forced through origin. Small signals (<LOQ) were overestimated.

Conclusions

- All neutral precursor compounds were detected in English air samples. Highest values were found for 8:2 FTOH. Concentrations in urban air were higher than in semi-rural air.
- 10:2 FTOlefin is reported for the first time in air samples. Values are probably strongly underestimated due to severe losses in the extraction and concentration process.
- Several ionic compounds are present in the particle phase of the air samples. They could undergo atmospheric long-range transport. Highest concentrations of all analysed compounds (including the precursors) were found for PFOA.

Results from English air samples

Table 4. Results from air samples from Hazelrigg/UK (2 samples, semi-rural site) and Manchester/UK (2 samples, urban site). All concentrations (pg/m³ air) are field blank deducted.

	10:2 FTOlefin*	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	N-Me-FOSA	N-Et-FOSA	N-Me-FOSE	N-Et-FOSE
Hazelrigg Filter 1	<0.4	0.69	<1	<1	<1	<1	0.35	12.1	6.9
Hazelrigg Filter 2	<0.4	nd	<1.1	<1.1	<1.1	<1.1	0.35	<4.2	<3.2
Hazelrigg PUF/XAD 1	<0.2	<50	15.9	9.0	25.2	2.1	1.6	19.2	13.3
Hazelrigg PUF/XAD 2	0.24	56.5	147	196	125	8.9	14.2	29.1	5.1
Manchester Filter 1	0.32	2.1	<1.2	<1.2	0.83	<1.2	0.42	14.6	4.6
Manchester Filter 2	0.21	nd	1.8	5.8	4.6	1.5	0.92	33.3	18.0
Manchester PUF/XAD 1	0.38	59.3	315	326	88.8	<0.6	11.2	20.0**	<12**
Manchester PUF/XAD 2	1.0	17.4	58.2	148	40.7	6.1	7.9	27.4	6.4

* Quantification of 10:2 FTOlefin by GC/NCI-MS

** Values obtained by GC/NCI-MS-MS, due to interference in PCI-MS

	PFBS	PFHxS	PFOS	PFDCs	6:2 FTS	PFHxA	PFHpA	PFOA	PFNA	PFDCa	PFUnA
Hazelrigg Filter 1	<3.2	<5.8	<43.9	<0.45	nd	<54.9	14.4	828	<13.6	14.3	<4.5
Hazelrigg Filter 2	<3.2	<5.9	<44.5	<0.45	nd	<55.6	<6.3	276	<13.8	2.4	<4.6
Manchester Filter 1	2.5	1.0	41.1	0.75	9.2	<26.0	11.6	455	<26.6	5.4	nd
Manchester Filter 2	2.0	0.91	51.0	<0.45	9.7	<19.1	4.9	226	<19.6	nd	nd



Figure 3. Extraction of PUF/XAD/PUF



Figure 4. Extraction of filters

Chromatograms of Manchester sample

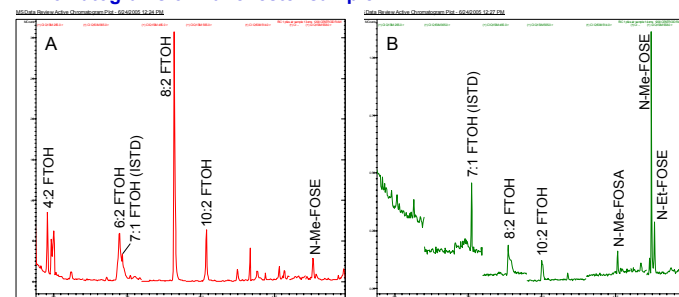


Figure 5. Total ion current chromatograms of GC/PCI-SIM-MS analysis of A) Manchester PUF/XAD 2 and B) Manchester Filter 2 sample

References

- [1] M. Smithwick et al., Environ. Sci. Technol. 39 (2005) 5517-5523 [3] J.W. Martin et al., Anal. Chem. 74 (2002) 584-590
 [2] D.A. Ellis et al., Environ. Sci. Technol. 38 (2004) 3316-3321 [4] U. Berger et al., Eur. J. Mass Spectrom. 10 (2004) 579-588