The use of Tenax® films to demonstrate the migration of chemical contaminants from cardboard into dry food.

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The use of Tenax® films to demonstrate the migration of chemical contaminants from cardboard into dry foodstuffs.

Contaminants in food packaging are a challenge of our time since the packaging material itself has been found to represent a source of food contamination through the migration of substances from the packaging. Before first use, packaging materials destined for the packaging of dry foods can be evaluated by performing migration experiments with the simulant for dry foods: Tenax®. This simulant is commercially available as a powder that is more difficult to handle during the migration experiments. In this contribution a Tenax® film was developed. The film can be applied to the cardboard surface to conduct the migration test. After the migration is completed, the film can be easily extracted to determine the concentration of the contaminants in the film. Finally, the performance of the Tenax® film was compared to the conventional Tenax® powder for the evaluation of 15 model migrants.

Keywords: Tenax®; film; food simulant; migration testing; food contact material

Introduction

Recent improvements in food production and distribution have led to an increased sophistication of food packaging. Unfortunately, non-inert materials, like paper and board, can be a direct source of chemical contaminants. Chemical partitioning from the packaging into the food is known as migration. In 1999, Boccacci et al. showed that diisopropylnaphtalene (DiPN) was transferred from cardboard to rice, pasta and maize flour already after three days at ambient temperature (Boccacci et al. 1999). Inevitably, several alerts for food contamination caused by migration have been reported in the past. Examples are the presence of photo-initiator 2-isopropylthioxanthenone (2-ITX) in instant baby milk and photo-initiator 4-methylbenzophenone (4-MBP) in breakfast cereals, leading to the temporary withdrawal of these products from the market (IBFAN 2005, EFSA 2009).

Therefore, a careful evaluation of food contact materials and their interactions with food is needed to ensure consumers' safety. Evaluation of the migration of chemical contaminants in food is necessary but 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 not yet in contact with food, the contact material can be checked for compliance using food simulants. According to the European Regulation No 10/2011, the official simulant for dry food is poly(2,6-diphenylphenylene oxide), also known under its commercial name Tenax® (Regulation (EU) N° 10/2011).

Numerous studies have been reported on the migration of contaminants from FCM into Tenax®. A few examples are the migration of phthalates (Aurela et al. 1999), diisopropylnaphthalene (Summerfield & Cooper 2001), dihydroabietic and abietic acids (Ozaki et al. 2006), alkylbenzenes (Aurela et al. 2001) and fatty acid esters (Richter et

al. 2009). Furthermore, Cannelas et al. demonstrated the use of Tenax® in the determination of non-intentionally added substances in acrylic adhesives (Cannelas et al. 2012) and Zurfluh et al. studied the use of Tenax® for the analysis of mineral oil saturated hydrocarbons (MOSH) from recycled paperboard (Zurfluh et al. 2013). Furthermore, Triantafyllou (Triantafyllou et al. 2007), Bradley (Bradley et al. 2014) and Nerín (Nerín et al. 2007a) demonstrated the use of Tenax® for a kinetic evaluation of certain migrants.

Before use, Tenax® is usually cleaned multiple times by soxhlet and dried afterwards. Next, Tenax® is applied on the food contact material surface for a certain contact time and contact temperature. According to the internationally recognised standard on overall migration from plastic materials and articles in contact with foodstuffs, 4 gram of Tenax® per square decimetre of surface area of the test specimen is required to cover the food contact surface sufficiently (EN 1186-13:2002). Nevertheless, it was demonstrated that 1 gram of Tenax® is equally sufficient to cover a 0.15 dm² circular sample (Jakubowska et al. 2014). After the migration is completed, Tenax® is removed from the food contact material surface and extracted. Extracts are usually analysed using gas or liquid chromatography. The use of the Tenax® powder as a simulant for dry foodstuffs is rather inconvenient since the Tenax® powder has to be entirely collected in a recipient prior to contaminant extraction. Hence, the concept of a practical Tenax® film was introduced.

In 2010, Alfeeli et al. developed thin Tenax® films as adsorbent material for micro preconcentration applications (Alfeeli et al. 2011). Tenax® was dissolved in dichloromethane and used to coat the embedded high-aspect-ratio three-dimensional micro pillars of the micro preconcentrator at room temperature or at frozen conditions (Alfeeli et al. 2011). Furthermore, Alfeeli et al. concluded that there was no difference

in the adsorption properties between the powder and the film form (Alfeeli et al. 2010).

