Reduction of adsorption phenomena of volatile aldehydes and aromatic compounds for static headspace analysis of cellulose based packaging materials

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Abstract

Headspace analysis of solid samples is frequently hampered by severe matrix effects due to adsorption phenomena of the analytes on polar matrix surfaces. Since adsorption can give rise to incorrect results, a possible alternative can be provided by a transfer of the adsorption system into a partition system. This can be accomplished by the addition of substances, which exhibit higher affinity to the matrix than the analyte, thus acting as displacer or modifier.The effect of water as displacer for a quantitative static headspace analysis of straight chained saturated aldehydes and mononuclear aromatics (benzene, toluene, xylenes and ethylbenzene) in cellulose based packaging material has been investigated. Special emphasis was given to an establishment of distribution equilibrium conditions. For this, the influence of the amount of added displacer was studied by means of a multiple headspace extraction procedure coupled to gas chromatography with mass spectrometric detection and selected ion monitoring. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The control of the composition of products which are intended for use as packaging materials is essential, particularly, when they come into direct or also indirect contact with packed foodstuff. Transfer of substances from the packaging material into the enclosed goods will potentially affect product quality. Depending on the arrangement of the packaging

materials and the physical properties of the migrating substances, the process of transfer can occur through the gas phase as well as by direct contact of the packing and the product of value [1]. Until now, most investigations on this topic concern the migration of residual monomers, plasticizers and anti-oxidants from plastic packaging into the food [2–5]. Regulations of the European Union require that ''there should not be a transference of substances from the packaging into the food, which could endanger humans health, which change the foods composition characteristically and which deteriorate sensorial properties'' [6]. Especially the last requirement has to be investigated thoroughly, since the

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threshold values of taste and odour of a large number of substances, including volatile carbonyls, are quite low [7].

The aim of this work was the analysis of volatile aldehydes (C4–C7), which have low threshold odour concentrations and volatile aromatic compounds like benzene, toluene, xylenes and ethylbenzene (BTEX), which are of hygienic concern in recycling cardboard, by means of static headspace analysis. The origin of aldehydes in cardboard is mainly to be reasoned with the peroxidation of lipids, while traces of BTEX aromatics may occur as residual solvents from a previous printing process [8,9].

Several alternatives are available for the analysis of volatile carbonyls from solid sample matrices. Common techniques include a solvent extraction of the aldehydes followed by derivatization with either 2,4-dinitrophenylhydrazine (DNPH) and analysis by HPLC with UV detection [10], or derivatization with *O*-pentafluorobenzylhydroxylamine (PFBHA) and gas chromatographic analysis [11]. Liquid extraction and derivatization require several operation steps, a direct analysis will be preferable for routine application, therefore. In principle, static as well as dynamic headspace extraction procedures directly coupled with gas chromatographic analysis are suited for this purpose. Recently, an approach based on static headspace extraction combined with solid-phase microextraction (SPME) has been introduced [12].

A crucial point with the direct gas phase extraction of solid samples by static headspace techniques, however, is the presence of matrix effects which are quite frequently responsible for incorrect, or irreproducible results. The polar surface of cardboard makes an adsorption of polar as well as moderately polar compounds very likely. Adsorption also changes the partition characteristics of the analytes. A direct establishment of the headspace equilibrium may be impossible, or at least very time consuming. Therefore, special emphasis has to be given a proper establishment of headspace distribution equilibrium.

Different approaches are suggested to overcome such matrix influences. The ''solution approach'', proposed by Rohrschneider [13], is based on a dissolution of the solid sample in an appropriate solvent, thus breaking the adsorption bonds by solvation of the analyte molecules. A potential disadvantage in trace analysis can be reduced head-

space sensitivity owing to analyte dilution and the change of the partition coefficient. Since cardboard is not soluble, a valuable alternative for the reduction of the matrix effects is the addition of a displacer, usually a liquid like carbon disulfide, benzyl alcohol or water, which competes for the polar adsorption sites on the solid surfaces [14]. Under optimized conditions, a true distribution system can be established in this way.

