Quantitative screening of possible migrants from paperboard packaging material by solid-phase micro extraction coupled to gas chromatography-mass spectrometry

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Introduction

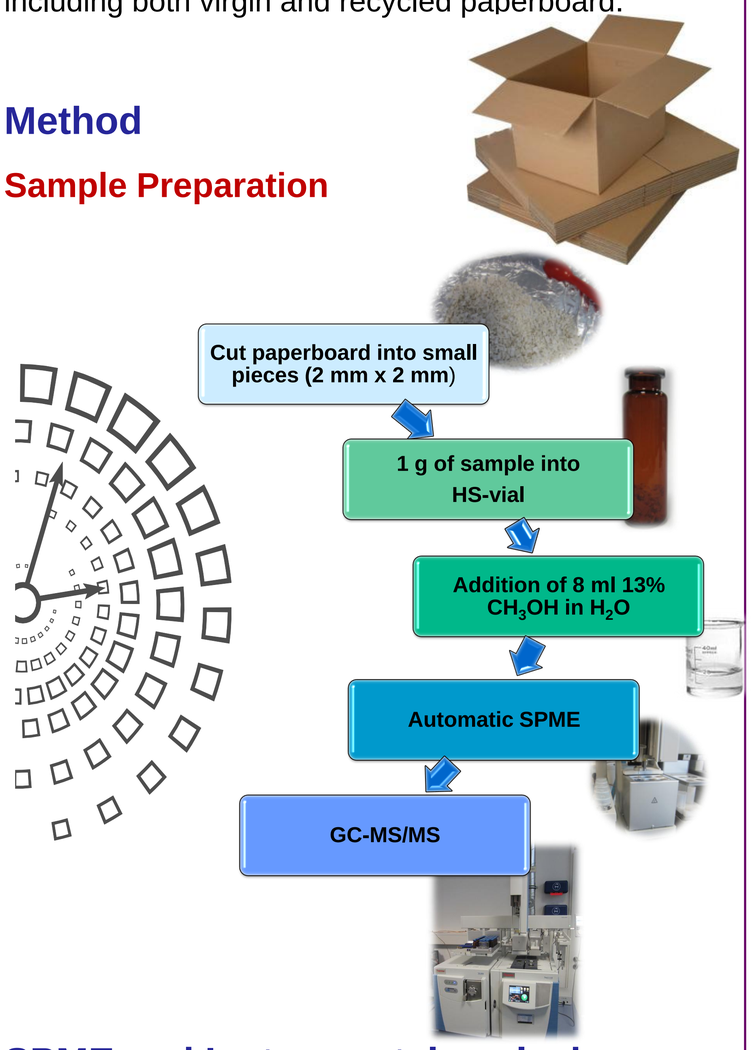
The reported method was developed for the determination of possible migrants from paperboard packaging material by usage of solid phase micro extraction and gas chromatography coupled to mass spectrometry. The method can be used for monitoring the content of unwanted compounds in paperboard intended for use in the contact with food. During method development were investigated all important parameters in order to reach the best method performance for the group of 19 important compounds covering the representatives of phthalates, photoinitiators, phenols, and off-flavors deriving from the degradation of paperboard components including printing, coating and adhesives.

The final method was successfully validated as a quantitative screening method for a group of 12 target contaminants.

The final method was applied in a small survey covering paperboard samples of various quality including both virgin and recycled paperboard.

Method

Sample Preparation



SPME and Instrumental analysis

Automated SPME

Fiber: 100 µm PDMS (polydimethylsiloxane)

Extraction time and temperature: 45 min at 65°C

Desorption time and temperature: 7 min at 270 °C

Conditioning fiber: 20 min

Swirling the vial: all the time

Instrumentation

System: Thermo Scientific™ TSQ 8000 Triple Stage Quadrupole MS coupled to Trace 1310 GC equiped with TriPlus RSH Autosampler

Column: TG – 5 SilMS(0.25mm x 30m; 0.25 µm)