Next, in 2013, Tenax®-coated silica nanoparticles were incorporated as an adsorbent bed in silicon based micro-thermal preconcentrator chips (Akbar et al. 2013). Tenax® was dissolved in dichloromethane and again evaporated to leave a thin film of the polymer adsorbent on the cavity surfaces of the micro-thermal preconcentrator chips (Akbar et al. 2013).

Recently, Tenax® was combined with the zeolite material ZSM-5 in order to form a thin film microextraction device that was used as a novel alternative tool for headspace volatile organic compound extraction and preconcentration (Goda et al. 2014). Tenax® was dissolved in chloroform and used to apply thin flat films via dip coating. The coating took place at room temperature in ambient air (Goda et al. 2014).

In this contribution, Tenax® films were constructed by dissolvation in chlorinated solvents, followed by evaporation under air. The Tenax® films were evaluated for their application in compliance testing of cardboard food contact materials.

Materials and methods

Chemicals

Neat certified standards of acetophenone (AP, 99%) benzophenone (BP, purity 99.9%), benzyl butyl phthalate (BBP, 98%), dibutyl phthalate (DBP, 99%), dibutyl sebacate (DBS, 97%), 2,6-diisopropylnaphthalene (DiPN, CPR), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 99%), trans,trans-1,4-diphenyl-1,3-butadiene (DPBD, 98%), 2,6-di-tert-butylphenol (DTBP, 99%), 2-ethylhexyl-4-dimethylaminobenzoate (EDB , 98%), 4-methylbenzophenone (MBP, 99.9%), methyl stearate (MS, 99%), naphthalene

(NPT, 99%), 4-phenylbenzophenone (PBZ, 99.8%) were purchased from Sigma-Aldrich (Bornem, Belgium). 2-Isopropyl-9H-thioxanthen-9-one (ITX, 100%) was supplied by Rahn (Zürich, Switzerland). Chemical structures are given in Figure 1.

Tenax® (60/80 Mesh) was also purchased from Sigma-Aldrich (Bornem, Belgium). Acetonitrile, chloroform, dichloromethane and methanol were purchased from Biosolve (Valkenswaard, Netherlands). All solvents were HPLC-grade.

All stock solutions were prepared in methanol at a concentration of 1 mg mL^{-1} and stored at -20°C for 6 months.

Development of the Tenax® film

Prior to its use, Tenax® was cleaned by soxhlet extraction with acetonitrile for at least 6h, followed by drying in an oven (BINDER, Bohemia, NY). Next, Tenax® was dissolved in chloroform or dichloromethane in concentrations ranging from 0.00625 up to 0.05 g mL^{-1}. After filtration using a 0.45 µm PVDF filter (GRACE) and a 1-0.45 µm glass fibre + PVDF prefilter (CHROMAFIL®), a fixed volume (2, 4 or 6 mL) was brought into a glass recipient and the solvent was evaporated at room temperature in air. A petri dish with a diameter of 58 mm was chosen as a recipient. To construct visibly flat and smooth films, any form of air circulation such as fumehoods was avoided.

Set-up migration experiment

Since a petri dish was chosen as a recipient, the Tenax® films could remain fixed on the glass to perform migration testing using a previously described set-up by Jakubowska et al. (Jakubowska et al. 2014). The Tenax® film was brought in contact with 0.15 dm^2 of spiked blank circular cardboard sample. The cardboard was spiked on the side of the cardboard intended for printing by homogeneously dotting 100 µL of a solution with a concentration of 25 µg mL^{-1} of the following contaminants: AP, BP, BBP, DBP, DBS,

DiPN, DMPA, DPBD, DTBP, EDB, ITX, MBP, MS, NPT and PBZ. A smaller petri dish with a diameter of 52 mm was used to cover the sample and the complete set was wrapped in aluminium foil. Migration conditions were according to European Regulation No 10/2011 (Regulation (EU) No 10/2011) for long-term storage of dry foodstuffs at room temperature, resulting in a migration of 10 days at 60°C. Afterwards, both film and cardboard were analysed and the concentration of the contaminants was determined.

