Determination of partition behavior of organic surrogates between paperboard packaging materials and air

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Abstract

The suitability of recycled paperboard packaging materials for direct food contact applications is a major area of investigation. Chemical contaminants (surrogates) partitioning between recycled paper packaging and foods may affect the safety and health of the consumer. The partition behavior of all possible organic compounds between cardboards and individual foodstuffs is difficult and too time consuming for being fully investigated. Therefore it may be more efficient to determine these partition coefficients indirectly through experimental determination of the partitioning behavior between cardboard samples and air. In this work, the behavior of organic pollutants present in a set of two paper and board samples intended to be in contact with foods was studied. Adsorption isotherms have been plotted and partition coefficients between paper and air have been calculated as a basis for the estimation of their migration potential into food. Values of partition coefficients ($K_{paper/air}$) from 47 to 1207 were obtained at different temperatures. For the less volatile surrogates such as dibutyl phthalate and methyl stearate higher $K_{paper/air}$ values were obtained. The adsorption curves showed that the more volatile substances are partitioning mainly in air phase and increasing the temperature from 70 to 100 °C their concentrations in air (C_{air}) have almost doubled. The analysis of surrogates was performed with a method based on solvent extraction and gas chromatographic-flame ionization detection (GC-FID) quantification.
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1. Introduction

Recycling is an opportunity to limit environmental pollution and to make an important contribution to attaining a more sustainable economy. In addition it helps to preserve the earth's resources. For this purpose the use of recycled packaging materials for food-packaging applications are of increasing interest in the last years [1–3].

The production of paper and board for food contact use in Europe involves 44% of virgin pulp and 40% of recycled. However, depending on the category of material, the latter percentage can rise to 90% [4,5]. To ensure the safety of such materials, food-packaging regulations in Europe require

that the packaging materials must not cause mass transfer (migration) of harmful substances to the food [4].

Studies on the virgin paper used for food packaging have shown that the levels of chemicals that can potentially migrate into food are very low [6,7]. In case of recycled paper the use is more risky. The possible sources of contamination of a recycled paper package can mainly be found in additives and in components linked to the printing and labeling process undertaken for the previous use of the package. Thus, substances like dialkylamino benzophenone, suspected to be carcinogenic and used in UV-cured printing inks for cartonboard, diisopropylnaphthalene (DIPN), used as solvent for carbonless copy paper and thermal paper manufacture, partially hydrogenated terphenyls (HTTP), phthalates, azo colorants, fluorescent whitening agents, primary aromatic amines, polycyclic hydrocarbons (PAH) and benzophenone, all involved

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in the labeling process, can be introduced via the recycling process to the package [8–11]. These studies make evident that there are many potential contaminants in recovered paper and even if there are production stages in the treatment of recovered fibers where contaminants can be removed quite effectively, poorly water-soluble compounds still remain in the recovered paper [12,13]. As a result, once present in the packaging they could migrate into the food content under certain conditions, posing health concerns for the consumers.

To predict the migration from the packaging into the food, the knowledge of the adsorption isotherms and the partition coefficients between paperboard and air of each of the potential migrants are necessary. Partitioning of organic compounds between cardboard samples and air is important for the migration behavior of cardboard based food packaging and therefore for quality control of food packaging [14,15]. As part of an EU research project FAIR-CT-98-4318 investigations on paper and board as food contact material were carried out [16]. The investigations were focused and divided into two phases. At the first phase the migration behavior of contaminants from paper samples into a food simulant, Tenax, and into several dry foods was studied [2]. The second phase was focused on the determination of adsorption isotherms and partition coefficients of selected contaminants between paper samples and air at several time–temperature exposure conditions. The main goal was to evaluate the ability of contaminants to migrate from paperboard matrices into foods and/or food simulants.

In this work, a method for the determination of partition coefficients of a group of organic compounds between cardboard and air has been developed using solvent extraction followed by GC-FID analysis. Adsorption isotherms were also plotted. Measurements were carried out in two different paper and board samples under various time/temperature conditions. Thus the tendency of substances to be preferably in air or packaging could be evaluated and subsequently the migration ability of chemicals from paper packages into food could be estimated. Obtained results were discussed in terms of the possibility from a safety point of view to use recycled fiber based materials for food contact applications.

