Analytical method for PFOA (and higher homologues) in articles - challenges and current status.

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Acknowledgement

I would like to express my sincere gratitude to my colleagues at

The Norwegian Climate and Pollution Agency

Ms. Ingunn Corell Myhre and Mr. Lars Haug Andersen in particular

The Norwegian Institute for Air research (NILU)

Ms. Dorte Herzke in particular

who made this presentation and product case study possible.

The challenge

- Versatile uses in articles

- Unknown exact compositions of PFCs

- Perfluorinated compounds (PFCs) are used in several industrial branches, but they also occur in a large range of consumer products.

- Due to their extraordinary properties (chemically inert, non-wetting, very slippery, nontoxic, nonstick, highly fire resistant, very high temperature ratings, highly weather resistant) they are applied in fluoropolymer coated cookware, sports clothing, extreme weather military uniforms, food handling equipment, medical equipment, electronic devices (e.g Li-ion batteries, toys etc) as well as water repellent products.

- Our present knowledge of the exact chemical PFC compositions in articles using perfluorinated compounds is limited or unknown.

Information to consumers on articles that may contain PFCs

some examples

Description	**PFC content information on the consumer article**
Privilege pan	Teflon Pro Platinum non-stick coating, professional use
Tefal pan ø 28	PFOS/PFOA free
Rast camping pan	Teflon coated
IKEA pan	Teflon classic convenience
Eva cake form	SLIP-LET®
Table cloth, Princess	Teflon fabric protector
Carpet brown; Element	Teflon treated

Analytical procedures for PFCs in articles (solid items)

Both volatile and non-volatile PFCs are analysed using well established analytical methods applying GC/MS and LC/MS (*LC/MS/MS or LC/TOF-MS*) techniques.

(*NOT: Analytical equipment in brackets are expensive and not common*)

Quality assurance measures are applied to ensure best possible quality of the data. Samples are diluted and extracted for both volatile and ionic PFCs, followed by a cleaning step with activated carbon.

Solid samples are homogenized prior to extraction and then treated similar to liquid samples.

Reported LOD levels in litterature from approx. 0,1 ng/g to 20 ng/g dependent on matrixes analysed.

Sample extraction

- At least two different methods are employed for the chemical analysis of the compounds of interest (volatile and non-volatile PFC).
- Both methods use similar sample pre-treatment and extraction step differing in choice of solvent, internal standard and analytical instrument.
- The analytical method applied is similar to the CEN standard for the determination of PFOS

Cleanup and quantification

Neutral volatile compounds

- The sample extracts are prepared according to a procedure established for the analysis of volatile PFCs, involving treatment with activated carbon.
- For heavily contaminated samples an additional dilution step is necessary.
- Separation and quantification are done by gas chromatography coupled to mass spectrometry (GC/MS). Quantification was based on the use of ^{13}C-labeled standards.
- Special care is taken to control thermal compound degradation in the GC injector and on the GC column.

Cleanup and quantification

Ionic non volatile compounds

The sample extracts containing ionic PFCs are cleaned up according to an established procedure for the analysis of PFOS and PFOA and other ionic PFCs with varying chain length. This includes purification with activated carbon.

Separation and quantification are done by liquid chromatography coupled to a **T**ime-**O**f-**F**light mass spectrometry (LC/TOF-MS).

The applied method is in accordance with the standardized analytical method developed for CEN /EU to analyse PFOS.

Quantification was based on the use of ^{13}C-labeled standards.

Analysed PFCs

Ionic PFCs that are analysed:

- PFCAs with a chain length of C4 to C14
- PFSs with a chain length of C4 to C10
- Other PFCs like 6:2 and 8:2 FTS, PFOSA and some FOSE/FOSA.

