Development of screening methods for fluorinated coatings of food contact materials and other everyday commodities

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Abstract

Screening methods were tested and developed to identify fluorinated coatings on food contact materials and other everyday commodities. Sliding spark spectroscopy (SSS) and Headspace GC-EI-MS turned out to be reliable and fast screening tools. A third approach, P&T-GC coupled with EPED gives more detailed information about the fluorinated compounds and is also reasonable fast (<1h). An important advantage of the GC-EPED is its capability to directly quantify the halogen content.

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. Beside already well-known approaches like wavelength dispersive X-ray fluorescence (XRF), X-ray microanalysis coupled to a scanning electron microscope (SEM) or fluorine NMR there were three additional screening methods used:

Sliding spark spectroscopy (SSS)
Headspace GC-EI-MS
Purge &Trap GC-EPED

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.

Analytical Methods

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].

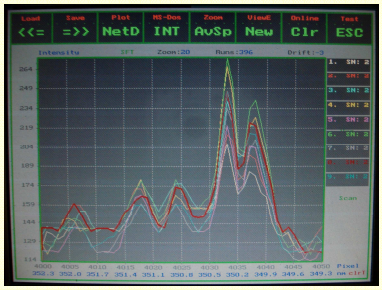

Fig. 1: SSS-result of a fluorine coated sandwich paper (PF-0036)

Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface. The analysis time for one sample is a few seconds. False positive measurements due to inorganic fluorine are possible.

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.

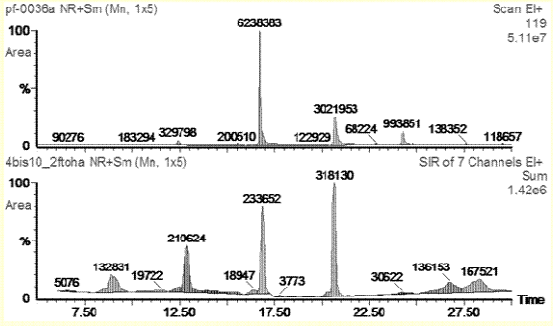

Fig. 2: HS-GC-MS-Chromatogram of a real sample compared to 500ng of each native Standards 4:2-, 6:2-, 8:2- and 10:2-FTOH

The use of EI (electron impact ionization) instead of CI allows the monitoring of typical C_nF_m fragments (i.e. m/z 119, 131, 169, 195, 231, 331, corresponding to FC-43 cal-gas fragments). This allows not only to detect the presence of known PFC, it allows also a detection of even unknown fluorinated organic compounds. The screening with Headspace GC-EI-MS can be automated and is reasonable fast (<1h), but each individual sample can be measured only once.

P&T GC-EPED:

The newly developed Plasma Emission Detector with Echelle Spectrometer (EPED, IMT Innovative Messtechnik GmbH, http://www.imtgmbh.de/eped-e.htm) was coupled with gas chromatography (AG6890, Agilent) and a purge & trap sampler (PTA3000, IMT) [3].

Fig. 3: Picture of a EPED-Detector

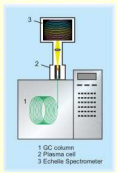

Fig. 4: GC/EPED scheme

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. The simultaneous measurement of fluorine and sulfur confirmed the presence of perfluorinated thiols like HDFT (heptadecafluoro-1-decanthiol) and homologues in some samples.

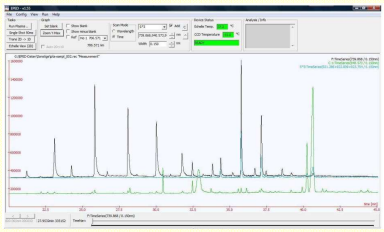

Fig. 5: EPED-chromatogram showing carbon-, fluorine- and sulfur-traces of a real sample containing FTOH and fluorinated thiols (FTSH)

Results and discussion

SSS and Headspace GC-EI-MS were compared for a set of 141 samples. In 105 of 141 investigated food contact materials and other everyday commodities both methods show equivocally the absence of fluorinated compounds (74.5%). In 31 cases (22.0%) both methods identified fluorinated compounds.

HS-GC/MS	+	31	2
	-	3	105
		+	-
		SSS	

Fig. 6: Comparison of the screening results of 141 FCM-samples

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 C_nF_m 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. 2)
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 rapidness (<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). Important advantages of the GC-EPED are the capability to directly quantify the halogen content as well as the simultaneous measurement of fluorine and sulfur .

Acknowledgments

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