2. Experimental

2.1. Reagents and solutions

A systematic study has been carried out with a group of semi-volatile model contaminants with different polarity, structure, molecular weight and boiling points. The model compounds were chosen to represent surrogates commonly present in paper and board packages originating for instance from printing inks. The selected chemicals are the following: (1) acetophenone, b.p. 203 °C; (2) naphthalene, b.p. 218 °C; (3) benzophenone, b.p. 306 °C; (4) dibutyl phthalate (DBP), b.p. 340 °C; (5) methyl stearate, b.p. 443 °C. All chemicals were of analytical grade and were purchased from Sigma (Taufkirchen, Germany) and Fluka (Buchs, Switzerland). Standard solutions of these reagents in HPLC grade absolute ethanol purchased from Merck (Darmstadt, Germany) at concentrations ranging from 1 to 25 μg/ml were analyzed with external calibration as a basis for quantification. Five spiking solutions in diethyl ether (Merck) of the surrogates in mixture at five different concentrations (ranging from 1 to 10 μg/μl) were used to fortify the samples. Absolute ethanol was also used as extraction solvent.

2.2. Paper samples

For the partition studies, two different paper samples were used having different pulp percentage of recycled matter (100 and 0%, respectively). Their characteristics are listed in Table 1.

2.3. Analytical procedure

Paper strips of both paper types with approximate dimensions 1 cm × 7 cm and an average weight of approximately 200 mg for S1 and 100 mg for S2 were placed in 22 ml septum glass vials. The vials were sealed with Teflon-coated septa (both vials and septa were purchased from Supelco, U.S.A.) and 1 μl of each of the spiking solutions was injected with a 5 μl Hamilton micro syringe. The solution was carefully introduced on the walls of the vial as it is shown in Fig. 1, in order to avoid liquid droplets to come in direct contact with the paper strip, and to favor a faster equilibrium. After the injection the glass vials were placed in an oven under the following optimum kinetic conditions: 70 °C for 4 h, and 100 °C for 1 h. The determination of these conditions has been described elsewhere [15].

The determination of the concentration of the sorbed surrogates into the paper strips was performed as follows: contaminated paper strips were cut in two pieces and the pieces were placed immediately in 5 ml glass vials containing 3 ml of ethanol as extraction solvent and the vials were sealed. Extraction of surrogates into ethanol was performed by gentle agitation of the vials for about 30 min at room temperature, using a horizontal shaker (purchased from Sigma–Aldrich Ltd., Germany). Absolute ethanol was found to give complete

Table 1
Properties of the paper samples used in the present study

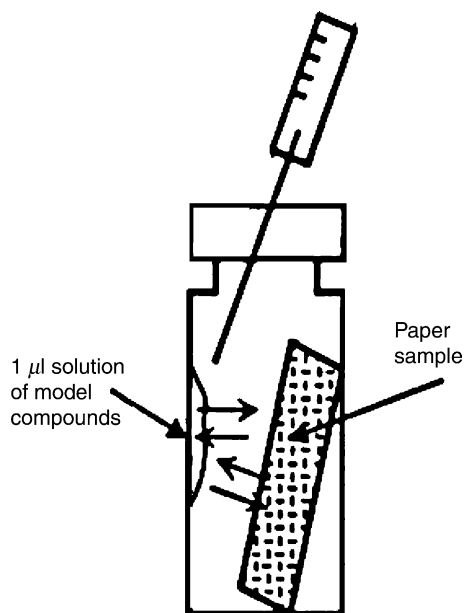| Sample	Type	Pulp	Recycled (%)	Grammage (g/m^2)	Thickness (μm)
S1	Testliner	Recycled	100	128	191
S2	Liquid board triplex	Bleached kraft + CTMP[a]	0	267	478

[a] CTMP: chemithermomechanical pulp.