Volatile PFCs that are analysed:

- FTOHs with C4, C6, C8 and C10 chains
- FOSE/FOSA

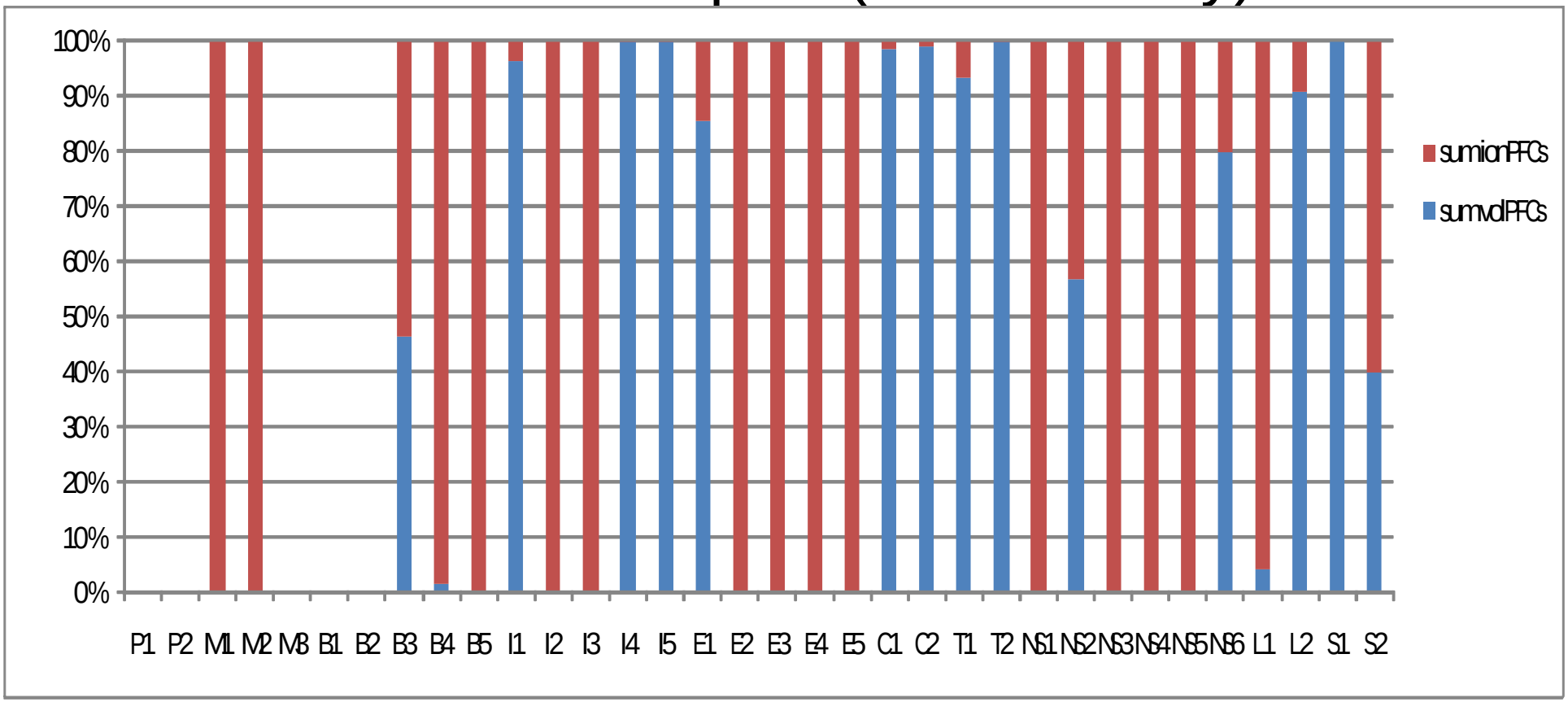
Analysed PFCs

Abbreviation	Full name	CAS #	Detection method
Fluortelomer alcohols			
4:2 FTOH	4:2 Fluorotelomer alcohol	2043-47-2	GC-MS
6:2 FTOH	6:2 Fluorotelomer alcohol	647-42-7	GC-MS
8:2 FTOH	8:2 Fluorotelomer alcohol	678-39-7	GC-MS
10:2 FTOH	10:2 Fluorotelomer alcohol	865-86-1	GC-MS
Fluortelomer sulfonates			
6:2 FTS	6:2 Fluorotelomer sulfonate	27619-97-2	HPLC-MS
8:2 FTS	8:2 Fluorotelomer sulfonate	39108-34-4	HPLC-MS
Fluortelomer carboxylates			
6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylate	$C_8H_2F_{12}O_2$*	HPLC-MS
8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylate	70887-84-2	HPLC-MS
Perfluoro sulfonates			
PFBS	Perfluorobutane sulfonate	375-73-5	HPLC-MS
PFHxS	Perfluorohexane sulfonate	432-50-7	HPLC-MS
PFOS	Perfluorooctane sulfonate	1763-23-1	HPLC-MS
PFDcS	Perfluorodecane sulfonate	335-77-3	HPLC-MS
N-Et-FOSE	N-Ethyl-heptadecafluorooctane sulfonamidoethanol	1691-99-2	HPLC-MS

Analysed PFCs

Abbreviation	Full name	CAS #	Detection method
Perfluoro carboxylates			
PFBA	Perfluorobutanoate	375-22-4	HPLC-MS
PFPA	Perfluoropentanoate	2706-90-3	HPLC-MS
PFHxA	Perfluorohexanoate	307-24-4	HPLC-MS
PFHpA	Perfluoroheptanoate	375-85-9	HPLC-MS
PFOA	Perfluorooctanoate	335-67-1	HPLC-MS
PFNA	Perfluorononanoate	375-95-1	HPLC-MS
PFDcA	Perfluorodecanoate	335-76-2	HPLC-MS
PFUnA	Perfluoroundecanoate	2058-94-8	HPLC-MS
PFDoA	Perfluorododecanoate	307-55-1	HPLC-MS
PFTrA	Perfluorotetradecanoate	376-06-7	HPLC-MS
Fluorooctane sulfonamides/ sulfonamidoethanols			
PFOSA	Perfluorooctane sulfonamide	754-91-6	HPLC-MS
N-Me-FOSA	N-Methyl-heptadecafluorooctane sulfonamide	31506-32-8	HPLC-MS
N-Et-FOSA	N-Ethyl-heptadecafluorooctane sulfonamide	4151-50-2	HPLC-MS
N-Me-FOSE	N-Methyl-heptadecafluorooctane sulfonamidoethanol	24448-09-7	HPLC-MS

Analysed PFCs, either ionic or volatile, were found in all but 5 samples (a case study)



NS: non stick ware, P: paper, T: textiles, L: leather, C: carpets, E: Electronics

