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Study on mass transfer ways of UV printing ink ingredients into foodstuffs

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Abstract

The ITX case (isopropylthioxanthone) showed conclusively that ingredients of UV inks may migrate into packaged foodstuffs. For multi-layered materials like beverage cartons the only way that mass transfer can occur is by the so called set-off effect. In contrast, in the case of rigid plastics like yoghurt cups, two other methods of mass transfer, permeation and gas phase, have to be considered. In cooperation with producers of ink, plastic cups and yoghurt, a project was conducted in order to elucidate the mass transfer of ink ingredients. In addition, the influence of storage time and age of UV lamps on the migration level was examined. The suitability of 50% ethanol as a simulant for yoghurt was tested, as well. ITX was chosen as a model migrant, as it is easily detectable. Furthermore, the migration of two other substances, the photoinitiator 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MTMP) and the amine synergist ethyl-4-(dimethylamino)benzoate (EDAB), which may be used in combination with ITX, was studied. Prior to being filled with yoghurt or 50% ethanol the printed cups were stored under different contact conditions, with and without contact between the inner layer and printed surfaces, in order to distinguish between the possible mass transfer ways. All analyses were performed by means of HPLC-DAD/FLD. It was shown that contamination with ITX and EDAB occurs via set-off and that the degree of migration increases with lamp age and storage time of the unfilled cups. Migration of MTMP was not detectable. The results show, that besides the careful selection of the appropriate raw materials for printing ink, a close monitoring of the process also plays a major role in migration control. In addition, the results proved that 50% ethanol is a suitable simulant for yoghurt.

Keywords

UV printing inks; migration; photoinitiator; mass transfer ways; yoghurt; 50% ethanol; isopropylthioxanthone; 2-methyl-4'-(methylthio)-2-morpholinopropiophenone; ethyl-4-(dimethylamino)benzoate

Introduction

Recently, migration of printing ink and varnish ingredients into foodstuffs has become a focus of interest. This was especially caused by the detection of isopropylthioxanthone (ITX) in baby milk, milk products and cloudy juices packaged in beverage cartons in 2005. But also the latest findings of 4-methylbenzophenone and benzophenone migrating from printed carton packages into cereals highlight that contamination of foodstuffs through printing inks is still a problem. All these packages were printed with ultraviolet (UV) inks which contain monomers and oligomers, pigments, additives and photoinitiators such as ITX. Under UV radiation photoinitiators start the polymerization of monomers and oligomers, thereby causing curing of the ink. UV printing inks and varnishes have a broad range of application in food packaging and are used in all kinds of materials like paper and cartonboard, plastics and multi-layered materials. Rothenbacher et al. 2007 showed that besides multi-layered cartons, also rigid plastic materials like yoghurt cups or plastic foils for sausages are printed with UV inks containing ITX, where contamination of the foodstuffs could take place. Several other studies also deal with the migration of ITX and/or photoinitiators and amine synergists like benzophenone, 4-hydroxybenzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 1-hydroxycyclo-hexyl-1-phenyl ketone, dimethylbenzyl ketal, 2-ethylhexyl-4-dimethylaminobenzoate, 2-methyl-1(4-(methylthio)phenyl)-2-morpholino propan-1-one, ethyl-4-dimethylaminobenzoate from various packaging materials into foodstuffs (Anderson et al. 2003, FSA 2006, MAFF 1995, Sagratini et al. 2008, Sanches-Silva et al. 2008 a+b). For example, migration into foodstuffs of up to 7.3 mg kg^{-1} benzophenone and up to $214 \text{ } \mu\text{g kg}^{-1}$ 2-ethylhexyl-4-dimethylaminobenzoate was shown (Anderson et al. 2003, Sanches-Silva et al. 2008 b).

The reported results in literature conclusively show that ingredients of printing inks and varnishes especially with low molecular weights which are not fully incorporated into the polymer matrix, e.g. photoinitiators and monomers/oligomers like acrylates, may migrate from the packaging into the packaged foodstuffs under certain conditions (Anderson et al. 2003, Papilloud et al. 2002). Contamination of the packed food can take place by three different mass transfer ways: set-off, permeation and gas phase. Set-off may occur during the storage of printed packaging material on reels or in stacks. The internal layer comes into contact with the external layer and ink ingredients can then be transferred to the food contact surface and finally migrate into the foodstuff after packaging. An example is the storing of printed multi-layered material in reels before the production of single beverage cartons. In the case of permeation the ink ingredients migrate from the outside through the packaging material to the inside, if there is no functional barrier like aluminum, e.g. yoghurt cups. Indirect transfer via the gas phase is possible if the substances are (semi-)volatile, e.g. migration of benzophenone and 4-methylbenzophenone into foodstuffs packaged in carton packages with inner plastic bags (EFSA 2009, Hartman et al. 1999, Pastorelli et al. 2008, Rothenbacher et al. 2007, Sanches-Silva et al. 2008 b).