Additionally, a conventional migration experiment with 1 gram Tenax® powder was conducted by bringing spiked blank cardboard (100 µL of a AP, BP, BBP, DBP, DBS, DiPN, DMPA, DPBD, DTBP, EDB, ITX, MBP, MS, NPT and PBZ solution with a concentration of 25 µg mL^{-1}) in contact with Tenax®. Prior to its use, Tenax® was cleaned by soxhlet extraction. After the migration (10 days at 60°C) was completed, Tenax® and cardboard were analysed and the rate of migration was determined.

Analysis of contaminants

Analysis of contaminants in the cardboard:

Cardboards were cut into pieces and extracted using 20 mL acetonitrile in 100 mL flasks for 24h at 70°C (Sanches-Silva et al. 2008). Analyses were carried out using GC-MS. Quantification was done using a five point calibration curve ranging from 0.625 to 2.5 µg per cardboard circle, external calibration. The calibration curve was constructed in the matrix. Hence, the cardboard was enriched with 100 µL of the contaminant solution (0, 6.25, 12.55, 18.75 and 25 µg mL^{-1}). The enriched cardboards were also kept in petri dishes for 10 days at 60°C to encounter the loss of substances due to evaporation. Afterwards, cardboard samples were extracted prior to calibration.

Analysis of contaminants in Tenax® film:

Tenax® films were cut into pieces and extracted with 20 mL acetonitrile in 100 mL flasks for 24h at 70°C. Analyses were carried out using GC-MS. Quantification was done using a five point calibration curve ranging from 0.625 to 2.5 µg per film, external calibration. The calibration curve was constructed in the matrix. Hence, after bringing 4 mL of a 0.05 g Tenax® mL^{-1} in the petri dish, the 'calibration-film' was spiked with 100 µL of a contaminant solution (0, 6.25, 12.55, 18.75 and 25 µg mL^{-1}) before evaporating into a Tenax® calibration-film. The calibration-films were also placed in the oven for 10 days at 60°C prior to extraction for calibration purposes.

Analysis of contaminants in Tenax®

After the migration experiments, the simulant Tenax® was analysed and the concentration of the model migrants was determined. A previously optimised method by Van Den Houwe et al. (Van Den Houwe et al. 2014) was used. Tenax® was extracted twice with 20 mL of acetonitrile. Both extracts were combined and further diluted to 50 mL. For the quantification, a five point calibration curve in the matrix was constructed using 1.0 g Tenax® spiked at a concentration ranging from 0.625 µg g^{-1} up to 2.5 µg g^{-1}. Calibration samples were also kept in the migration oven for 10 days at 60°C before being extracted.

GC-MS analysis

GC-MS analyses were carried out using a Agilent 7683 Automatic Liquid sampler (Agilent Technologies, Palo Alto, USA). The GC-MS analyses were performed on an Agilent 6890N gas chromatograph coupled to an Agilent 5973N single quad mass selective detector. 2 µL was injected into the GC-MS system in split injection mode (split ratio 3,0:1). A VF-5ms column (Factor four, Agilent, California, VS) of 30 m (Ø

184 0.25 mm and film thickness of 0.30 μm) was used. Helium was delivered as carrier gas
185 at a constant pressure of 14.65 psi with an initial flow of 1.3 mL min^{-1}.
186 The temperature gradient started at 80°C (held for 2 min) and rose with 20°C
187 min^{-1} to reach 290°C, which was held for 10 min. The total run time was 22.5 min.
188 Temperatures of injection port, ion source, quadrupole and interface were set at 160,
189 230, 150 and 280°C, respectively. For quantification of compounds, the mass
190 spectrometer was operated in selective ion monitoring (SIM) mode (100 ms dwell
191 times). Table 1 presents the specific m/z ratios and the retention times.
192 Instrument control and data acquisition were performed by Agilent software
193 (Enhance Chemstation 2004, Agilent).

194 **Results and discussion**

195 ***Selection of contaminants***

196 The contaminants were selected based on a literature search on contaminants in paper
197 and board. It was found that photo-initiators and phthalates are one of the most common
198 groups of compounds present in paper and board food packaging (Aurela et al. 1999;
199 Jakubowska et al., 2014; Jung et al., 2013; Summerfield et al. 2001; Van Den Houwe et
200 al., 2014). Hence, two phthalates (BBP and DBP) and six photo-initiators (BP, DMPA,
201 EDB, ITX, MBP and PBZ) were selected. Futhermore, the following contaminants were
202 also frequently studied: AP, DBS, DiPN, DPBD, DTBP, MS and NPT (Aurela et al.,
203 2001; Bradely et al., 2014 and 2015; Isella et al., 2013; Nérin et al., 2007b; Poças et al.,
204 2011; Sanches Silva et al., 2006 and Triantafyllou et al., 2007).
205