In the present work the displacement characteristics of water were investigated for the analysis of the target analytes in recycling quality cardboard.

2. Experimental

2.1. Chemicals

The aldehydes butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal were purchased from Merck (Darmstadt, Germany), the quality was pro analysis. Benzene, toluene, ethylbenzene, xylenes and glyceryl triacetate, which was used as a solvent for the preparation of standards, were obtained from Aldrich (St. Louis, MO, USA), all with a purity better than 99%. Deionized water was prepared with a Barnstead Nanopure Ultrapure Water System from International PBI (Milan, Italy).

2.2. Standards and samples

For calibration purposes an external vapour standardization was applied. Standards were prepared by appropriate dilution of a stock solution containing the aldehydes butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal as well as the aromatics benzene, toluene, ethylbenzene and xylenes (about 8 µg/µl of each) dissolved in glyceryl triacetate to a final concentration of 88 ng/µl up to 798 ng/µl. Portions of 10 µl were pipetted into 22.5 ml headspace vials (Perkin-Elmer, Norwalk, CT, USA) in order to obtain the gas phase standards. The phase ratio in the vials was kept constant by substitution of the sample volume with inert glass beads when sole gas phase standards were processed. For this purpose the solid-phase volume was determined by displacement measurement.

DIN A4 sized cardboard samples of 280 g/m^2

were taken directly from the production process and cut in the laboratory by means of a commercially available annihilator (EBA 1226C, Adolf Ehinger, Balingen, Germany) to a size of 1.5 mm width and 15 mm length. If necessary, samples were stored at −20°C in fully filled and tightly sealed 1 l glass flasks. For analysis, portions of 1.5 g were weighed into 22.5 ml headspace sample vials. To investigate the influence of water onto the headspace equilibrium, volumes of 50 μl, 100 μl and 200 μl were added to the samples with piston-type pipettes of appropriate volumes (Brand, Wertheim/Main, Germany) and the results were compared with those of untreated samples. Sample vials were tightly sealed with a butyl rubber septum and an aluminium crimped cap (Perkin-Elmer).

2.3. Instrumentation and conditions of analysis

Liquid volumes up to 100 μl were handled by means of calibrated capillaries (Brand), while larger volumes were transferred with adjustable 1000 μl Transferpettors (Brand).

For headspace equilibration and sampling, a Perkin-Elmer HS 40 automatic headspace sampler and 22.5 ml headspace vials sealed with butyl septa and crimp caps were used. For equilibrium studies the sampler was operated in 4-step multiple headspace extraction mode. Open split coupling was chosen for connection of the headspace sampler interface to a Hewlett-Packard 5890 Series II gas chromatograph (Hewlett-Packard, Wilmington, DE, USA), which was equipped with a split/splitless injection port and connected to a Hewlett-Packard 5971A mass selective detector. Separation was achieved with a DB 624 capillary column from J&W Scientific, 30 m× 0.25 mm internal diameter and 1.4 μm film thickness (Folson, CA, USA). A brief compilation of the operational parameters of the analysis is given in Table 1.

The target analytes were ionized by electron impact ionization at 70 eV and detected in single ion monitoring mode. Characteristic fragment masses, grouped in run time windows, were selected for detection. Qualifier fragments were measured simultaneously to check for potential interference. This was done automatically during data analysis by calculation of the ratios of target ion signals to the qualifier ion signals. A second qualifier ion was measured for the aldehydes to obtain additional information about peak purity. The low masses of the fragment ions and less selective fragmentation of the investigated compounds necessitates this procedure. A summary of the selected ion masses of the

Table 1
Experimental parameters of the headspace sampler and gas chromatograph

Headspace sampler	
Pressurization gas	He 5.0 quality
Head pressure	110 kPa
Equilibration temperature	80°C
Equilibration time	90 min
Pressurization time	3 min
Injection time	0.2 min
Hold up time	0.4 min
Vent time	24 s
Needle and transference line temperature	120°C
Gas chromatograph	
Injection port temperature	200°C
Splitless time	1 min
Head pressure	90 kPa
Temperature program	40°C hold for 0.4 min, 7°C per min up to 150°C, than 30°C per min up to 250°C, hold for 3 min
Detector temperature	250°C
Electron multiplier voltage offset	106 V starting at 2.4 min
Solvent delay	2.4 min
Detector off	19 min

