Semi-quantitative determination of potential migrants in food packaging materials - Part 2: Semi-volatile compounds

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Introduction

The importance of screening methods is more and more increasing e.g. for analysis of non intentionally added substances (NIAS). In other cases migration of substances, e.g. oligomers, shall be evaluated but reference substances are lacking. In all these cases semi-quantitative methods are necessary to enable food regulatory evaluation or at least the decision if a peak in an extract or migration solution is negligible or not.
The signal of the flame ionization detector (FID) correlates in theory linearily with the mass of carbon in the column output. Therefore the FID should be calibratable with an universal internal standard. Many labs use such techniques, but data on accuracy of such a semi-quantitative estimation are lacking. We use the antioxidant BHA (2-*tert*-butyl-4-hydroxyanisole) with a molecular weight of 180 g/mol as internal standard for calibration. BHA contains oxygen as hetero atom and should therefore give a more conservative estimation than a pure hydrocarbon.
More than 50 different substances have been analyzed in seven level calibrations and their relative response factors versus the response of BHA have been determined. Thus the confidence interval for such an semi-quantitative approach using an "universal" internal standard can be estimated which is an important step for the evaluation of screening results.

Method

55 representative substances related to food packaging materials and adhesives were selected. Standard solutions of each substance were prepared in dichloro-methane (DCM) with concentrations of 0.1, 0.5, 1.0, 5.0, 10, 25 and 50 mg/l BHA as internal standard. These standards were analyzed by using GC-FID equipped with DB-1 column (30 m × 0.32 mm i.d. × 0.25 µm film thickness). The oven temperature was programmed to start from 40 °C (4 min) at rate 5 °C/min to 340 °C (10 min). The injection and detection temperature were kept at 300 °C and at 320 °C. The relative response factor (RRF) was defined as the signal/concentration ratio between analyte and the internal standard BHA. The RRF was calculated for mass related concentration (mg/l, RRF w/w).

$$\text{Relative response factor (RRF)} = \frac{Area_s}{C_s} * \frac{C_{is}}{Area_{is}}$$

Area $_s$: Peak area of the analyte
C_s: Concentration of analyte (mg/l)
Area $_{is}$: Peak area of the internal standard
C_{is}: Concentration of internal standard (mg/l)

Results

The DB 1 column (dimethylpolysiloxane) is a non-polar phase and separates substances according to their molecular weight (Figure 2). Polar substances like alcohols (glycol, polyol) or amines show a bad peak shape (Figure 1) and therefore low sensitivity. The relative response of the alcohols except resorcinol was poor (0.14 ~ 0.45).

1, Methyl acrylate	2, Vinyl propionate	3, Ethyl acrylate	4, Ethylene glycol	5, Methyl methacrylate	6, Propylene glycol	7, Ethyl acrylate	8, *para*-Xylene
9, Styrene	10, Butyl acrylate	11, 1,4-Butanediol	12, Diethylene glycol	13, *alpha*-Methylstyrene	14, Butyl methacrylate	15, Glycerol	16, N-vinyl-2-pyrrolidone
17, Hexamethylene diamine	18, Caprolactam	19, Ethylhexyl acrylate	20, Resorcinol	21, Isophoron diamine 2nd peak	22, Isophron diamine main peak	23, Glycerol triacetate	24, Toluene-2,4-diamine
25, Butyl diglycol acetate	26, 2,6-Di-tert-butyl-4-methylphenol	27, Benzophenone	28, 2-Octyl-2H-isothiazol-3-one	29, Diisobutyl phthalate	30, Dibutyl phthalate	31, 4,4'-Methylene dianiline 2nd peak	32, 4,4'-Methylenedianiline main peak
33, Benzoflex 284	34, Bisphenol A	35, Docusate sodium	36, 2-Ethylhexyl diphenyl phosphate	37, Diethylhexyl adipate	38, Diethylene glycol dibenzoate	39, Dipropylene glycol dibenzoate	40, Benzoflex 354
41, Diethylhexyl phthalate	42, Triethylene glycol dibenzoate	43, BADGE	44, 4,4'-bis(4-glycidyloxyphenyl) propane	45, Irgafos 168	46, Irganox 1076	47, Benzoxazole, 2,2'-(2,5-thiophenediyl) bis(5-(1,1-dimethylethyl)	48, Irganox 1330

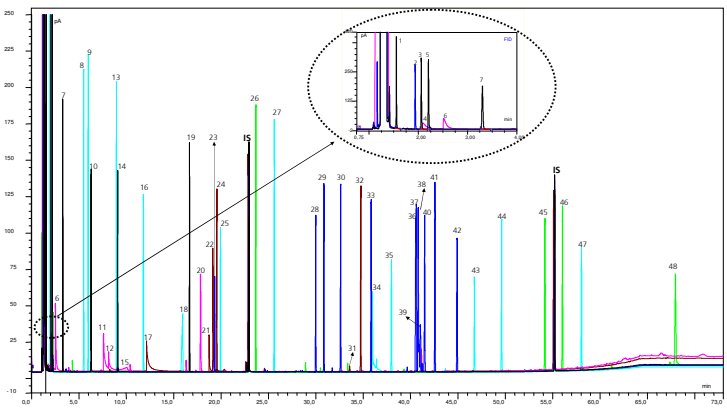

Figure 1: Representative chromatograms of the adhesive related substances detected by using GC-FID equipped with DB 1 separation column after injection of 5.0 µl of a standard solution containing 50 µg/ml

