Non-target screening of contaminants in paper-paperboard for food contact materials

Lukas Vapenka[*], Adam Vavrous[**], Lenka Votavova[*], Kristina Kejlova[**], Jaroslav Dobias[*], Jitka Sosnovcova[**]

[*] Department of Food Preservation, Institute of Chemical Technology in Prague, Technicka 5, 166 28 Prague 6, Czech Republic
[**] National Institute of Public Health, Srobarova 48, 100 42 Prague 10, Czech Republic

Introduction

The application of paper based materials for food packaging is not covered by a harmonized EU legislation on food contact materials. There is still a lack of systematic information on the occurrence of xenobiotics in paper and/or paperboard used for food packaging in EU member states. For this reason the EFSA Scientific Cooperation (ESCO) Working Group was set up in February 2010 in order to collect the information present at Member State level and to make proposals to anticipate emergency situations linked to presence of substances released by non-plastic food contact materials and for which no harmonised risk assessment is available.

The most important contaminants in paper and paperboard for food packaging are anthraquinone, bisphenols, phthalates, mineral oil saturated hydrocarbons (MOSH), mineral oil aromatic hydrocarbons (MOAH), photoinitiators, etc. Most of them originate from recycling process, the contaminants from paper pulp processing are also present.

The aim of this work was non-targeted screening of xenobiotics in paper and paperboard packaging materials used for food packaging in the Czech Republic.

EXPERIMENTAL PROCEDURE

Samples

- 83 samples of paper and paperboard used for food packaging in the Czech Republic (printed and/or unprinted with different content of recycled pulp).

Samples preparation

- Solvent extraction
  - Solvent: methanol
  - Extraction: 10 ml solvent + 0.5 g sample (cut up paper)
    30 min ultrasonic bath
    Concentration of extract
- Direct analysis of sample
  - 0.5 g sample (cut up paper) → solid phase microextraction (SPME)
  - Extraction conditions: headspace, temperature, 40 °C; time, 30 min; SPME fibre, divinylbenzene/carboxen/polydimethylsiloxane (DVB/ CAR/ PDMS)

GC-MS analysis

- Liquid injection
  - Gas chromatograph Agilent 6890 with mass selective detector Agilent 5973N
  - Capillary column DB-5ms (30 m × 0.25 mm × 0.25 μm)
  - Mobile phase: Helium; constant flow 1 ml/min; linear velocity 36 cm/s
  - Injection: 1 μl; Split 1:1; temperature, 250 °C
  - Oven temperature programme: 40 °C for 1 min; 40 °C to 325 °C at 10 °C/min; 325 °C for 15 min
- Headspace SPME
  - Gas chromatograph Agilent 7890 with mass selective detector Agilent 5975C
  - Headspace SPME: fiber DVB/CAR/PDMS, temperature, 40 °C; extraction time,1800 s
  - Capillary column, mobile phase and oven temperature programme were identical to liquid injection GC-MS.

Data processing

- Data were collected and processed by Agilent GC ChemStation software using NIST 11 Mass Spectral Library.

RESULTS

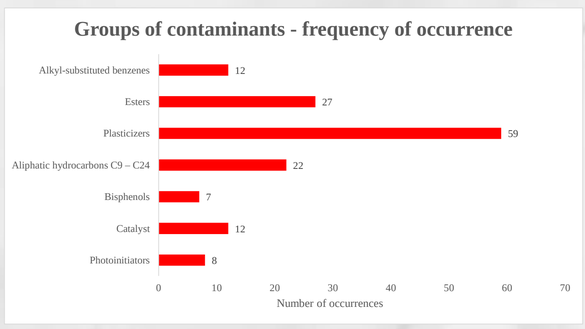

Figure 1. Groups of contaminants and their frequency of occurrence.