Table 2
List of measured target and qualifier ions grouped in run time windows

Compound	Group start time (min)	Target ion (mass/charge)	Qualifier ions (mass/charge)
Butanal	2.4	41	39 and 72
Benzene	4.7	78	77
Pentanal	5.8	44	41 and 39
Toluene	7.1	91	92
Hexanal	8.3	72	67 and 82
Ethylbenzene	9.6	91	106
m- and p-Xylene	10.0	91	106
o-Xylene	10.7	91	106
Heptanal	11.7	70	55 and 81

target and qualifier ions is listed in Table 2. Data acquisition was carried out with a G1034C Hewlett-Packard MS ChemStation, V. C 02.00.

2.4. Characterization of the headspace equilibrium and quantitative analysis

The headspace equilibrium conditions were investigated by means of a four step multiple headspace extraction (MHE) procedure which was applied on all individual samples. In an ideal partition system, the amount of a volatile analyte in the headspace above the sample decreases with increasing extraction cycles according to an exponential relationship. If the system is in equilibrium, a plot of the logarithms of the headspace concentrations expressed by the chromatographic peak areas versus the number of the extraction steps will produce a linear function [14]. The equation of the curve was determined by linear regression of the data points in Microsoft Excel for Windows 95 (V7.0). Consequently, the numerical value of the linear correlation coefficient (r^2) will be reflecting the quality of the distribution equilibrium, any significant deviation from unity is indicative of interferences.

The two parameters phase ratio (β) and partition coefficient (K) of the volatiles are essential to express the establishment of a partition equilibrium. Since vial size and sample volume were not altered throughout the experiments, the phase ratio, which was calculated according to Eq. 1, was kept constant. The addition of displacer reduced the volume of the gas phase less than 1% and required no further corrections, therefore:

$$\beta = \frac{V_v - V_s}{V_s} \qquad (1)$$

where β is the phase ratio, V_v the volume of the sample vial and V_s the sample volume.

The partition coefficients were calculated by application of the vapour phase calibration multiple headspace extraction (VPC–MHE) method [14]. A substantial variation of the distribution coefficient is reflecting a deviation from equilibrium conditions. In order to reduce the influence of statistical random variations of the individual data points on the area ratio values (Q), which represents the ratio of the peak areas of two consecutive extraction steps, the slopes (q) of the regression curves according to Eq. 2 were used:

$$Q = e^{-q} \qquad (2)$$

where Q is the ratio of peak areas of a single component after consecutive extraction and q the slope of regression curve.

Eq. (3) was applied for calculation of the partition coefficient according to the VPC–MHE method:

$$K = \frac{Q_{st} - Q_s}{Q_s - 1} \cdot \beta \qquad (3)$$

where K is the partition coefficient, β the phase ratio, Q_{st} the area ratio value of the standard and Q_s the area ratio of the sample.

The total amount of analyte in the sample can be determined by extrapolation of the regression curve to infinity. The corresponding signal is the total peak area, which would be obtained if the whole amount of analyte in the sample could be injected into the

GC within one extraction. Calculation of this value was performed according to Eq. (4) [15]:

$$\sum_{n=1}^{n=\infty} A_n = \frac{A_1^*}{1 - e^{-q}} \qquad (4)$$

where n is the number of extractions, A_n the total peak area, A_1^* the intercept of regression curve with the y-axis and q the slope of the regression curve.

The limits of detection were calculated from calibration data of three replicate measurements of standard mixtures at four concentration levels using the ValiData macro for MS-Excel V 1.04 (Rohrer & Wegscheider, Graz, Austria) [16].

3. Results

3.1. Effect of the addition of displacer onto the headspace equilibrium

A prerequisite for all further analyses was a proper separation and identification of the target compounds by combined headspace analysis and gas chromatography with mass spectrometric detection. A typical chromatogram of standard mixture recorded under conditions as pointed out in the Experimental section is depicted in Fig. 1. Apparently, selectivity of separation and detection are sufficient for the required purpose.

