

PHOTOINITIATORS IN DRY FOODSTUFFS: RESULTS OF BELGIAN MARKET SURVEY & A KINETIC EVALUATION OF THE MIGRATION

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Introduction

Mixtures of photoinitiators are widely used as catalysts for photo-polymerisation. After exposure to light, the photoinitiator decomposes into free radicals, thereby triggering the polymerization reaction that causes the ink to cure onto the substrate. However, the photoinitiators are not always completely utilised or removed after the printing process. As a result, migration of low molecular weight photoinitiators, applied on the outer surface of the packaging material, into the food can still occur [1]. Several alerts for food contamination caused by UV-curable inks have been reported in the past. Examples are the presence of 2-Isopropylthioxanthone (2-ITX) in instant baby milk [2] and breakfast cereals [3], leading to the temporary withdrawal of these products from the market.

At present, there is no specific European legislation for the use of printing inks on food contact materials. However, all materials and articles intended to come into contact with food should comply with the general requirements laid down in the European Framework Regulation 1935/2004, i.e. they should not transfer their constituents into food in quantities that could endanger human health or bring about unacceptable changes in composition or characteristics of foodstuffs [4]. A specific European Regulation exists only for plastic materials and articles intended to come into contact with food [5], mentioning a specific migration limit (SML) of 0.6 mg kg⁻¹ for the use of benzophenone (BP) as additive, while the application of the other photoinitiators is not mentioned in this legislation [5]. Evaluation of the migration of chemical

contaminants in food is necessary but very challenging due to the complexity of the matrix and the wide variety of foods that need to be analysed. If a food contact material is in contact with the food, the food itself is analysed for compliance. If no contact has been established yet, the food contact material can be checked for compliance using food simulants. According to Regulation (EU) No 10/2011, the official simulant for dry food is poly(2,6-diphenylphenylene oxide), also known under its commercial name Tenax® [5].

In this study, a Belgian market survey was conducted in order to investigate the presence of photoinitiators in dry food. As most samples were far from the end of the shelf life and migration might still occur, migration kinetics of photoinitiators towards dry foodstuffs were also investigated.

Materials and methods

All Belgian market dry foodstuffs were extracted using acetonitrile, followed by the addition of inorganic salts to precipitate fatty residues. After filtration, the extract was analysed using Ultra performance liquid chromatography in combination with tandem mass spectrometry (UPLC-MS/MS) [6].

Migration kinetics experiments were performed using the standard operation procedure developed by the European Reference laboratory for food contact materials, Joint Research Centre in Ispra (Jakubowska et al. 2014). One g of Tenax® was brought in contact with spiked blank circular cardboard sample (non- food contact side) in a petri dish and spiked on the side of the cardboard intended for printing by homogeneously

dotting a photoinitiator solution. Another petri dish was used to cover the sample and the complete set was wrapped in aluminium foil. Migration conditions were according to European Regulation (EU) No 10/2011 (Regulation (EU) No 10/2011) for long-term storage at room temperature, resulting in a migration of 10 days at 60°C [7]. After the migration experiments, the simulant Tenax[®] was analysed and the concentration of the photoinitiators was determined. A previously optimised method by Van Den Houwe et al. was used [8].

In order to obtain a complete overview of the migration as a function of time, samples were stored at 60°C and analyzed on a daily basis up to 20 days.

Results and discussion

In March 2010, 97 samples of dry foods packed in cardboard boxes and stored at ambient temperature were collected from the Belgian market and a survey on the occurrence of photoinitiators was performed [6]. At least one photoinitiator was found in 89% of the food samples (86 out of 97). Since most samples were still far from the expiration date, migration kinetics of photoinitiators were studied.

Different migration patterns for the different photoinitiators were shown. Figure 1 presents the results for the migration of 4,4'-bis(diethylamino)benzophenone (DEAB), Ethyl-4-dimethylaminobenzoate (EDMAB) and 2-Isopropyl-9H-thioxanthen-9-one (ITX) as a function of time into Tenax[®], showing significantly different migration patterns, even though the photoinitiators have comparable properties such as molecular weight, molecular size, polarity, boiling point, ... ITX migration from cardboard in Tenax[®] reached an equilibrium after 12 days, while EDMAB has not reached an equilibrium yet and DEAB probably never will.

Photoinitiators 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) and Michler's ketone (MK) have similar low Tenax[®]-migration profiles as DEAB. Therefore these two photoinitiators were never detected in the market survey if they were even present in the cardboard at all. Furthermore it is

expected that 4-hydroxybenzophenone (4-HBP) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HMMP), which were detected at the ppb level in several samples, will not exceed legal limits near expiration dates since these photoinitiators also show analogous profiles to the DEAB-migration profile.