1 For composite materials with an internal aluminum layer, e.g. for beverage cartons, contamination
2 with packaging ink ingredients can only occur by set-off. In contrast, in the case of rigid plastics like
3 yoghurt cups, the two other methods of mass transfer, permeation and gas phase, have to be con-
4 sidered. In cooperation with producers of ink, plastic cups and yoghurt, a project was conducted to
5 elucidate the mass transfer of ink components. In addition, the influence of other factors of the pack-
6 aging production and filling process on the migration level such as the age of the UV lamps during
7 printing and the storage time of the cups before being filled with yoghurt were examined. ITX was
8 chosen as a model migrant, as it can easily be detected and some analytical methods exist. Another
9 photoinitiator, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MTMP), and the amine synergist
10 ethyl-4-(dimethylamino)benzoate (EDAB), which are often used together with ITX were examined, as
11 well. Furthermore, 50% ethanol was used as a migration simulant, according to Council Directive
12 (EEC) No. 1985/572 (EEC 1985) and its amendments.
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24 **Materials and methods**

25 *Chemicals*

26 HPLC-grade acetonitrile and tert-butyl methyl ether, isohexane for gas chromatography, and ethanol
27 absolute and toluene for analysis were purchased from Merck (Darmstadt, Germany). Nanograde
28 acetone was purchased from Mallinckrodt Baker (Griesheim, Germany). Demineralized water was
29 produced by a Milli-Q water purification system (Millipore, Schwalbach, Germany). Standards of 2-
30 isopropylthioxanthone (ITX, CAS 5495-84-1, purity 99%) were purchased from IGM Resins (Krefeld,
31 Germany), 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MTMP, CAS 71868-10-5, purity
32 98%) from Sigma-Aldrich (Steinheim, Germany), ethyl-4-(dimethylamino)benzoate (EDAB, CAS
33 10287-53-3, purity 98%) and thioxanthone (TX, CAS 492-22-8, purity 98.5%) as the internal standard
34 for ITX from Fluka (Sigma-Aldrich, Steinheim, Germany) and 2-ethylhexyl-4-dimethylaminobenzoate
35 (EHDAB, CAS 21245-02-3, purity 98.5%) as the internal standard for EDAB and MTMP from Merck
36 (Darmstadt, Germany). All other chemicals were, at least, of analytical quality. To prepare the 0.1 M
37 citrate phosphate buffer (pH 6.0), 21 g citric acid monohydrate and 14.2 g disodium hydrogen phos-
38 phate were dissolved in approximately 900 ml water. After adjusting to pH 6.0 with concentrated so-
39 dium hydroxide, the solution was diluted to 1000 ml with water. Solutions of analytical standards were
40 prepared in acetonitrile and stored at 4 °C in the dark.
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53 *Samples and migration tests*

54 For all tests, deep drawn polypropylene cups with a capacity of 250 g were used. Printing was per-
55 formed by a dry offset process. To examine the influence of the printing ink on migration, the cups
56 were printed with two different model UV inks, a yellow and a black one, with different quantities of
57 photoinitiators and curing behavior. A banderole was chosen as the print layout to have a nearly fully
58 printed surface as worst case. In addition, the cups were printed using two different UV lamps and
59 reflectors, new and used (ca. 1500 h), and the printed, unfilled cups were stored for two different time
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1 periods, 1 and 21 days, at room temperature. These storage times were chosen according to the in-
2 formation of the plastic cup producer who delivers the printed cups normally just in time or in between
3 three weeks after production. For migration tests, the cups were filled with 250 g yoghurt (fat content
4 ca. 3.8%) and 50% ethanol (v/v), respectively, covered with aluminum foil and stored for 10 days at
5 5 °C. At the end of the storage time the migrates were bottled into glass flasks and stored at -18 °C
6 and 5 °C for yoghurt and ethanol, respectively, prior to analysis. All tests were carried out fivefold. To
7 examine the mass transfer four different methods of cup contact were used. First, printed cups were
8 stacked into each other as in the normal production process, i.e. the inner layer was in partial contact
9 with the printed outer layer (Figure 1a). Second, single printed cups were covered with a piece of
10 aluminum foil, so that the inner layer had no contact with a printed surface and no contamination via
11 the gas phase could occur (Figure 1b). Third, a printed cup was stacked into an unprinted one and the
12 unprinted one was subjected to analysis at end of the storage time (Figure 1c). Fourth, to simulate the
13 possible transfer of ingredients via the gas phase, a printed cup was stacked into an unprinted one in
14 such a way that the surfaces had no contact. This construct was stored in a preserving glass for 10
15 days at 40 °C prior to being filled with 50% ethanol (Figure 1d).
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34 *Preparation of the model ink*