206 ***Optimisation of the production of the Tenax® film***

207 Among different organic solvents that were tested, Tenax® or poly(2,6-
208 diphenylphenylene oxide), was best dissolved in chloroform or dichloromethane

209 (DCM). Since it was practically not feasible to dissolve Tenax® at higher concentrations
210 than 0.05 gram per millilitre chloroform, solutions ranging from 0.00625 g mL^{-1} to 0.05
211 g mL^{-1} were used to construct films of 25, 50, 100, 150 and 200 mg by evaporating 4
212 mL of a Tenax® solution in a petri dish (Figure 2). In parallel, Tenax® films of 100, 200
213 and 300 mg were constructed by evaporating different volumes (2, 4 and 6 mL) of a
214 0.05 g mL^{-1} chloroform solution (Figure 3). Tenax® films lighter than 200 mg were too
215 thin and broke easily when removed from the petri dish. Hence, films containing 200
216 mg and 300 mg Tenax® were found suitable to proceed.
217 Next, the performance of 200 mg and 300 mg films (evaporation of 4 mL and 6 mL of a
218 0.05 g mL^{-1} solution) was compared for Tenax® films constructed from chloroform and
219 Tenax® films constructed from DCM. The results for ITX, BBP and NPT are given in
220 Figure 4. The results, an average of triplicate experiments, demonstrated that the choice
221 of dissolution solvent, nor the weight of the film had an important impact on the
222 migration performance, for all compounds investigated. Additionally, 200 mg films
223 were more homogenous compared to 300 mg films because less evaporation time was
224 needed. Hence, 200 mg films constructed by evaporation of 4 mL of a chloroform
225 solution (0.05 g mL^{-1}) were chosen for further experiments.
226
227 ***Impact of the amount of Tenax® in a conventional migration experiment***
228 In the conventional migration experiment 1 gram Tenax® is brought into contact with
229 0.15 dm^2 of cardboard sample (Jakubowska et al., 2014). The optimised Tenax® film
230 only contained 200 mg Tenax®. Hence, the conventional migration from the selected
231 compounds in 1 gram Tenax® powder was compared to the migration in 0.2 gram
232 Tenax® powder. The results for ITX, BBP and NPT are shown in Figure 5. Despite the
233 fact that the cardboard surface is barely covered using 0.2 gram Tenax®, the migration

234 results of the selected contaminants towards 0.2 gram Tenax® are comparable with the
235 migration results towards 1 gram Tenax® for all contaminants investigated. Hence, the
236 performance of the optimised Tenax® films can be compared with the conventional
237 migration experiment using 1 gram Tenax® powder.
238
239 ***Evaluation performance Tenax® film***
240 Finally the performance of the Tenax® film was compared to the performance of the
241 conventional 1 gram Tenax® powder for two available blank cardboards (cardboard A
242 and B) destined for the packaging of dry foodstuffs. Hence, the spiked cardboards were
243 each brought into contact with a Tenax® film for 10 days at 60°C. In parallel, spiked
244 cardboard was brought into contact with 1 gram Tenax® powder for the same contact
245 time and temperature. The experiment was performed in triplicate, using calibration
246 curves constructed in the matrix. The results for ITX, BBP and NPT are given in figure
247 6. Except for NPT, all compounds showed a comparable or even a higher migration
248 towards the Tenax® powder for cardboard A. Since different cardboards have different
249 properties, different migration results were observed for both migration into the
250 conventional 1 gram Tenax® powder and the 200 mg Tenax® film. Nevertheless,
251 cardboard A is rather rough and probably a more intense contact is established between
252 the cardboard and the Tenax® powder compared to the contact with the Tenax® film.
253 For cardboard B; BP, DTBP, EDB, ITX and MBP have a higher migration potential for
254 the Tenax® powder, while DiPN, MS, NPT and PBZ migrate more towards the designed
255 Tenax® film . Probably the effect of a more intense contact between the cardboard and
256 the powder is lost because cardboard B was found to be much smoother compared to
257 cardboard A. Hence, the migration in Tenax® powder compared to the migration in the

Tenax® film is influenced by the surface properties of the cardboard with a more favourable migration in Tenax® powder for rough surfaces.