All other product categories mentioned in the table above but not explained are preparations.

Unknown PFCs (case study)

- All samples were screened for unknown PFCs according to the PFOS replacements identified by the Stockholm Convention on Persistent Organic Pollutants POPs review committee (POPRC).

- Due to the nature of the used analytical instrumentation, additional ionic PFCs could be screened for. However, not many unknown PFC could be extracted from the fullscan chromatograms.

- Polyfluoroalkyl phosphonic acids and phosphoric acids and their diesters (PAPs and diPAPs), used mainly in packaging, could not be found by the applied means in the paper samples.

- A lot of signals in the analysed samples remain unknown and the chemical structure could not be solved during this case study.

Conclusions and recommendations

- Even with a limited number of samples, this screening of polyfluorinated products shows the extreme versatility and application in a variety of industrial materials and consumer applications and products.

- A complete list of all respective compounds does not exist as well as trace analytical methods capable for all compounds mentioned. More work and requirements of chemicals information from the distribution chain is needed in order to be able to enforce a new regulation.

- Impurities, transfer during production, storage, transport or other sources could contribute to the overall PFC load.

- It is strongly recommended to have a continuous follow–up on product groups since our knowledge and best practiced analytical performance of PFC content are limited.

- More screening is suggested for carpets, leather and textiles in order to assess the possible exposure. Even if levels might seem low in some products, the amount of these products used and deposited could lead to a considerable source of emission into ecosystems, especially as waste.

- New PFCs will be introduced into the European and global market, eventually turning up in consumer households

Thanks for your attention!