35 Ca. 50 mg of the ink was diluted with 50 ml acetonitrile with the addition of the internal standards. For
36 HPLC analysis this solution was diluted again at 1:100 with acetonitrile.
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40 *Preparation of ink solutions from not cured cups*

41 To determine the quantity of photoinitiators and the amine synergist brought onto the cups with the
42 printing ink, uncured printed cups were taken from the offset printing press. These were put into
43 screw-top jars containing ca. 150 ml acetone, where the ink was washed off of the cups by swiveling
44 the jars around. The solution was subsequently poured into 500 ml volumetric flasks, and the jar and
45 cup were washed several times with acetonitrile. An aliquot with the addition of internal standards was
46 subjected to HPLC analysis.
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53 *Preparation of cup extracts*

54 The cup was cut into small pieces (ca. 1 x 1 cm) and subsequently extracted with 100 ml toluene con-
55 taining internal standards in an ultrasonic bath for 2 h. After filtration of the extract the solvent was
56 evaporated in a rotary evaporator at 77 mbar and 40 °C water bath temperature. The residue was ex-
57 tracted threefold with acetonitrile and filtered through glass wool into a 50 ml volumetric flask. For
58 HPLC analysis, 100 µl and 200 µl of the black and yellow cup extracts, respectively, were filled up to
59 1 ml with acetonitrile.
60

Preparation of yoghurt migrates

Extraction of the yoghurt was performed with acetonitrile, following a liquid-liquid clean-up according to a method published by Rothenbacher et al. 2007, with the following modifications. Instead of 2,4-diethylthioxanthone TX was used as internal standard and EHDAB was added as the second internal standard. Furthermore instead of filter paper glass wool was used due to problems with the internal standard TX in case of filter paper and at the end the solvent was evaporated to dryness under a gentle stream of nitrogen at 60 °C.

To approximately 5 g of homogenized yoghurt, the internal standards and 5 ml 0.1 M citrate phosphate buffer solution (pH 6.0) were added and the sample was extracted by shaking intensively for 1 min. After addition of 30 ml acetonitrile, the mixture was shaken for 10 min and quantitatively filtered through glass wool. Flask and glass wool were rinsed with 10 ml acetonitrile/water (3:1, v/v). After addition of 1.5 g sodium chloride and intensively shaking for 30 s, the filtrate was mixed with 20 ml tert-butyl methyl ether/isohehexane (80:20, v/v) before gently shaking again. The lower aqueous phase was discarded. The organic layer was washed two times with 20 ml water. After addition of 10 ml tert-butyl methyl ether/isohehexane (50:50, v/v) and, if necessary, separation of the aqueous phase, the organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated to dryness under a gentle stream of nitrogen at 60 °C. Finally, the residue was dissolved in 1 ml acetonitrile and directly subjected to HPLC analysis.

Preparation of 50% ethanol migrates

Internal standards were added to approximately 10 g ethanol migrate. Then the solvent was reduced to 1 ml under a gentle steam of nitrogen at 60 °C. After addition of 1 ml acetonitrile, the mixture was shaken extensively for 1 min and then subjected to HPLC analysis.

High performance liquid chromatography with diode array and fluorescence detection (HPLC–DAD/FLD)

Analysis was performed on an Agilent 1100 high performance liquid chromatograph (Agilent, Waldbronn, Germany) equipped with a Luna C18(2) (100 mm; 2 mm I.D.; 3 µm) column (Phenomenex, Aschaffenburg, Germany) coupled with a diode array (260 nm and 310 nm; spectra recorded from 190 to 400 nm) and a fluorescence detector (excitation 264 nm/emission 440 nm) connected in a series. The system was run at 40 °C (stop time 18 min) in gradient mode with demin. water/acetonitrile: 0 min 40% acetonitrile, 12 min 85% acetonitrile, 16 min 100% acetonitrile, 18 min 100% acetonitrile with a post time of 6 min, a flow rate of 0.3 ml/min and an injection volume set to 10 µl.

Limits of detection and quantification, as well as the range of linearity, were determined for MTMP and EDAB by HPLC–DAD analysis, and for ITX by HPLC–FLD analysis using standard solutions in acetonitrile in the absence of matrix interferences, according to DIN standard 32645 (DIN 2008).

Spiking procedure

Recovery tests were conducted by adding standard solutions directly into yoghurt and 50% ethanol, respectively, both of which were proven to be free of the photoinitiators and the amine synergist being investigated. The spiked matrices were shaken briefly and left to stand for 5 min before extraction and concentration, respectively, to enable dispersion. Yoghurt was spiked five times at levels of 10, 30, 50, 70 and 90 $\mu\text{g kg}^{-1}$; 50% ethanol was spiked five times at levels of 10, 20, 40, 60, 80 and 100 $\mu\text{g kg}^{-1}$.