Fig. 1. Procedure (on-glass injection) for the determination of partition coefficients.

extraction of sorbed surrogates under these conditions as continued extraction and a repeat analysis of the extracts revealed no increase in surrogate concentrations. The recovery of the method was determined in the range 90.5–105%. The ethanol extracts were analyzed by GC and the concentrations were determined from the respective calibration graph, using the external standard method. Triplicate determinations were carried out. The relative standard deviation (R.S.D.) of the method was 4–11%.

2.4. Gas chromatography (GC) analysis

The GC unit was a Fisons 9000 series gas chromatograph (Fisons Instruments, Rodano, Italy) equipped with an auto injector and a flame ionization detector (FID). The separation column was a 30 m × 0.32 mm internal diameter fused silica capillary DB-1 with a film thickness of 0.25 μm, purchased from J&W Scientific (Folsom, CA, USA). The following GC parameters were kept constant: detector temperature, 290 °C; injector temperature, 240 °C; injection mode: split with split ratio ca. 15:1; injection volume, 1 μl. The column temperature program was: 60 °C (3 min), from 60 °C at a rate of 10 °C/min to 270 °C (3 min). Carrier gas: He (99.999% purity), at a flow rate of 1.45 ml/min.

3. Results and discussion

3.1. Adsorption isotherms

Since paper is porous the diffusion of contaminants inside the matrix occurs mainly through the gas phase. Conse-

quently, the knowledge of the partition coefficient of a certain compound between paper and air can be a powerful instrument for the estimation of its migration ability [17,18]. Besides, it may also give useful information about the time a
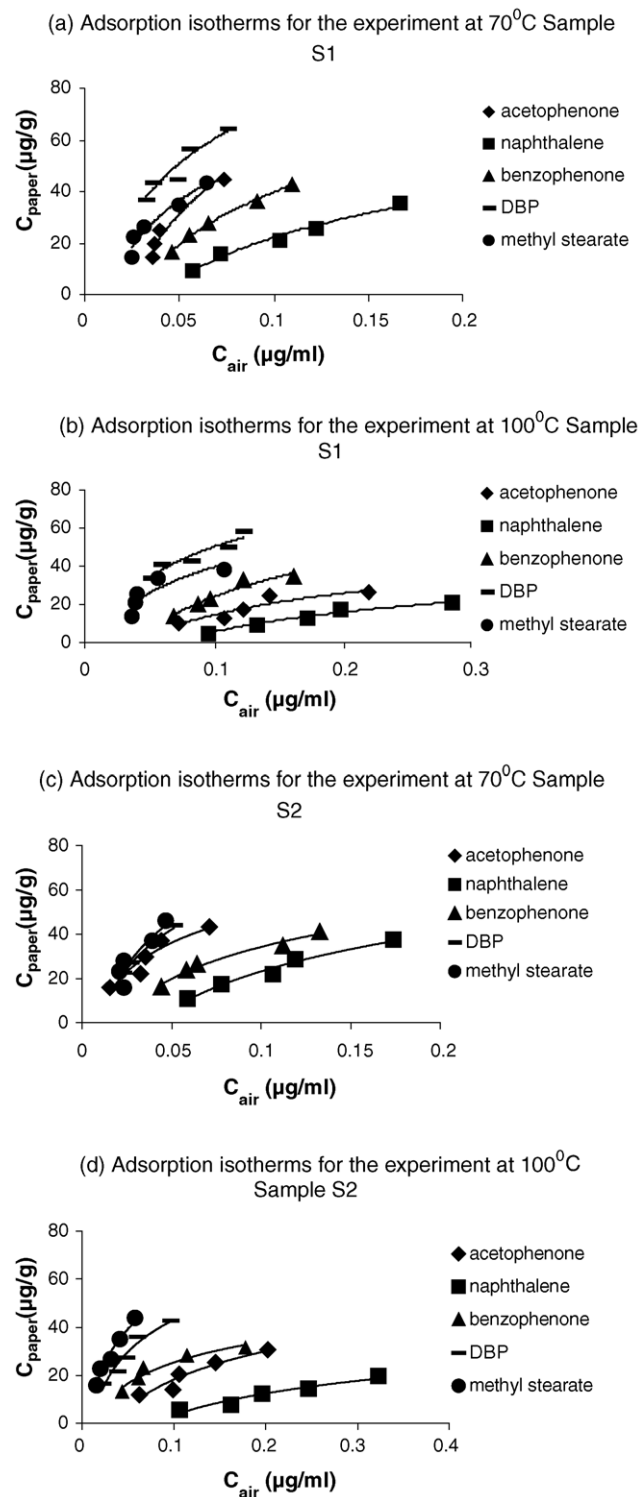

