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Migration of Photoinitiators by Gas Phase into Dry Foods

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Photoinitiators are components widely used in UV-cured inks for printing food packaging. In the present study, the migration of seven photoinitiators through the vapor phase was investigated. To perform the migration test, an additive enriched polyethylene wax was used as a source to release photoinitiators. The method was applied to evaluate the migration of the photoinitiators into five selected dry foods (cake, bread, cereals, rice and pasta). The highest level of migration was found in the cake. Parameters affecting the migration process were evaluated, and high migration level was found to correlate with both the porosity and the fat content. In addition, the kinetics of migration of the photoinitiators from the additive enriched wax into the cake were studied under accelerated conditions.

KEYWORDS: Photoinitiators; migration; vapor phase; dry foods

INTRODUCTION

Last February a notification from the German authorities concerning the migration of 4-methylbenzophenone from cardboard to certain breakfast cereals was issued on the Rapid Alert System for Food and Feed (RASFF). As a result of the notification the European Commission asked European Food Safety Authority (EFSA) to evaluate if the presence of 4-methylbenzophenone found in cereals constituted a risk for the health and also to evaluate if the existing Tolerable Daily Intake (TDI) for benzophenone and hydroxybenzophenone could be applied to 4-methylbenzophenone. The Scientific Panel on food contact materials, enzymes, flavorings and processing aids (CEF) concluded that short-term consumption of cereals contaminated with 4-methylbenzophenone at the levels reported did not constitute a risk for the health; but also indicated that if the use of 4-methylbenzophenone is to be continued, more data are required to carry out a full risk assessment. On the other hand, the Panel concluded that the TDI of benzophenone could not be applied to 4-methylbenzophenone and in addition hydroxybenzophenone should not be included in the TDI of benzophenone because of the lack of supporting data (*1*).

Benzophenone-based derivatives are widely used as photoinitiators for UV-cured inks. These types of printing inks are environmentally friendly since no organic solvents are included in their formulation (*2*, *3*). In the food packaging field, UV-cured inks, like the one including benzophenone as photoinitiator, are widely used for printing the external face of the packaging. If there is not an effective barrier, ink components, like photoinitiators with low molecular weights, can permeate through the material and migrate to the food (*4*, *5*).

Several studies have demonstrated the migration of benzophenone from paper and board to food and food simulants via direct contact (*5*−*8*); however information about the migration through the vapor phase is very scarce (*9*−*12*).

Johns et al. (*5*) studied the migration of ink components from cartonboard to food during frozen storage; and they observed that under low temperature conditions (−20 °C) the migration of benzophenone occurs even when there is no direct contact between the packaging and the food.

The development and validation of accurate and sensitive methods to analyze potential migrants is essential in order to guarantee the food safety. The techniques commonly used to determine photoinitiators are liquid chromatography with UV detection and gas chromatography with flame ionization detector (*7*, *13*, *14*). Chromatographic techniques coupled to mass spectrometry have also been successfully applied in the analysis of these contaminants (*4*, *15*).

Pastorelli et al. (*13*) reported a rapid and specific reverse-phase liquid chromatographic method with diode-array detector to quantify benzophenone in packaging materials and cake samples.

Sagratini et al. (*15*) developed a multicomponent method to analyze five ink photoinitiators in packaged beverages. Analyses were performed by gas chromatography−mass spectrometry. The presence of benzophenone in the samples was confirmed by liquid chromatography atmospheric-pressure photoionization mass spectrometry (APPI)/MS/MS).

In the present paper the migration of seven benzophenone-based photoinitiators including 4-hydroxybenzophenone, methyl-2-benzoylbenzoate, benzophenone, 2-hydroxybenzophenone,

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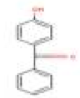
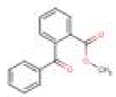
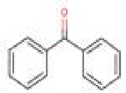
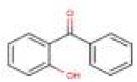
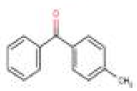
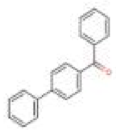
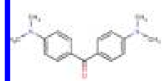
Table 1. Chemical Structures and Physicochemical Properties of the Photoinitiators[a]