Furthermore 2-chloro-9H-thioxanthen-9-one (CTX), 2-ethylanthraquinone (EA), 2-ethylhexyl-4-dimethylaminobenzoate (EDB), ITX and 4-methylbenzophenone (MBP) were found in low concentrations (ppb level) in about 5% of the Belgian market samples. BP, 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and EDMAB were most frequently found. Most samples resulted in concentrations lower than 0.01 mg kg⁻¹ for DMPA and EDMAB. Nevertheless, two out of three rice samples of brand X contained high amounts of EDMAB and DMPA (X1: 0.009 mg kg⁻¹ EDMAB, 0.242 mg kg⁻¹ DMPA, X2: 0.204 mg kg⁻¹ EDMAB, 0.818 mg kg⁻¹ DMPA). BP was detected in 68 samples and concentrations remained below 0.02 mg kg⁻¹. Except one rice sample (brand Y) contained a significant concentration of BP (Y: 0.262 mg kg⁻¹). The sample, containing a plastic film, was analysed approximately one year before expiration date.

Both EDB and DMPA Tenax[®] migration profiles show significant migration and do not reach migration equilibria after 10 days migration at 60°C. BP, CTX, EA and MBP have comparable migration profiles to the profile of ITX. Consequentially, regulatory limits can be exceeded for BP, CTX, DMPA, EA, EDB and MBP near expiration dates. Especially for products X1, X2 and Y. BP migration towards Tenax[®] is completed within the 10 days migration period. Hence, product Y was purchased in 12-fold and analysed every month till the end of shelf life.

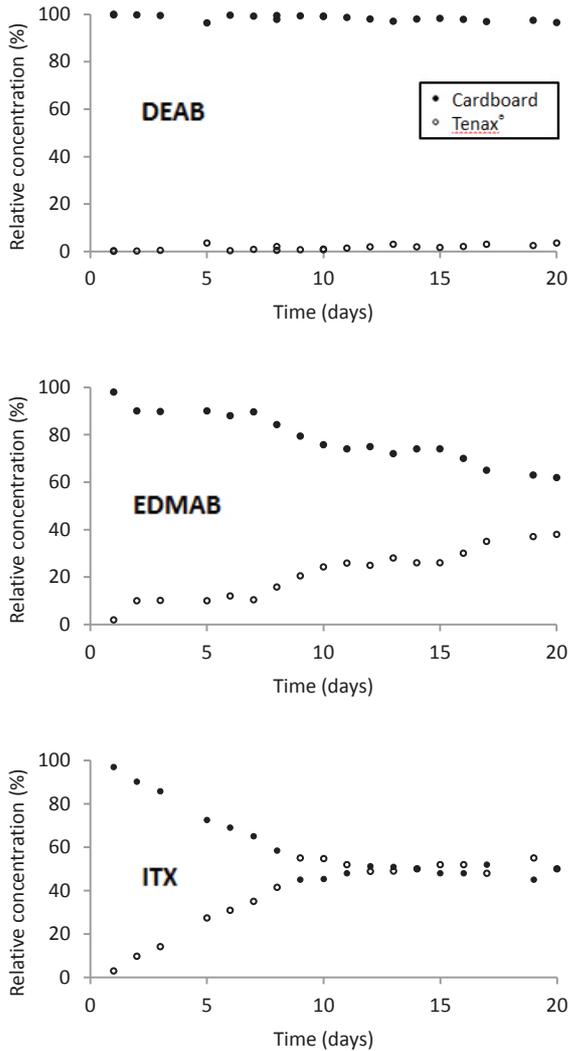


Fig. 1. Migration kinetics for DEAB, EDMAB and ITX from cardboard in Tenax[®] at 60°C.

Figure 2 presents the results for the migration of BP in product Y as a function of time before the end of shelf life, showing the migration equilibrium had already settled approximately one year before the end of shelf life.

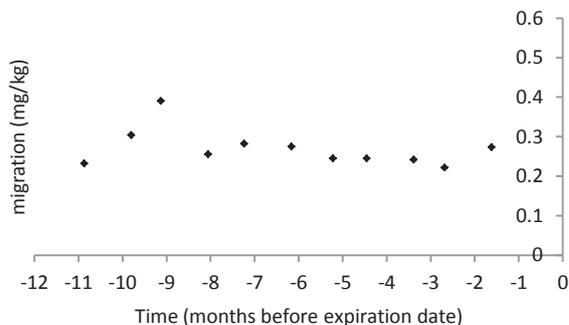


Fig. 2. Migration of BP (in mg/kg) of BP for product Y.

Conclusion

The absence of CPTX, DEAB and MK in dry food samples found on the Belgian market was explained through the evaluation of the migration of these photoinitiators in the simulant for dry foods Tenax[®]. Different migration patterns were found for different photoinitiators. Hence, it was confirmed that BP already reached migration equilibrium for product Y near the end of shelf life.

This study specifically focussed on the migration of photoinitiators from cardboard towards cereals. Nevertheless, dry foodstuffs should be screened on a regular basis, especially near expiration date. Moreover, further research is needed, especially with other migrants, having different physical and chemical properties.

References

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