Injection: S/SL injector – splitless mode, at 270°C

Carrier flow: 1.2 ml/min

Transfer line: 250 °C

MS/MS parameters: EI Positive

SRM ion mode

at 70 eV

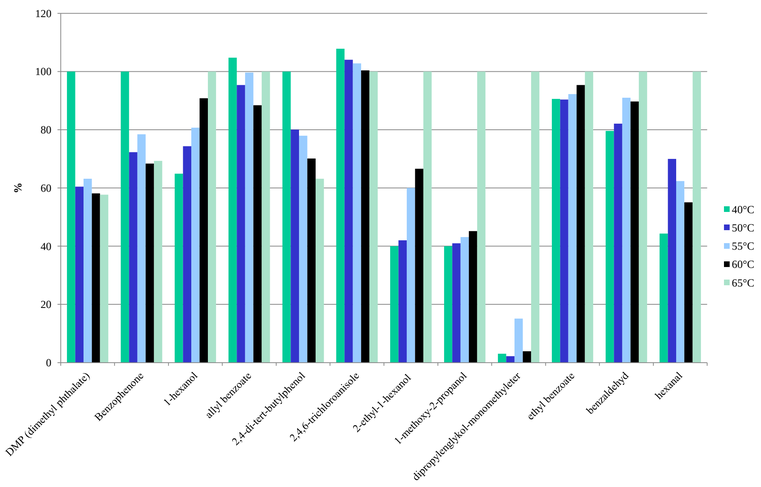
TABLE 1. Validation results: method recovery (%), method repeatability expressed as RSD (%) for spiked paperboard samples at three different spike levels with six replicates and intermediate precision expressed as RSD (%) measured at one level with three sets with six replicates in three days

Compound	Spiking levels (µg/kg)			Repeatability (%)			Recovery (%)			Intermediate precision at Level II. (%)			LOD (µg/kg)	LOQ (µg/kg)
	Level I.	Level II.	Level III.	Level I.	Level II.	Level III.	Level I.	Level II.	Level III.	Day I.	Day II.	Day III.		
1-hexanole	750	2000	4000	8	13	2	83	100	103	8	15	11	100	300
1-methoxy-2-propanol	75	200	400	15	4	2	86	95	103	15	14	2	20	60
2,4-di-tert-butylphenol	7.5	20	40	11	19	16	77	82	81	11	7	21	0.3	1
2-ethyl-1-hexanol	75	200	400	16	8	2	90	109	103	16	14	1	20	50
Allyl benzoate	7.5	20	40	9	12	5	89	98	94	9	8	6	0.3	1
Benzaldehyd	75	200	400	19	7	3	85	112	102	19	14	5	2	5
Benzophenone	7.5	20	40	20	19	5	92	118	98	20	21	17	16	50
Dipropylenglykol-monomethyleter	7500	20000	40000	19	10	18	97	78	70	19	28	21	2500	7500
DMP (Dimethylphthalate)	75	200	400	9	9	3	104	101	100	9	8	9	8	20
Ethyl benzoate	7.5	20	40	7	10	3	88	99	97	7	9	3	1.5	5
Hexanal	7500	20000	40000	14	13	15	108	119	120	14	20	8	35	100
2,4,6-trichloroanisole	7.5	20	40	20	22	19	94	88	86	20	7	22	0.03	0.1

Method Development

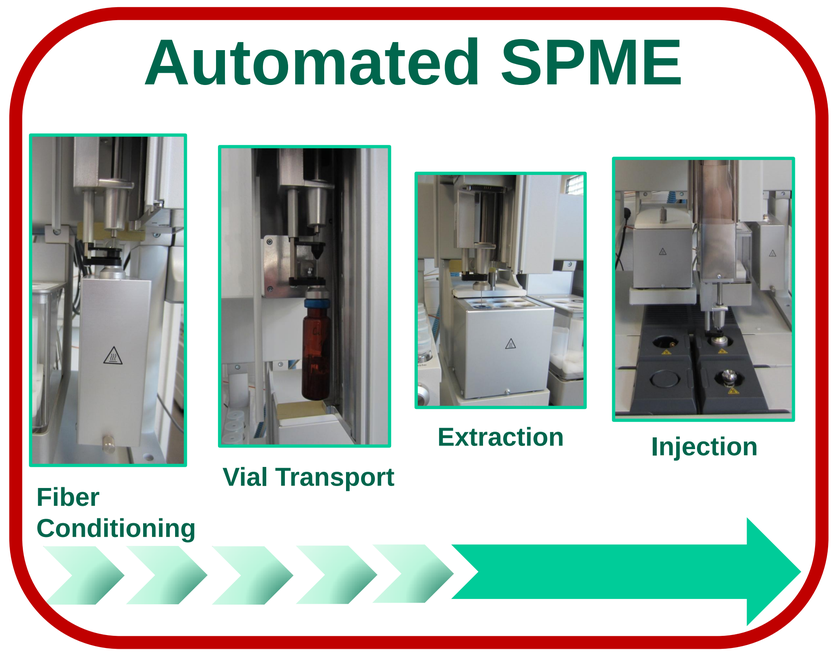
Different commercial SPME fibers and other parameters affecting the performance of extraction process including extraction temperature (see the Figure 1) were investigated during method development.