Structure	Formula	Name	CAS No	Molecular weight	Melt Point (ºC)	Boil Point (ºC)	log P (octanol-water)	Vap Press (mm Hg) 25ºC	Henry's Law Constant (atm-m3/mole) 25ºC
	$HOC_6H_4COC_6H_5$	4-hydroxybenzophenone	1137-42-4	198.22	132-135	150-160	3.07	1.00E-05*	2.02E-10*
	C15-H12-O3	methyl-2-benzoylbenzoate	606-28-0	240.254	52	351	2.7	1.53E-05*	1.25E-08*
	C13H10O	benzophenone	119-61-9	182.22	47.8	305.4	3.18	8.2E-04*	0,00000194*
	C13-H10-O2	2-hydroxybenzophenone	117-99-7	198.22	40	127-133	3.52	4.39E-04*	2.54E-08*
	C14-H12-O	4-methyl benzophenone	134-84-9	196.2	59.5	328.1*	3.690*	1.94E-4*	–
	C19-H14-O	4-benzoylbiphenyl	2128-93-0	258.3	100	420	4.827*	3.11E-7*	–
	C21 H28 N2 O	4,4'-bis(diethylamino)benzophenone	90-93-7	324.4	95.5-96.5	475.7±30.0*	5.994±0.394*	3.25E-9*	–

[a] (*) Estimated. (—) Not found.

4-methylbenzophenone, 4-benzoylbiphenyl and 4,4′-bis(diethylamino) benzophenone through the vapor phase was studied. To perform the migration test an additive enriched polyethylene wax was used as the releasing source for photoinitiators. The method was applied to evaluate the migration of the photoinitiators into five selected dry foods. Parameters that influence the migration process were evaluated. Migration kinetics were studied under accelerated conditions.

MATERIALS AND METHODS

Reagents and Standard Solutions. Standards of 4-hydroxybenzophenone (purity 98%), methyl-2-benzoylbenzoate (purity 97%), 2-hydroxybenzophenone (purity 99%), 4-methylbenzophenone (purity 99%), 4-benzoylbiphenyl (purity 99%) and 4,4′-bis(diethylamino) benzophenone (purity 99%) were supplied by Aldrich, and benzophenone (purity 99%) was provided by Fluka.

Chemical structures and physicochemical properties of the photoinitiators studied are shown in **Table 1**. The data was collected from different databases (SciFinder 2007, ChemIDplus Advanced).

Polyethylene wax Licowax PE 520 (nonpolar and low-molecular 105 polyolefin waxes; drop point, 120 °C; density, 0.93 g/cm^3) was obtained from Clariant Ibérica, S. A. (Barcelona, Spain).

All solvents were HPLC-grade. Acetonitrile was provided by Merck (KgaA, Darmstadt, Germany), and ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA).

Stock standard solutions (300 mg/L) of photoinitiators were prepared in acetonitrile and stored at 4 °C in the darkness.

Food Samples. For migration studies five dry foods were selected: cake (naturally leavened baked cake), toasted bread, breakfast cereals (corn flakes), pasta (durum wheat semolina pasta) and rice (white parboiled).

All foodstuffs were bought in a local supermarket.

Migration Studies. An additive enriched polyethylene wax was used as a photoinitiator release system. It was prepared according to the procedure reported by Sanches-Silva et al. (*16*) with a slight modification. Briefly, a solution containing about 2 mg of each photoinitiator was carefully added to 3 g of wax. Once the solvent was evaporated, the mixture was heated at 140 °C for 2 h. The enriched wax was then cooled at room temperature. To verify the concentrations of the photonitiators, a small piece of the wax was extracted with the procedure mentioned below and analyzed by HPLC-DAD.

Food samples were placed on a metallic net and were separated from each other with a glass ring (∅ = 3.5 cm and the height = 0.9 cm). The additive enriched wax (area = 46.6 cm^2) was placed on the bottom of a glass container (V = 720 mL) without direct contact to food to ensure that the migration of the photoinitiators occurred through the vapor phase. The migration studies were performed under accelerated conditions (70 °C, 48 h).

