DEVELOPMENT OF SCREENING METHODS FOR FLUORINATED COATINGS OF FOOD CONTACT MATERIALS AND OTHER EVERYDAY COMMODITIES

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Introduction

Perfluorinated chemicals (PFCs) and their precursors are a group of chemicals widely used to create non-stick coatings on items such as cooking pans and food packaging as well as stain repellant coatings on goods like carpets, clothing and furniture. Because PFCs are extremely persistent and partly also bioaccumulative chemicals there is a need to identify the presence of fluorinated compounds in everyday live. Therefore it was the aim of the presented work to develop screening methods to identify fluorinated coatings on food contact materials and other everyday commodities.

Materials and methods

Investigated samples:

Food contact materials and other everyday commodities were collected mainly in Freising, situated north-east of Munich in Bavaria, Germany.

Sliding spark spectroscopy (SSS):

SSS (SSS2, IoSys) is normally used for plastic characterization and sorting. The basic principle of the method is the thermal vaporization of a small amount of the sample surface using a train of defined high-current sliding sparks. The material components in the spark plasma are vaporized, atomized and activated to emit radiation[1]. Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface.

Headspace GC-EI-MS:

Alternatively, a screening method with headspace GC-EI-MS (PE Clarus 600 C, PerkinElmer) was developed and tested [2]. About 1 dm² of the material was placed into a 10 ml headspace vial. At a temperature of 150°C volatile compounds are released into the headspace. An aliquot of the headspace volume is transferred onto a GC column and detected by EI-MS after chromatographic separation. Typical C_nF_m fragments (i.e. m/z 119, 131, 169, 195, 231, 331) were monitored in order to identify the presence of PFC.

P&T GC-EPED:

The newly developed Plasma Emission Detector with Echelle Spectrometer (EPED, IMT Innovative Messtechnik GmbH) was coupled with gas chromatography (AG6890, Agilent) and a purge & trap sampler (PTA3000, IMT) [3]. The EPED detector combines a long term stable pulsing plasma cell with a high resolution Echelle spectrometer. The resulting multi-element gas chromatographic 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.

Results and discussion

SSS and Headspace GC-EI-MS were compared for a set of 138 samples. In 105 of 138 investigated food contact materials and other everyday commodities both methods show equivocally the absence of fluorinated compounds (76.1%). In 31 cases (22.4%) both methods identified fluorinated compounds. Only for two cases of folded box materials which were known as fluorine-containing the SSS could not detect fluorine whereas HS-GC-MS showed significant traces of FC in gas phase. It turned out that the fluorine-containing coating was covered by a further layer. For three samples SSS detected fluorine, whereas HS-GC-EI-MS could not identify typical CnFm fragments. These samples might be contaminated by fluorine salts, which give a good response in SSS-detection but not in the headspace GC-MS system.

With headspace GC-EI-MS 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. (Fig. 1)

59 of the samples (all of them food contact materials) were analyzed with P&T GC-EPED. The results were in coincidence with the other methods. The EPED method also allowed the quantification of the total fluorine content. The maximum value found was 1888 ng fluorine / dm² for a butter wrapper. The simultaneous measurement of sulfur confirmed the presence of perfluorinated thiols (HDFT and homologues[4]) in some samples.

Comparing the methods the main advantage of the SSS is its fastness (<1 min). Headspace GC-EI-MS and P&T-GC coupled with EPED give more detailed information about the fluorinated compounds and are also reasonable fast (<1h). An important advantage of the GC-EPED is its capability to directly quantify the halogen content.

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References

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Fig. 1: HS-GC-MS: Chromatogram of a real sample compared to 500ng of each native Standards 4:2-, 6:2-, 8:2- and 10:2-FTOH

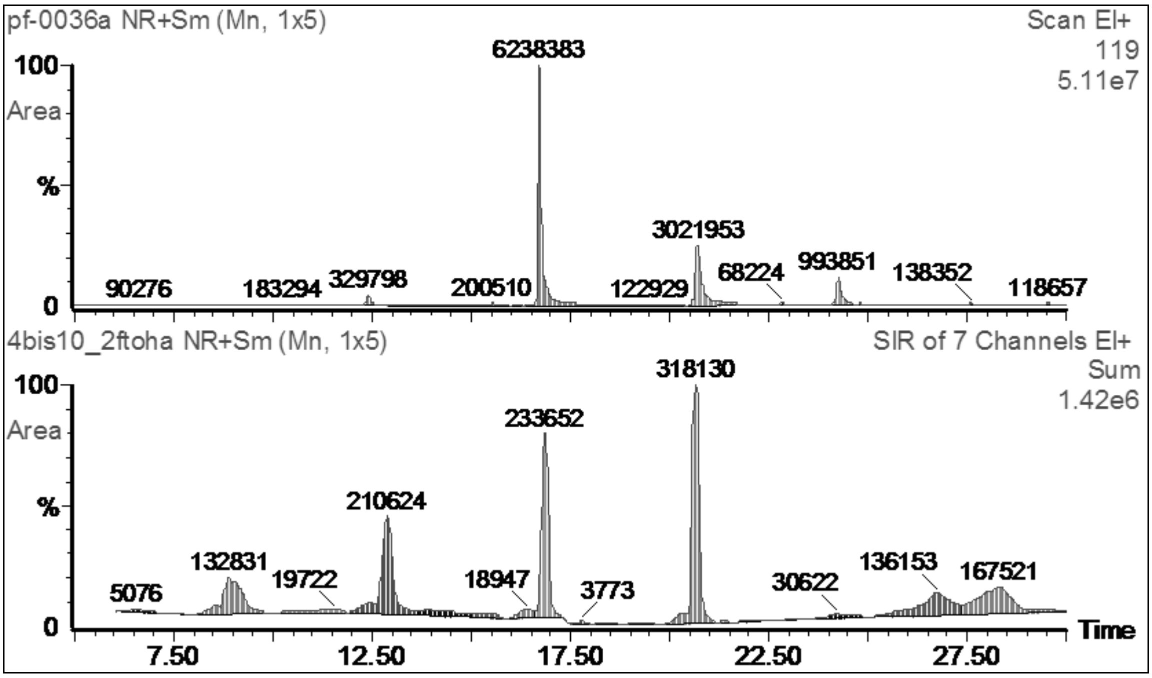

Fig. 2: Scheme of a EPED detector

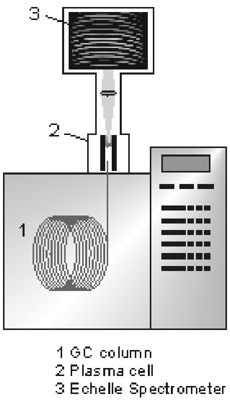

Fig. 3: EPED-chromatogram showing C-, F- and S-trace of a real sample containing FTOH and fluorinated thiols