FIGURE 1. Peak areas for 12 target compounds determined at different extraction temperatures (65°C was chosen as optimal)



Survey Samples

After validation method was applied on the small group of survey samples covering virgin and recycled paperboard in printed and non-printed version. The results confirmed the presumption of higher content of packaging contaminants in recycled and printed paperboard samples as it is shown in the Table 2.



Method Validation

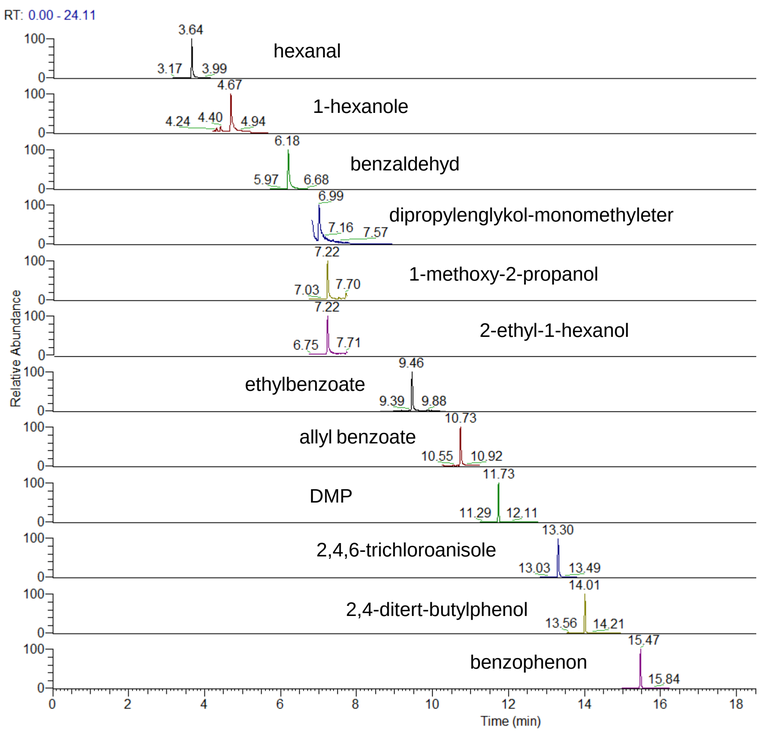
In-house validation of the developed method was carried out for paperboard and 12 target compounds. Due to the difficulty to gain a pure blank paperboard for quantitation the standard addition procedure was employed. The measured parameters were specificity, linear range, precision, accuracy, limit of detection and limit of quantification (LOD and LOQ). The partial results are shown in the Table 1. The example of chromatogram with 12 target compounds is shown in the Figure 2.

TABLE 2. Levels (in µg/kg) of packaging migrants in the survey samples (C1 – C12)

Analyte	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
1-hexanole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	313	< LOQ	< LOQ	< LOQ
1-methoxy-2-propanol	91	95	187	273	< LOQ	3881	476	103	6160	1388	5886	1411
2,4-di-tert-butylphenol	8	8	7	< LOQ	10	18	10	7	19	< LOQ	15	12
2-ethyl-1-hexanol	96	99	85	278	50	3880	480	109	6237	1409	5967	1446
Allyl benzoate	< LOQ	< LOQ	< LOQ	3	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5	< LOQ	< LOQ
benzaldehyd	263	659	373	1546	97	299	831	637	1052	1282	575	1094
Benzophenone	36	< LOQ	94	103	< LOQ	92	2765	984	2718	1342	2362	3002
Dipropylenglykol-monomethyleter	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	14825	< LOQ	< LOQ	< LOQ
DMP	< LOQ	< LOQ	< LOQ	21	< LOQ	< LOQ	72	32	87	< LOQ	74	28
ethyl benzoate	< LOQ	< LOQ	< LOQ	23	< LOQ	8	5	< LOQ	11	12	6	9
hexanal	4199	528	13610	4398	1687	2799	6099	3788	14707	5369	2278	2079
2,4,6-trichloroanisole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Note. C1 – C5: not printed virgin paperboard, good – high quality; C6: printed virgin paperboard, good quality; C7 – C8: not printed recycled paperboard, low quality; C9 – C12: printed recycled paperboard, low – bad quality

FIGURE 2. Example chromatogram of spiked paperboard with 12 packaging migrants (c = 0.024 – 30 mg/kg)



Conclusion

- The reported method enables determination and quantification of 12 possible migrants from paperboard
- The method is fully automated thanks to the usage of automated SPME
- Thanks to the usage of automated SPME the developed method is very fast, robust and saving significantly manpower
- The good results obtained from in-house validation confirmed the suitability of this method for monitoring the content of unwanted contaminants in paperboard intended to be use in contact with food

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