In order to establish the suitability of water as a displacer, a set of homogenized cardboard samples with different amounts of water added was analyzed. The correlation coefficients of the regression curves for the MHE analysis are listed in Table 3. The values represent the mean of three replicate samples including also their standard deviations. The lowest correlation coefficients are obtained for the untreated samples. With an increasing amount of added water also, the values of r^2 rose and reached nearly unity in the case of the aldehydes. Closest approximation to ideal linearity was observed for hexanal. Remaining deviations from unity are the result of statistical random variations of the measurements.

For a visualization of the displacer effect, pentanal was chosen as representative target analyte. The result of the appropriate MHE analyses is shown in Fig. 2 by plotting the logarithms of the peak areas from all displacer dosage experiments versus the number of extraction steps minus one. To character-
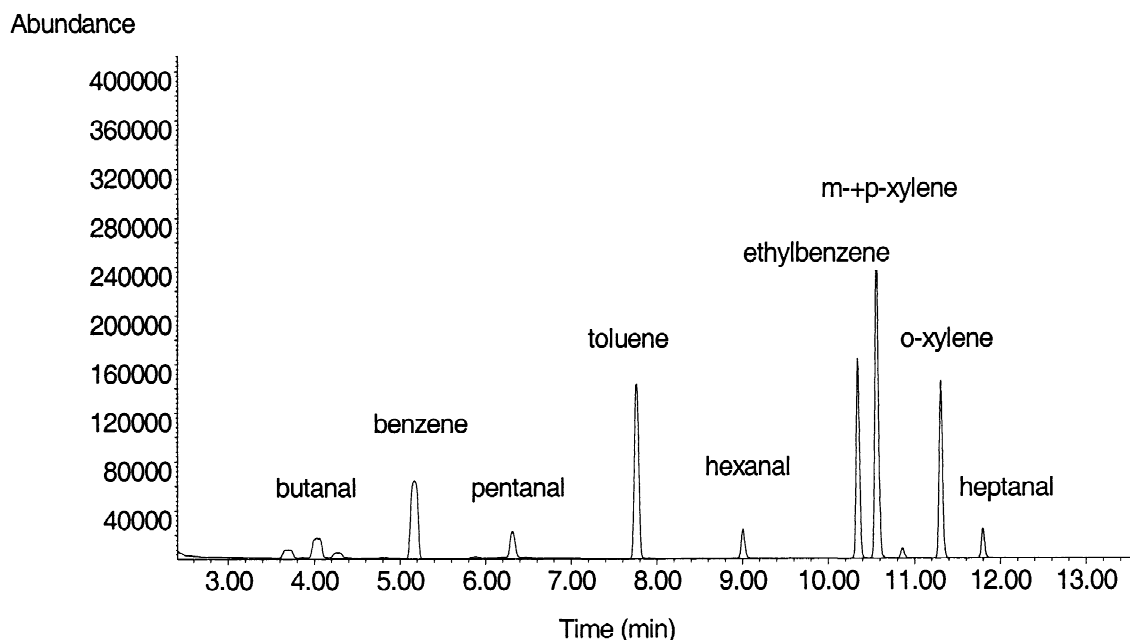
Fig. 1. Typical chromatogram of standard mixture.

Table 3
Mean values (Mean) and standard deviations (SDs) of the regression coefficients r^2 of MHE regression curves of three replicate measurements in dependence of the added displacer volume