Fig. 2. Adsorption isotherms for the five surrogates in both paper samples at 70 and 100 °C.

packaging can be used under determined conditions without appreciable risk of undesirable compounds release.

For this purpose as mentioned above adsorption isotherms were constructed. Adsorption isotherms were plotted as concentration of surrogates in paper, C_{paper} (μg/g, *y*-axis) versus concentration in air, C_{air} (μg/ml, *x*-axis). The concentrations of the surrogates in the air have been calculated from the difference from the total quantity of surrogate in the paper minus the surrogate found in the GC analysis of the extract from the paper at equilibrium. Curves were constructed for different temperatures and paper samples. Fig. 2 shows the adsorption isotherms obtained at 70 and 100 °C for the five surrogates in both paper samples. Obtained results showed the ability of contaminants of various chemical structures and various volatilities to partition in the headspace and thus to potentially transfer to dry foods during temperature fluctuations in distribution or storage.

From Fig. 2 considerable differences between the adsorption behaviors can be recognized. The adsorption curves showed that, as expected, the more volatile substances partitioned more readily in the headspace at any given temperature and low absorption in paper matrix was noticed. Naphthalene for example with boiling point 218 °C partitioned mainly in air phase. The cellulose fibers have an overall negative charge due to carboxyl groups from the carbohydrates and the hydroxyl groups of the lignins. As a consequence electron rich

substances such as naphthalene will suffer a net repulsion and will not be fiber-retentive and therefore low absorption values in the paper were observed. On the contrary dibutyl phthalate and methyl stearate with higher boiling points partitioned strongly into the condensed phase on the paper and board. For the more polar surrogates, such as acetophenone (highest volatility of the group) especially at 70 °C higher absorption to the board matrix was observed than expected according to its boiling point, due to the high affinity of substance for the fibers.

As can be seen the concentration of surrogates in the paper was higher at 70 °C than at 100 °C. This is due to the fact that 100 °C is enough to promote readily partition in headspace.

Obtained isotherms show a typical Langmuir behavior reaching asymptotically upper limits of C_{paper} (saturation of the cardboard phase) for all surrogates.

3.2. Determination of partition coefficients

Partition coefficients ($K_{paper/air}$) of surrogates between paper and air were calculated using the following expression

$$K_{paper/air} = \frac{C_{paper}}{C_{air}}$$

C_{paper} is the concentration of each surrogate in paper-board sample at equilibrium expressed as μg/g, C_{air} is the

Table 2
Values of partition coefficients of surrogates between paper and air

Compounds	70 °C, 4 h				100 °C, 1 h			
	S1		S2		S1		S2	
	$K_{paper/air}$	R.S.D. (%)	$K_{paper/air}$	R.S.D. (%)	$K_{paper/air}$	R.S.D. (%)	$K_{paper/air}$	R.S.D. (%)
Acetophenone	390	4.1	1016	6.9	136	4.0	187	4.4
	537	4.7	679	5.5	120	4.2	140	4.1
	629	5.5	837	5.0	141	4.5	193	4.9
	677	4.9	840	4.8	174	5.0	174	5.6
	605	5.0	518	4.4	119	4.0	151	5.2
Naphthalene	161	4.2	182	6.1	52	4.0	51	5.0
	219	4.6	223	5.5	71	5.5	47	4.1
	206	4.7	204	4.9	74	5.0	62	4.6
	208	5.9	241	4.1	89	4.9	58	5.1
	212	6.0	215	4.8	73	4.5	61	5.2
Benzophenone	351	7.5	362	5.4	197	7.0	292	5.0
	421	7.4	407	5.5	233	7.4	300	5.4
	424	8.8	413	4.1	239	6.9	345	4.6
	394	6.1	309	4.6	268	6.5	245	4.3
	390	6.9	309	4.7	213	7.1	175	4.0
Dibutyl phthalate	1151	10.1	867	7.7	662	9.5	730	6.4
	1207	9.9	982	6.5	687	8.8	555	6.0
	921	9.0	1006	6.9	530	9.1	562	6.9
	1020	10.8	848	7.0	451	8.2	598	7.4
	944	10.5	857	6.1	477	8.5	542	7.2
Methyl stearate	578	5.9	680	6.8	380	4.1	983	7.0
	850	6.8	1118	7.1	532	4.9	1141	6.8
	845	7.4	1199	7.0	632	5.2	854	6.5
	699	7.0	940	7.5	597	5.0	840	6.0
	675	6.1	982	6.6	458	4.7	856	6.1