For the studies of migration kinetics, the cake was selected as the representative of dry food. The cake samples (m = ca. 3 g) were placed in 45 mL glass jars without direct contact with the wax (area = 2.9 cm^2). The glass jars were then hermetically closed and stored at 70 °C for 5, 10, 24, 34, 48, 144, and 360 h.

Photoinitiator Extraction. Food samples were extracted using the method described previously in the literature (*13*). Acetonitrile was used as extraction solvent.

Chromatography. HPLC analyses were performed on a HP1100 system (Hewlett-Packard, Waldbronn, Germany) equipped with a HP1100 quaternary pump, a degassing device, an autosampler, a column thermostatting system, a diode-array detector (DAD) and Agilent ChemStation for LC and LC/MS systems software.

The separation was performed on a Kromasil 100 C18 (25 × 0.4 cm i.d., 5 μm) column, using a binary mobile phase consisting of acetonitrile and water; the gradient elution program is shown in **Table 2**. The flow rate was 1 mL/min, and the injection volume was 20 μL. The selected wavelengths were 254 nm for 4-hydroxybenzophenone, methyl-2-benzoylbenzoate, benzophenone, 2-hydroxybenzophenone, 4-methylbenzophenone, and 4,4′-bis(diethylamino) and 290 nm for 4-benzoylbiphenyl. Data concerning the validation of the chromatographic method are described in a paper submitted for publication.

Table 2. HPLC Elution Profile Program[a]

time (min)	% A	% B
0	50	50
10	0	100
15	0	100
16	50	50[b]
20	50	50[c]

[a] A: water. B: Acetonitrile. [b] Return to initial conditions. [c] Re-equilibration.

RESULTS AND DISCUSSION

The migration of benzophenone and derivatives into dry foodstuffs through the vapor phase was investigated. The assays were carried out under accelerated conditions (70 °C, 48 h) (**Figure 1**). The foodstuffs used for the study were analyzed prior experiments (blank sample) and no detectable quantities of the migrants of interest were found from these blank food samples. All photoinitiators studied here were found to migrate into the food, except 4,4′-bis(diethylamino)benzophenone, probably due to its low vapor pressure (3.25×10^{-9} mmHg). The conditions used in the migration test here simulate the worst case.

The highest contents of migrated photoinitiators were found in cake. This is not surprising since the compounds are lipophilic. The fat content was approximately 10.7 times higher in cake than in pasta and about 3.6 times higher than in cereals (**Table 3**).

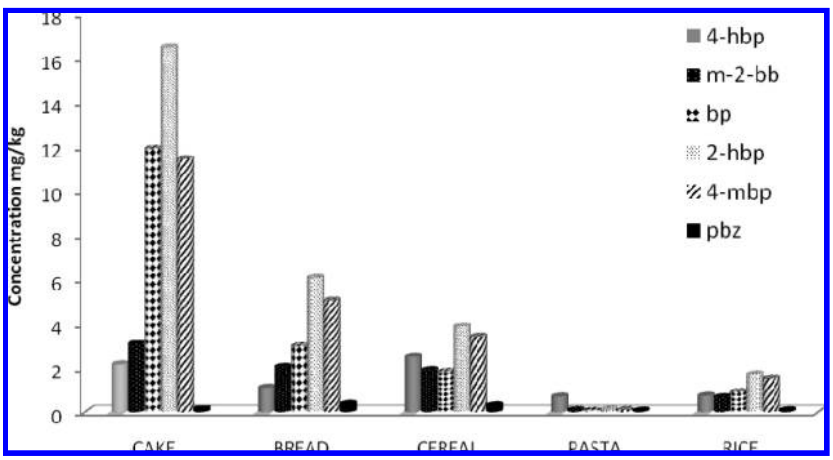


Figure 1. Migration of benzophenone-based derivatives into dry foodstuffs, at 70 °C for 48 h.