Compound	0 μl		50 μl		100 μl		200 μl	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Butanal	0.722	0.053	0.965	0.013	0.981	0.004	0.993	0.001
Pentanal	0.859	0.005	0.982	0.006	0.990	0.002	0.997	0.001
Hexanal	0.990	0.004	0.997	0.001	0.998	0.002	0.998	0.001
Heptanal	0.862	0.048	0.976	0.001	0.985	0.005	0.997	0.002
Benzene	0.557	0.071	0.868	0.028	0.934	0.016	0.978	0.018
Toluene	0.950	0.029	0.971	0.018	0.949	0.036	0.982	0.009
Ethylbenzene	0.896	0.057	0.993	0.001	0.992	0.005	0.995	0.005
m- + p-Xylene	0.964	0.035	0.995	0.004	0.963	0.014	0.987	0.005
o-Xylene	0.983	0.015	0.991	0.004	0.997	0.003	0.997	0.001

ize the shapes of the extraction curves, the corresponding data points are distinguished by different types of lines. The curvature of the continuous line connecting the data points of untreated samples is typical for adsorption systems, whereas the dashed line, which was obtained after addition of 200 μl water, exemplifies good approximation to a partition system. The fit of linearity expressed as a correlation coefficient is $r^2 = 0.858$ for the untreated sample and $r^2 = 0.999$ for the sample with an amount of 200 μl displacer for an 1.5 g cardboard sample quantity.

As can be seen from Table 3, similar results were obtained for volatile aromatic compounds. Especially for the most volatile compounds, benzene and toluene, equilibrium was not reproducibly established. This is indicated by an increase in the standard deviations of the correlation coefficients. A typical MHE plot is displayed in Fig. 3 which represents the influence of the displacer dosage onto the linearity for toluene. In a quite analogous manner as had been observed for the analysis of the aldehydes, headspace equilibria of the aromatic com-
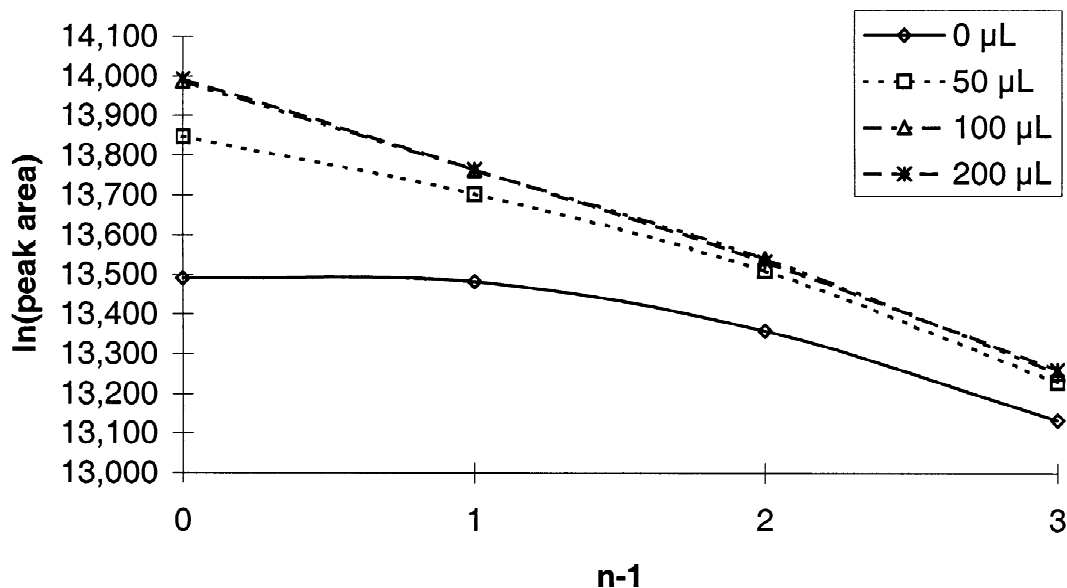