In 2016, Van Den Houwe et al. performed migration experiments for the migration of several photo-initiators from cardboard in cereals after a contact of 6 months at room temperature (Van Den Houwe et al., 2016). About 5.4% BP migrated in cereals after a six months contact between the cereals and the cardboard at room temperature (Van Den Houwe et al., 2016). The percentage of migration of BP in the Tenax® films was 26.1% using a smooth cardboard and 14.1% using a more rough cardboard to establish the migration contact for 10 days at 60°C. Although the migration rate in the Tenax® film (14.1% and 26.1%) is less compared to the migration in the powder form (38.8% and 36.9%), the Tenax® film migration rate might be better estimate of the migration in dry foods. Indeed, the migration of photo-initiators in other dry foodstuffs such as bread crumbs, pasta and rice was more realistically simulated by the use of the Tenax® film in comparison with the conventional migration (Table 2). However, a higher migration potential of photo-initiators towards rice was indicated in a rice matrix (Table 2). These results are of great consistency with the market survey performed in 2014 where significant amounts of photo-initiators were only found in several rice samples (Van Den Houwe et al., 2014).

Nevertheless, Tenax® films were fast and easily applied to the cardboard surfaces and ensure the entire collection of Tenax® adsorbent prior to extraction, making the developed Tenax® films wordy for further optimisation and investigation.

Conclusion

The use of Tenax® films as a food simulant for dry foodstuffs for the migration of 15 chemical contaminants from cardboard was evaluated. Initially, the construction of the

Tenax® films was optimised. Films with less than 200 mg Tenax® showed severe drawbacks, but 200 mg Tenax® films constructed from a Tenax®-chloroform solution were found suitable. The optimised films were brought into contact with two types of cardboard enriched with 15 chemical contaminants relevant for paper and board food contact materials.

Higher migration rates were observed towards conventional Tenax® powder compared to the migration in the designed Tenax® films. This tendency was explained by a more intense contact between the cardboard and the conventional Tenax® powder. Nevertheless, the designed Tenax® film is fast and easy applicable and can open new perspectives in the domain of testing food contact materials intended for contact with dry foodstuffs, since preliminary experiments have demonstrated that the migration rate is more realistic when compared to the migration in dry foodstuffs.

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382
383 ***Overview of the figures***
384 **Figure 1**
385 Chemical structures of the chemical contaminants.
386 **Figure 2**
387 Tenax® films constructed from different chloroform solutions with a weight of a) 25
388 mg, b) 50 mg, c) 100 mg, d) 150 mg and e) 200 mg.
389 **Figure 3**
390 Tenax® films constructed from a 0.05 g mL^{-1} chloroform soluton with a weight of a)
391 100 mg, b) 200 mg and c) 300 mg.
392 **Figure 4**
393 Comparison of the performance of 200 mg and 300 mg Tenax® films constructed from
394 DCM and chloroform, relative to the 200 mg film constructed from chloroform.
395 **Figure 5**
396 Comparison of the migration towards 1 gram and 0.2 gram Tenax® powder, relative to 1
397 gram Tenax®.
398 **Figure 6**

Comparison of the performance of Tenax® films and Tenax® powder for cardboard A, resulting in a higher migration rate towards the Tenax® powder for ITX, a comparable migration rate for BBP and a higher migration rate towards the Tenax® film for NPT.

Overview of the tables

Table 1

Overview of the specific m/z ratios and retention times of the selected chemical contaminants.

Table 2

Comparison of the conventional migration and the migration in Tenax® films with the actual migration in dry foodstuffs for several photo-initiators (average of 3 replicates).

Overview of supplementary data

Figure 1

Comparison of the performance of 200 mg and 300 mg Tenax® films constructed from DCM and chloroform, relative to the 200 mg film constructed from chloroform.

Figure 2

Comparison of the migration towards 1 gram and 0.2 gram Tenax® powder, relative to 1 gram Tenax®.

Figure 3

Comparison of the performance of Tenax® films and Tenax® powder for cardboard A, resulting in a) a higher migration rate towards the Tenax® powder, b) a comparable migration rate and c) a higher migration rate towards the Tenax® film.