concentration of surrogates in air after the test in μg/ml. Due to the applied ratio of weight to volume the dimension of $K_{\text{paper/air}}$ is ml/g.

The values of partition coefficients of all surrogates at both temperatures (70 and 100 °C) and for both paper samples are presented in Table 2. As can be seen $K_{\text{paper/air}}$ values decrease when the temperature increases. In most cases partition coefficient values at 100 °C were lower than $K_{\text{paper/air}}$ values at 70 °C. A similar behavior was found for all surrogates in both paper samples. This means that at high temperatures the adsorption ability of the paper is lower. On the other hand once the compounds are trapped onto the paperboard they are easily released when temperature increases which means that higher migration values would be expected and consequently higher risk for the paper samples used for food contact applications at high temperatures. Also for the less volatile model substances higher $K_{\text{paper/air}}$ values were observed. In general, the higher the partition coefficient value the more absorption takes place in the paperboard.

The partition of the surrogates in air does not always follow their boiling point temperature. As can be seen the substance with the highest concentration in air and consequently lower $K_{\text{paper/air}}$ value was naphthalene. On the contrary acetophenone, the surrogate with the highest volatility in the mixture, has higher $K_{\text{paper/air}}$ values than naphthalene. This can be attributed to different affinity of the surrogates for fibers as mentioned previously.

As can be also concluded from Table 2, paper sample S2 has higher partition coefficient values for most surrogates than sample S1. This can be possibly explained by the fact that among the two samples S2 has the higher thickness and grammage. As a consequence, the surrogates are better retained in the cardboard phase. On the contrary, the release (migration) of the compounds to the vapor phase is higher in the case of thinner samples. These results are in agreement with those obtained by other investigators [15].

In order to evaluate the contamination levels of a food packaged in a paper and board material, it could be assumed that the total amount of the surrogates in the air would be absorbed by the food. It should be stressed that this situation would represent the "worst-case scenario". According to this uncertain scenario it could be assumed that the higher the concentration in air, the higher is the contamination probability.

4. Conclusions

A number of interesting conclusions can be drawn from the present investigation:

(1) A simple and reliable solvent extraction procedure followed by GC-FID analysis has been developed to determine the partition behavior of selected model contaminants (surrogates) between paper and board samples and air at various time/temperature conditions as a base for the estimation of their ability to migrate into foodstuffs. The developed methodology can detect surrogates with a wide range of concentrations, boiling points and molecular weights.

(2) The adsorption isotherms of the studied compounds onto paper samples are of Langmuir type.

(3) High partition coefficient values were generally measured for most of the compounds indicating significant sorption levels of the studied surrogates into both paper samples.

(4) Partition coefficient values show significant differences, which depend on the boiling point of the compound, its chemical structure, as well as and the type of the paper sample. The partition coefficients of the surrogates decrease with increasing temperature, indicating that the use of paper and board samples as food-packaging materials at high temperatures is more risky. This would be more critical in case of using recycled paperboard packaging materials that might have been contaminated with various surrogates. It seems that the lower the partition coefficient values the higher the risk for the packaged commodities. However, for final conclusions, migration studies from contaminated paper and board packages into selected dry foods with varied composition should be awaited. Corresponding investigations have been recently accomplished and will be published in a forthcoming paper.

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