Fig. 2. Influence of the displacer addition onto MHE of pentanal. Plot of the logarithms of the peak areas of pentanal obtained in four consecutive headspace extractions of samples with varying displacer content versus the number of extractions (*n*) reduced by one.
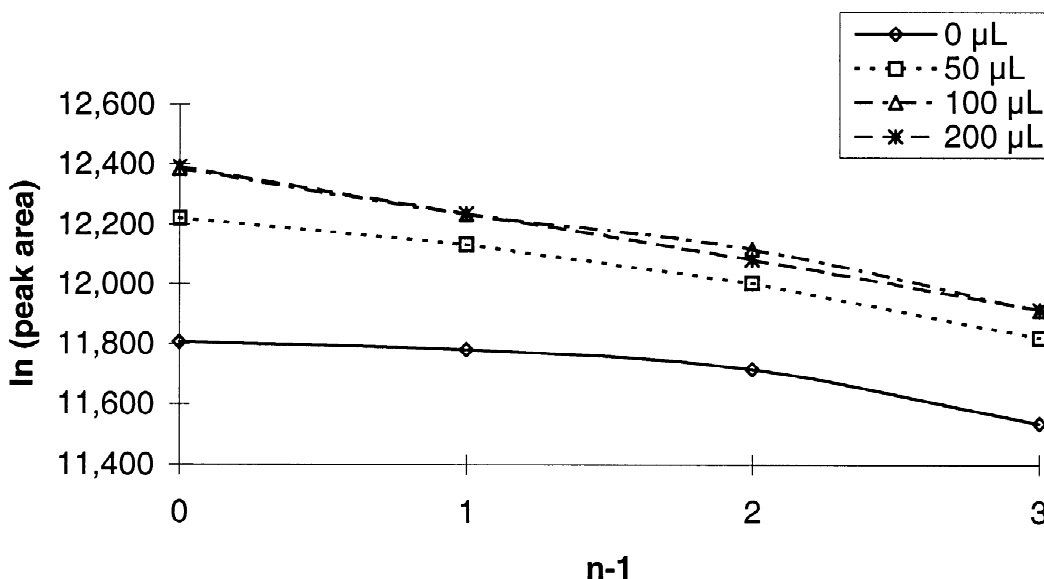
Fig. 3. Influence of the displacer addition onto MHE of toluene. Plot of the logarithms of the peak areas of toluene obtained in four consecutive headspace extractions of samples with varying displacer content versus the number of extractions (*n*) reduced by one.

pounds are significantly improved by the addition of water as displacer. For the given experimental set-up a minimum of 100 µl displacer is required.

3.2. Influence of the addition of displacer onto the partition coefficient

The correlation coefficients of the MHE regression curves are quite useful parameters for method development and system characterization. A valid confirmation of the static headspace equilibrium conditions can be established by a computation of the individual partition coefficients, which reflect the true influence of the displacer. Since hexanal and *o*-xylene exhibited the closest approximation to ideality at all levels of displacer dosage, they were chosen as model compounds for this purpose. The computationally obtained partition coefficients are listed in Table 4. Obviously, the data show a pronounced trend for the availability of the volatile sample components in the gas phase. The partition coefficients differ significantly depending on the amount of added displacer, the numerical values decrease and level off to constancy with increasing displacer concentration. This demonstrates clearly the overall importance of the displacer onto the

establishment of the static headspace equilibrium of this system. Thus, accuracy of the analytical results can only be obtained by a careful consideration of true equilibrium conditions.

3.3. Quantitative results

Not only the regression coefficient, but also the slope of the MHE curve is of relevance for quantitative analysis. The exchange rate of the gas phase of consecutive headspace extractions must be sufficient to attain a concentration gradient of the volatiles in order to permit a meaningful extrapolation of the total peak areas. The signal intensity of the first extraction, expressed as the intercept of the regression curve, does not automatically reflect the quality of the gas phase extraction. A typical set of the

Table 4
Calculated partition coefficients for hexanal and *o*-xylene in dependence of the displacer dosage

	Hexanal	*o*-Xylene
Untreated sample	47.64	53.83
50 µl displacer	24.92	31.96
100 µl displacer	24.28	24.09
200 µl displacer	21.29	18.14

Table 5
Regression curve parameters and calculated content of pentanal at selected displacer volumes

