The newly developed Plasma Emission Detector with Echelle Spectrometer (EPED) in combination with GC as a tool to analyse the emission of unknown fluorinated substances from consumer products and food contact materials

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Abstract
A new kind of detector was adapted to analyze unknown fluorinated substances with gas chromatography. The newly developed GC-EPED shows high sensitivity and selectivity for sulphur and the halogens chlorine, bromine, fluorine and iodine with detection limits for the above elements < 10 pg/s and will therefore be an important tool to analyse fluorinated and other halogenated substances. In combination with a P&T sampler the GC-EPED is a possible replacement for test chamber methods to analyze the emission of fluorinated substances especially from consumer products and food contact materials.

2 Introduction

The trace analysis of perfluorinated carboxylates and sulfonates in organic matter is still state-of-the-art, but knowledge about per- and polyfluorinated precursor compounds in biological matrices is limited. For example Yeung and coworkers [1] demonstrated the presence of substantial amounts of unidentified organic fluorine in human blood samples by the combination of an automated combustion unit and an ion chromatography system [2]. Aim of the presented work was to develop an analytical tool to be able to analyze unknown fluorinated substances with gas chromatography. A Plasma Emission Detector with Echelle Spectrometer (EPED) was coupled with GC.

2 Description of the EPED

The Echelle Plasma Emission Detector (EPED) combines a long term stable pulsing plasma cell with a high resolution Echelle spectrometer.

Fig. 1: Picture of the EPED-detector

The newly developed EPED detector was combined with gas chromatography (Agilent 6890 GC) by direct coupling of the GC capillary column.

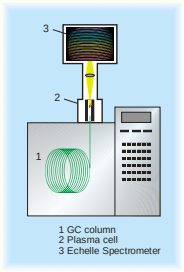

Fig. 2: Scheme of the EPED-detector coupled with GC

The detector principle is based on the excitation of atoms in a helium micro plasma at atmospheric pressure. The emission lines of the target atoms are continuously recorded by an echelle polychromator, which is directly adapted to the plasma cell. Due to the high energy of the pulsed plasma, all eluating molecules from the column are atomized in the plasma at temperatures of about 8000K and are emitting element-specific wavelengths.

The resulting multi-element detector shows high sensitivity and selectivity for sulphur and the halogens chlorine, bromine, fluorine and iodine with detection limits for the above elements < 10 pg/s and a linearity about 3-4 decades. Additionally carbon can detected but with less sensitivity. The detector response for the elemental concentrations is totally structure independent.

In further experiments the GC-EPED was combined with a purge & trap sampler (PTA3000, IMT). Former work [4] demonstrated that a modified purge & trap sampler combined with GC/FID can be used for the determination of the emission of volatile organic compounds from building products and furnishing as a replacement for the test chamber method according to ISO 16000-9. In combination with the EPED detector this methodology is able to analyse the overall emission of fluorinated substances e.g. from consumer products and food contact materials.

3 Results

In a first approach fluorine-containing waterproof/breathable fabrics and greaseproof paper products were investigated.

The emission of a large number of fluorine containing substances could be observed. Some of the fluorinated compounds could be identified as fluorotelomers (e.g. 6:2-, 8:2- and 10:2-FTOH) by comparison with native standards.

The simultaneous measurement of fluorine and sulfur confirmed the presence of perfluorinated thiols like HDFT (= 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanthiol) and homologues in some samples.

The EPED methodology also allowed the quantification of the total fluorine content. The maximum value found was 2101 ng fluorine / dm² for a butter wrapper. By comparing total fluorine with the sum of FTOHs and FTSHs the percentage of the unknown fluorine compounds amount is up to 96%.

4 Discussion

The first results with the EPED detector showed that there is a large number of fluorine containing substances emitted from waterproof/breathable fabrics and greaseproof paper products. Characterization, identification and quantification of these unidentified fluorinated compounds would be instructive.

The measurements with the GC-EPED demonstrated that the detector is a valuable tool for this purpose. The detector will allow to perform mass balances of perfluorinated compounds with their precursors and metabolic intermediates in biological matrices.

Further work will focus on structure identification of the still unknown emitted fluorinated substances and the validation of a universally-valid quantification method for unknown fluorocarbons.

Sample	Total	sum of FTOH	sum of FTSH	unknown fluorinated compounds	unknown fluorinated compounds	
	(ng F / dm²)	(ng F / dm²)	(ng F / dm²)	(ng F / dm²)	(%)	
PF-0133	1507	1159	10	338	22	baking paper
PF-0143	872	582	5	286	33	baking paper
PF-0003	435	15	2	418	96	fast food paper
PF-0117	622	510	1	111	18	baking paper
PF-0063 B	744	344	1	398	54	butter wrapper
PF-0063 C	915	202	1	712	78	butter wrapper
PF-0137	1562	410	91	1062	68	butter wrapper
PF-0096	2101	156	196	1749	83	butter wrapper

Fig.3: The table illustrates the amounts of total fluorine, total FTOHs and total FTSHs in selected samples. Further a sample description and the percentage of the unknown fluorine amount is shown.

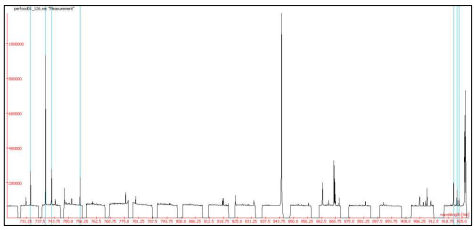

Fig.4: EPED spectral data of 10:2-FTSH

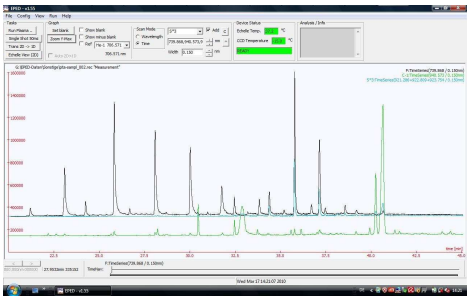

Fig. 5: EPED-chromatogram showing carbon-, fluorine- and sulfur-traces of a real sample containing FTOH and fluorinated thiols (FTSH)

References

[1] Yeung et al., 2008. Perfluorinated Compounds and Total and Extractable Organic Fluorine in Human Blood Samples from China, Environ. Sci. Technol., 2008, 42 (21)
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[3] EPED specification, see http://www.imtgmbh.de/eped-e.htm
[4] Scherer et al., 2007. Entwicklung eines Schnelltestverfahrens zur Bestimmung von VOC-Emissionen (2007). 36. Jahrestagung der GUS 2007: 14.-16. März 2007, pp. 201-210