Figure 4

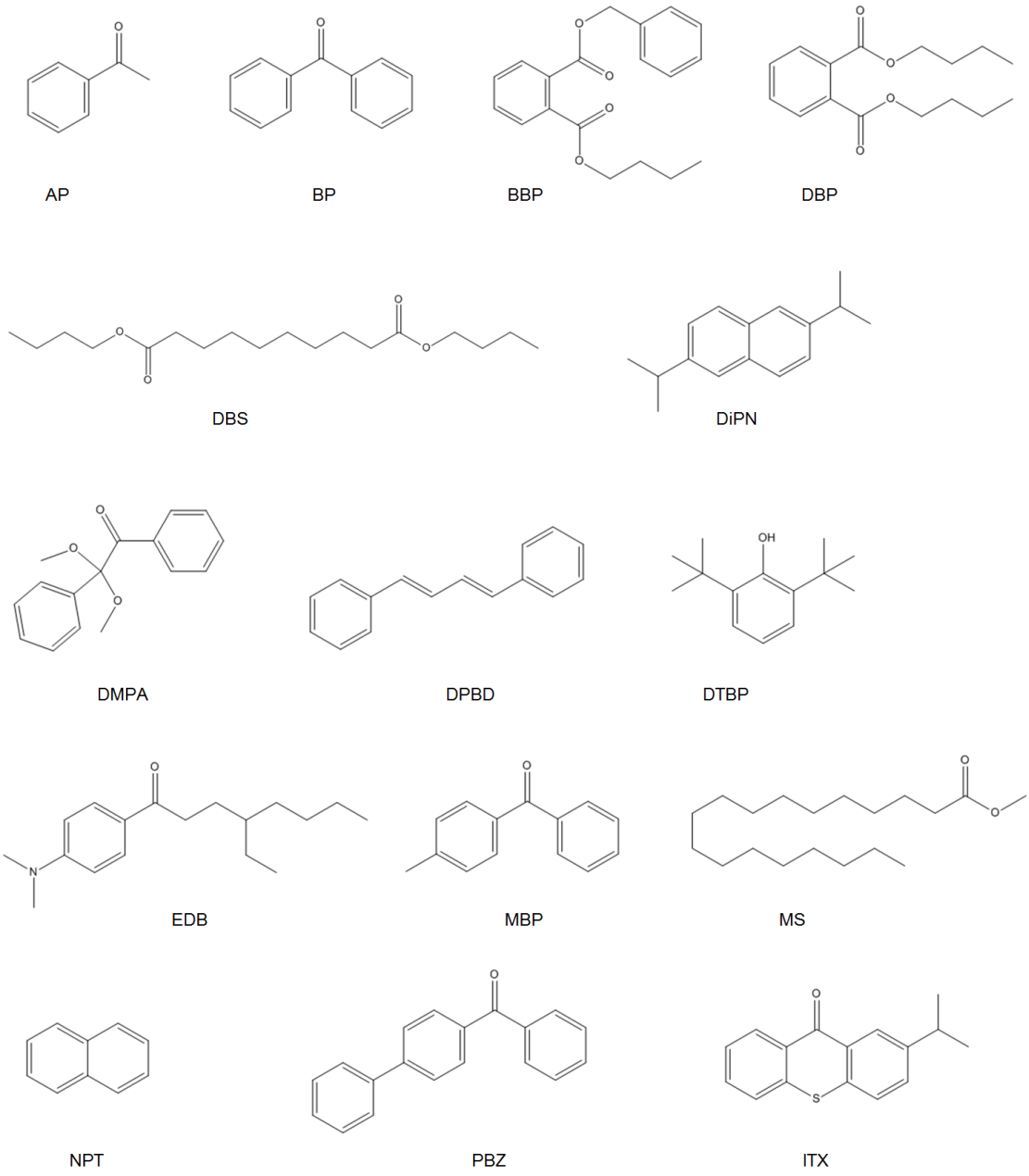
Comparison of the performance of Tenax® films and Tenax® powder for cardboard B resulting in a) a higher migration rate towards the Tenax® powder, b) a comparable migration rate and c) a higher migration rate towards the Tenax® film.