	0 μl	50 μl	100 μl	200 μl
Slope of regression curve	−0.1199	−0.2050	−0.2364	−0.2599
Intercept of regression curve	13.546	13.880	13.982	13.916
Correlation coefficient	0.858	0.978	0.991	0.998
Total peak area	6758416	5755902	5611995	4828609
Calculated pentanal content (μg/g)	6.48	5.18	4.93	4.34

relevant parameters is shown for the example of pentanal in Table 5. The effect of the displacer addition is not visible with the first gas chromatograms which yield comparable signal intensities. The data indicate the influence of the displacer on the characteristic data of the MHE curve, higher values for slope and correlation coefficients predict a reduction of the systematic error of quantitation. For the purpose of comparison, total peak areas and calculated pentanal contents are displayed despite insufficient equilibration of the untreated sample as well as for samples with 50 and 100 μl of water addition. As a result of the decrease of the calculated total areas with increasing displacer dosage, quantitative data decrease too. A compilation of the quantitative results including limits of detection and relative standard deviation for the analysis of all components at different levels of displacer dosage is given in Table 6. In order to visualize the effect of the displacer addition onto the reliability of the head-

space analysis, also data from the analysis under non-equilibrium conditions are included. Precision and accuracy are significantly enhanced by the addition of the displacer. Analyte contents of the samples, which were modified with 200 μl water, result in considerably lower values. The data for the aromatic compounds are less conclusive than those for the aldehydes. Analyte contents decrease with increasing amounts of displacer for benzene, ethylbenzene and *o*-xylene, but relative standard deviations are more pronounced. According to the mean value of the correlation coefficient of the MHE regression curve equilibrium conditions are sufficiently established for quantitation purposes.

4. Conclusion

The intention of this work was a thorough investigation of the influence of water as a displacer

Table 6
Limits of detections (LODs) and calculated mean values, standard deviations (SDs) and relative standard deviations (RSDs) obtained from three replicate analysis of cardboard samples at increased displacer volumes

Compound	LOD (μg/g)	0 μl			50 μl			100 μl			200 μl		
		Mean (μg/g)	SD (μg/g)	RSD (%)	Mean (μg/g)	SD (μg/g)	RSD (%)	Mean (μg/g)	SD (μg/g)	RSD (%)	Mean (μg/g)	SD (μg/g)	RSD (%)
Butanal	0.17	1.71	0.25	14.86	1.23	0.04	3.58	1.17	0.02	1.77	1.04	0.01	1.13
Pentanal	0.18	6.48	0.83	12.86	5.18	0.08	1.64	4.93	0.07	1.48	4.34	0.05	1.04
Hexanal	0.21	5.97	0.59	9.80	5.72	0.19	3.34	5.77	0.29	5.06	5.60	0.07	1.25
Heptanal	0.11	1.90	0.36	18.92	1.52	0.13	8.34	1.63	0.13	7.81	1.47	0.07	4.50
Benzene	0.15	0.97	0.07	7.62	0.65	0.02	3.68	0.57	0.01	1.79	0.48	0.01	2.94
Toluene	0.19	1.21	0.04	3.40	1.07	0.07	6.55	1.11	0.09	8.12	1.15	0.09	7.53
Ethylbenzene	0.12	0.94	0.13	13.90	0.59	0.01	1.96	0.55	0.05	9.05	0.50	0.03	6.86
m- + *p*-Xylene	0.25	0.89	0.12	13.72	0.97	0.35	36.17	0.95	0.06	6.81	0.87	0.11	12.33
o-Xylene	0.20	0.27	0.02	8.03	0.27	0.00	0.62	0.26	0.01	2.92	0.26	0.01	3.04

onto the headspace equilibrium of volatile aldehydes and aromatics in polar solid samples. The displacer has to establish a partition system and reduce adsorption phenomena which are responsible for systematic errors in quantitative analysis. In order to find out about the required saturation level of the displacer, measurements were accomplished with increasing volumes of added displacer and compared with the data obtained for untreated samples. For a characterization of the headspace equilibrium conditions, the technique of multiple headspace extraction was found to be useful. The effect of the displacer was evaluated by means of the characteristic parameters of the MHE regression curves and correlation coefficients. Apparently, the polar displacer improves significantly gas phase equilibration, thus resulting also in enhanced precision and accuracy of quantification. A confirmation of the actual shift of the equilibrium conditions could be obtained by a computation of the partition coefficients for the individual components. The data display clearly the marked influence of the displacer dosage onto the analysis of the volatiles in the polar cardboard matrix.

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