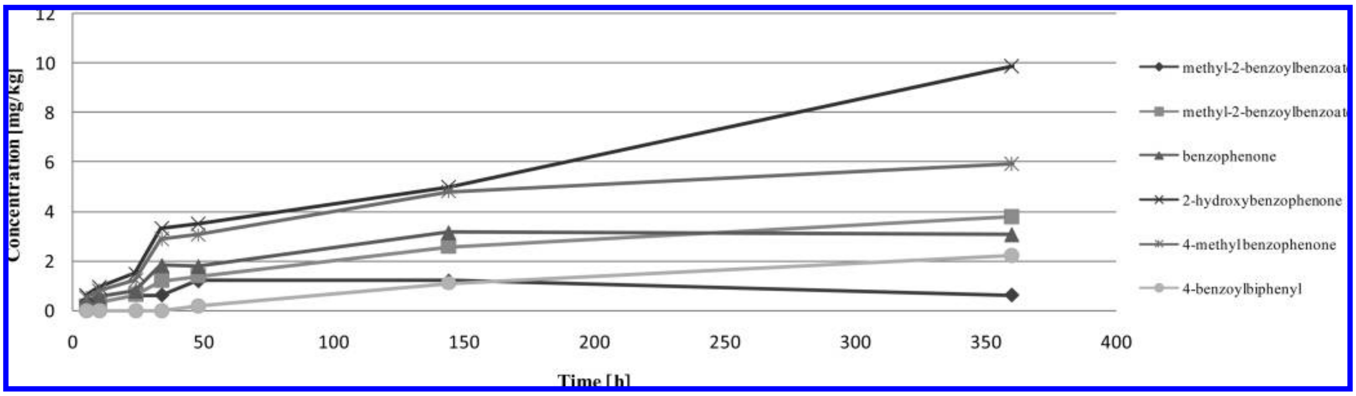


Figure 2. Kinetics of migration of photoinitiators into cake at 70 °C.

Table 3. Chemical Composition of the Foods Studied According the Nutritional Label

food	fat (%)	proteins (%)	carbohydrate (%)
cake[a]	11.6	4.4	78.1
bread	7	13	70.5
cereal	3.2	9	72.2
pasta	1.08	12.84	67
rice	0.5	7.84	77.2

[a] Data obtained from the USDA database (*17*).

These results are in good agreement with those reported by Anderson and Castle (*4*) and Triantafyllou et al. (*7*) for benzophenone. Anderson and Castle (*4*) analyzed 71 food samples selected randomly from a total of 143 samples packaged in printed carton board, in which benzophenone had been detected. The highest value corresponded to a high fat chocolate packaged in direct contact with cartonboard.

In the study conducted by Triantafyllou et al. (*7*), the migration of different contaminants from recycled paper and board into foods with different fat contents was evaluated. They observed that the highest migration levels were found in the foodstuff with the highest fat content.

Of these seven photoinitiators studied, the higher migration was observed for 2-hydroxybenzophenone, benzophenone and 4-methylbenzophenone. This could be explained with the higher vapor pressures of these compounds.

Another factor that seems to affect the migration process is the porosity. In order to evaluate the influence of this parameter, the true density of the selected food was measured using a helium pycnometer (Mycropicnometer, Quanta-Chrome, MPY-2). From the data of density, the porosity (ε) was calculated by means of this equation:

$$\varepsilon = (1 - d_{\text{apparent}}/d_{\text{true}}) \times 100$$

where d_{apparent} is the apparent density (mg/mL of the sample including air) and d_{true} is the true density (mg/mL of the sample excluding air).

The porosity values obtained for cake, bread, cereal, pasta and rice were 30.6%, 35.9%, 8.8%, 3.7% and 4.8%, respectively. It was observed that the foodstuffs with a porous structure, such as cake and bread, presented the highest migration values.

These results suggest that the porosity strongly influences the migration process; high porosity values contribute to high migration levels.

In the cake, the concentrations of the photoinitiators increased over time until the equilibrium was reached after approximately 150 h (**Figure 2**). However, for 2-hydroxybenzophenone not even that time was enough to reach the equilibrium. On the other hand, in the case of 4-benzoylbiphenyl, it was only after 48 h when the migration was on a detectable level. This could be due to the low vapor pressure compared to the rest of the photoinitiators.

In summary, the results obtained in this study show that the migration of benzophenone-based photoinitiators through the vapor phase occurs to a large extent. And furthermore, both the porosity and the fat content of the food have a strong influence on the migration process. Foods with high fat content and high porosity values are exposed to high migration levels.

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