Table 1

N°	Chemical contaminant	Abbreviation	Specific m/z ratio	Retention time (min)
1.	Acetophenone	AP	105	4.76
2.	Naphthalene	NPT	128	5.97
3.	2,6-Di-tert-butylphenol	DTBP	191	8.44
4.	Benzophenone	BP	105	9.36
5.	2,6-Diisopropylnaphthalene	DiPN	197	9.95
6.	4-methylbenzophenone	MBP	119	10.16
7.	2,2-Dimethoxy-2-phenyl acetophenone	DMPA	151	10.87
8.	Dibutyl phthalate	DBP	149	11.21
9.	Trans,trans-1,4-diphenyl-1,3-butadiene	DBPD	206	11.78
10.	Methyl stearate	MS	74	11.96
11.	Dibutyl sebacate	DBS	241	12.22
12.	2-Ethylhexyl-4-dimethylaminobenzoate	EDB	165	12.80
13.	Benzyl butyl phthalate	BBP	149	13.22
14.	2-Isopropyl-9H-thioxanthen-9-one	ITX	239	13.55
15.	4-Phenylbenzophenone	PBZ	181	13.94

Table 2

	Conventional migration in Tenax® powder (%) (10 days at 60°C)	Migration in Tenax® film (%) (10 days at 60°C)	Migration in dry foodstuffs (%) (6 months at room temperature)			
			Cereals	Bread crumbs	Pasta	Rice
BP	50.5	26.1	5.4	5.11	5.98	17.58
EDB	69.4	23.4	8.9	11.08	17.81	36.77
ITX	54.7	21.7	7.4	8.14	14.57	30.78
MBP	50.2	17.1	5.4	14.01	16.98	42.87



441

442 Fig1

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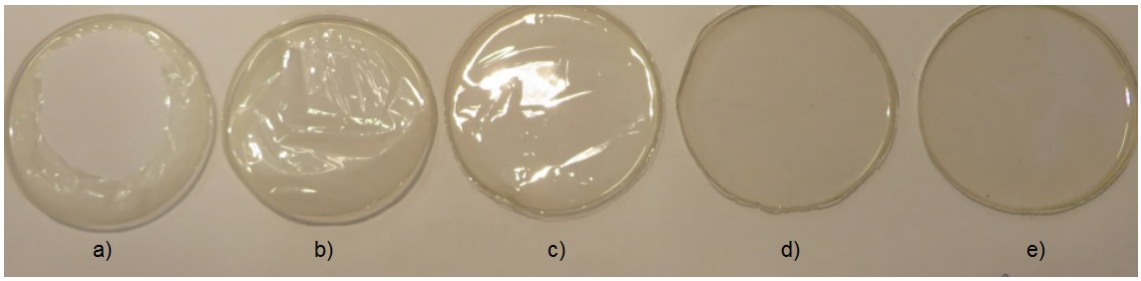


Fig 2

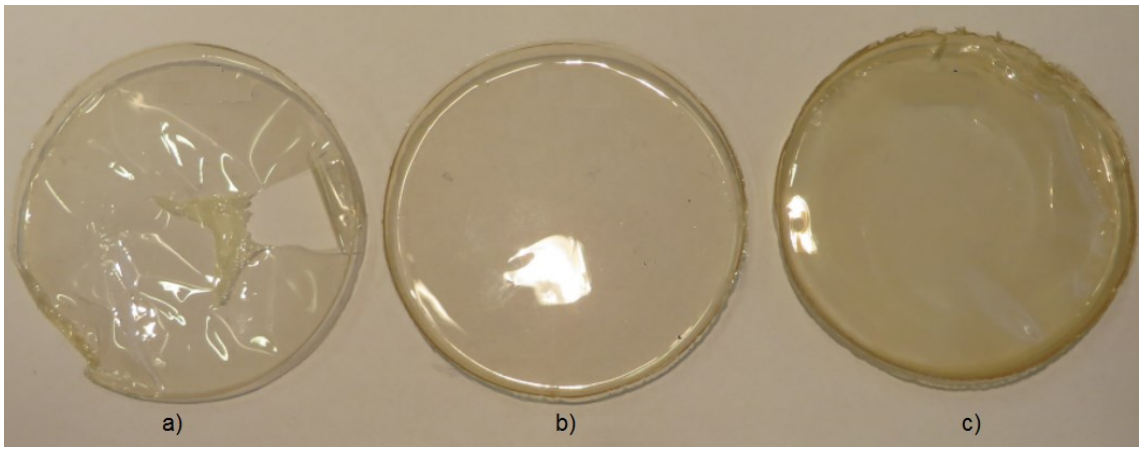
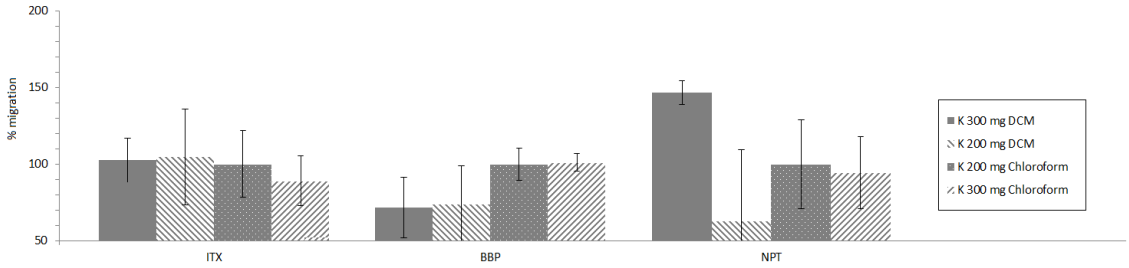