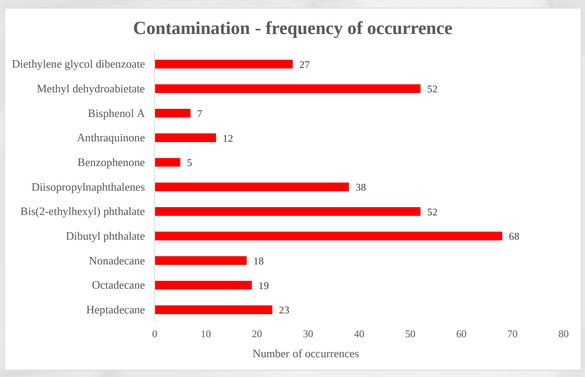

Figure 2. Typical contaminants in paper and their frequency of occurrence.

Table 1. Characterictics of the selected analysed sample.

Code	Food contact	Printed	% Recycled	Grammage (g/m²)
1	Direct	No	100	120
2	Direct	No	100	140
3	Direct	No	0	120
4	Direct	No	0	120
5	Direct	Yes	0	150
6	Indirect	No	100	170
7	Indirect	No	100	125
8	Indirect	No	100	125
9	Direct	Yes	0	135
10	Indirect	No	>90	140
11	Direct	No	<20	180
12	Direct	No	<20	200
13	Direct	No	0	27
14	Direct	No	0	35

Table 2. List of substances found in the selected sample.

		0 % recycled pulp						max. 20 % recycled pulp		>90 % recycled pulp					
Compounds		Sample code													
Aliphatic hydrocarbons	**CAS No.**	3	4	5	9	13	14	11	12	1	2	6	7	8	10
Heptadecane	629-78-7									+	+	+			
Octadecane	593-45-3									+	+	+	+		
Nonadecane	629-92-5									+	+	+	+	+	
Aromatic cyclic															
Dibutyl phthalate	84-74-2	+	+	+						+	+	+	+	+	+
Bis(2-ethylhexyl) phthalate	117-81-7				+				+	+	+	+	+	+	
Diisopropylnaphthalenes	2027-17-0								+	+	+	+	+		+
Ketones															
Benzophenone	119-61-9			+	+										
Anthraquinone	84-65-1							+	+					+	
Phenols															
Bisphenol A	80-05-7								+			+	+	+	+
Others															
Methyl dehydroabietate	1235-74-1	+		+	+				+	+	+	+	+	+	+
Diethylene glycol dibenzoate	120-55-8								+	+	+	+	+	+	+

CONCLUSIONS

- 93 compounds were identified in paper and paperboard by both the methods used.
- Anthraquinone (catalyst for lignin and cellulose separation), diisopropylnaphthalenes (solvents for carbonless copy paper), phthalates and diethylene glycol dibenzoate (plasticizers), methyl dehydroabietate (adhesive), benzophenone (photoinitiator), bisphenol A and aliphatic hydrocarbons were identified as typical contaminants in paper (Figure 2 and Table 2).
- Plasticizers represented the group of contaminants of the most frequent occurrence in tested samples (Figure 1) and dibutyl phthalate was the most prevalent contaminant (Figure 2) which was identified in 68 of 83 samples.
- Diisopropylnaphthalenes (DIPNs) and diethylene glycol dibenzoate were identified only in samples with content of recycled pulp above 20 % (Table 2). These contaminants could be used as suitable markers of addition of recycled pulp into paper.

References

Triantafyllou et. al., *Food Chemistry*, 2007, 101, pp. 1759-1769.
Binderup et. al., *Food Additives and Contaminants*, 2002, 19, pp. 13-28.
Suciu et. al., *Food Chemistry*, 2013, 141, pp. 4146-4151.
Song et. al., *J. Agric. Food Chem.*, 2000, 48, pp. 5856-5859.
Asensio et. al., *Packag. Technol. Sci.*, 2009; 22, pp. 311–322.

Acknowledgments

The authors are grateful for financial support provided by the Specific University Research (MSMT No. 20/2014): A1_FPBT_2014_006 and the Internal Grant Agency of the Ministry of Health of the Czech Republic (research project no. NT/14375 – 3/2013).