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Table 1: Relative response factors

Classification	Nr.	Substances	MW	RRF	Classification	Nr.	Substances	MW	RRF
Group A Acrylate	1	Methyl acrylate	86.09	0.71	Group E Amine	33	Toluene-2,4-diamine	122.17	0.81
	2	Ethyl acrylate	100.11	0.64		35	Hexamethylene diamine	116.21	0.65
	3	Methyl methacrylate	100.11	0.67		36	Isophorone diamine	170.30	0.54
	4	Ethyl methacrylate	114.14	0.82		37	4,4-Methylenedianiline	250.25	0.94
	5	Butyl acrylate	128.18	0.90	Group F Antioxidants	38	2,6-Di-*tert*-butyl-4-methylphenol	220.35	1.34
	6	Butyl methacrylate	142.19	0.96		39	Irganox 1076	531.00	1.28
	7	Ethylhexyl acrylate	184.28	1.25		40	Irgafos 168	646.93	1.16
Group B Plasticizers	8	Di-*iso*-butyl phthalate	278.35	0.99		41	Irganox 1330	775.21	0.89
	9	Dibutyl phthalate	278.35	1.00	Group G Others	43	Vinyl propionate	100.12	0.52
	10	Diethylhexyl phthalate	390.56	1.15		44	Styrene	104.15	1.31
	11	Diethylhexyl adipate	370.57	1.17		45	*para*-Xylene	106.17	1.36
	12	Glycerol triacetate	218.20	0.46		46	Caprolactam	113.16	0.69
	13	2-Octyl-2H-isothiazol-3-one	213.34	0.82		47	N-vinyl-2-pyrrolidone	114.14	0.72
	14	2-Ethylhexyl diphenyl phosphate	362.44	0.72		48	*alpha*-Methylstyrene	118.18	1.35
	15	Diethylene glycol dibenzoate	314.34	0.87		49	Benzophenone	182.23	1.25
	16	Triethylene glycol dibenzoate	358.40	0.75		50	Bis(4-diethyl-aminophenyl) methanone	324.46	0.93
	17	Dipropylene glycol dibenzoate	342.42	0.41		51	Butyl diglycol acetate	204.27	0.70
	18	Propylene glycol dibenzoate	284.30	0.99		52	Bisphenol A	228.29	1.23
	19	2,2,4-Trimethyl-1,3-pentanediol dibenzoate	354.45	1.12		53	BADGE	340.42	0.43
Group D Alcohol	26	Ethylene glycol	62.06	0.20		54	Uvitex OB	430.06	0.94
	27	Propylene glycol	76.10	0.30		55	Docusate sodium	445.63	0.44
	28	1,4-Butanediol	90.12	0.45	Group C Carboxylic acid	All substances were not detected in calibration range.			
	29	Diethylene glycol	106.12	0.15					
	30	Resorcinol	110.11	0.67					
	31	Glycerol	92.09	0.14					

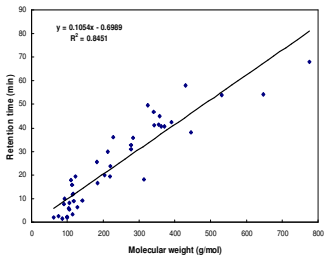

Figure 2: Correlation of the retention time with the molecular weight on GC-FID equipped with DB-1 column

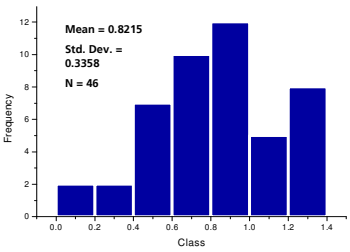

Figure 3: Frequency distribution of relative response factors

The amines showed a better relative response (0.54 ~ 0.94) but hexa-methylene diamine and isophoron diamine were not detected at a concen-tration of lower than of 5 mg/l. Carboxylic acids are not volatile enough and are not detectable by GC. The other substances showed detection limits between 0.2 mg/l and 2.5 mg/l. The relative response was between 0.41 and 1.36 (Figure 3 and Table 1) at a mean of 0.89 ± 0.28 (without alcohols). This means a BHA-equivalent of 1 mg/l corresponds to concentrations between 2.4 mg/l and 0.7 mg/l (mean 1.1 mg/l).

Conclusions

1) The screening method on DB 1 column is applicable to a broad range of substances except highly polar substances.
2) The retention time correlation to the molecular weight and can therefore be used for it's estimation in case of unknowns.
3) The semi-quantitative approach can be used with an acceptable range of uncertainty. For a conservative estimation, it should be multiplied by factor 3 (upper 95 % confidence interval).

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