Fig 3



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460 Fig 4

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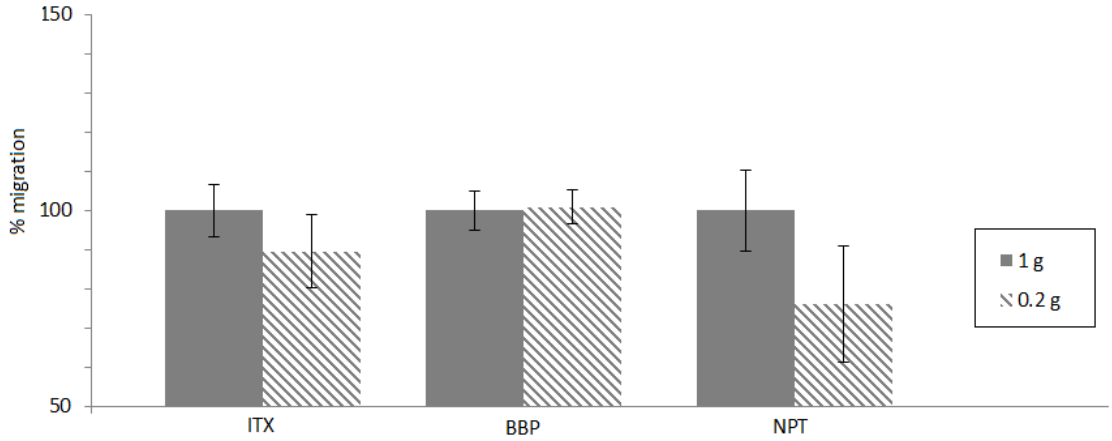

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463 Fig 5

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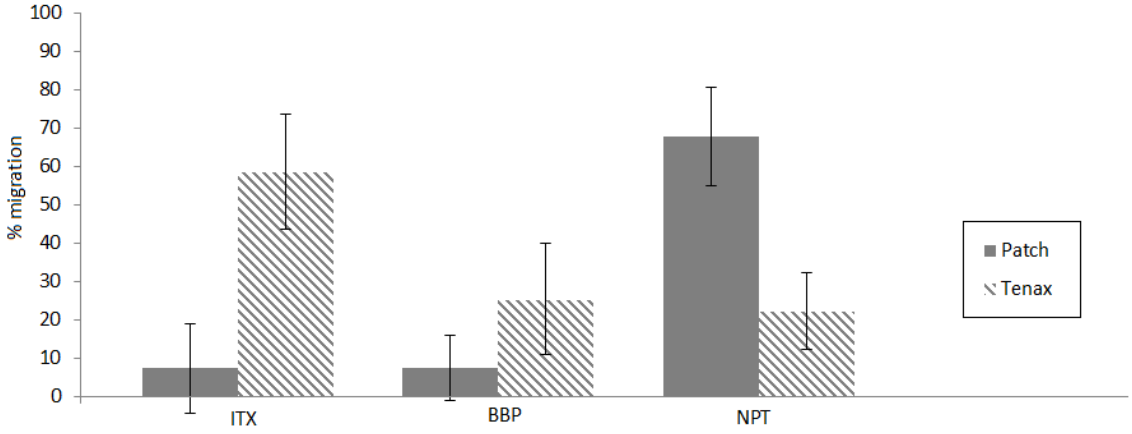

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468 Fig 6