Results and discussion

Limits of detection and quantification for yoghurt

All calculations were carried out by internal standard correction. TX was used for ITX and EHDAB for MTMP and EDAB. ITX was linear in the range of 25 to 500 $\mu\text{g l}^{-1}$ for the FLD-Signal, with a correlation coefficient of 0.9999. These values corresponded to 5 and 100 $\mu\text{g kg}^{-1}$ yoghurt. Limits of detection and quantification were determined at 2 and 13 $\mu\text{g l}^{-1}$ (0.4 and 2.5 $\mu\text{g kg}^{-1}$ yoghurt), respectively, in acetonitrile, according to DIN standard 32 645 (DIN 2008). Linearity could also be shown for MTMP and EDAB for the DAD Signal in the same range as for ITX, with correlation coefficients of 0.9998 and 0.9993. Limits of detection and quantification were determined at 19 and 60 $\mu\text{g l}^{-1}$ (3.8 and 11.9 $\mu\text{g kg}^{-1}$ yoghurt) for MTMP, and 18 and 54 $\mu\text{g l}^{-1}$ (3.5 and 10.7 $\mu\text{g kg}^{-1}$ yoghurt) for EDAB. Confirmation was achieved by comparing the UV spectra of the samples with the standard solutions spectra.

Limits of detection and quantification for 50% ethanol

Calculations for ITX and EDAB were made by internal standard correction. For MTMP the calculations were carried out by external calibration since it was shown that MTMP is not as much lost as EHDAB. All substances showed linearity in the range of 50 to 500 $\mu\text{g l}^{-1}$, corresponding to 10 and 100 $\mu\text{g kg}^{-1}$ 50% ethanol. Correlation coefficients were 0.9998 for ITX, 0.9998 for MTMP and 0.9994 for EDAB. Limits of detection and quantification were determined at 7 and 29 $\mu\text{g l}^{-1}$ (1.4 and 5.8 $\mu\text{g kg}^{-1}$ 50% ethanol) for ITX, 8 and 27 $\mu\text{g l}^{-1}$ (1.6 and 5.4 $\mu\text{g kg}^{-1}$ 50% ethanol) for MTMP and 12 and 41 $\mu\text{g l}^{-1}$ (2.5 and 8.2 $\mu\text{g kg}^{-1}$ 50% ethanol) for EDAB.

Recoveries

Recovery rates for ITX in yoghurt were achieved at between 91 and 93% with a relative standard deviation (RSD) of $\leq 4\%$ (Table I). For MTMP and EDAB the values were 87-93% with a RSD of $\leq 11\%$ and 76-102% with a RSD of $\leq 10\%$, respectively (Table I). Mean recovery rates for the internal standards TX and EHDAB in yoghurt were 86% with a RSD of $\leq 4\%$ and 88% with a RSD of $\leq 6\%$, respectively. Recovery rates for ITX in 50% ethanol were 83-101% with a RSD of $\leq 9\%$, for MTMP 89-93% with a RSD of $\leq 4\%$ and for EDAB 77-97% with a RSD of $\leq 10\%$ (Table II). For the internal standards TX and EHDAB mean recovery rates in 50% ethanol were 66% with a RSD of $\leq 8\%$ and 60% with a

1 RSD of $\leq 18\%$, respectively. It is assumed that the recovery of TX, ITX, EHDAB and EDAB in 50%
2 ethanol is low due to a increased volatility or a decreased solubility under the concentration condi-
3 tions. Nevertheless, the recovery rates of ITX and EDAB, as well as the relative standard derivations,
4 corrected by the internal standards are satisfactory.
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9 [Insert Tables I and II about here]
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11 *Analytical results of the model inks*

12 Table III summarizes the concentrations of the two photoinitiators and the amine synergist in the print-
13 ing inks and their quantity on the yoghurt cups before curing. The comparison of the concentration of
14 the photoinitiators in the yellow and black ink shows that the black contains more of the two photoini-
15 tiators: 1% more ITX and 2.9% more MTMP. This is in order to correct for the UV absorption of the
16 carbon black pigments. Especially MTMP is recommended for a good through curing of printing ink
17 films (RAHN 2005). Regrettably, the analyzed concentrations on the yoghurt cups are not consistent
18 with the determined concentrations in the ink. For instance, in the case of the yellow ink the con-
19 centration in the inks are nearly the same but the concentrations on the yoghurt cups show consider-
20 able fluctuation. A possible cause could be a variation in the production of the model printing inks
21 since the inks for the direct analysis and for the manufacture of the uncured cups were not derived
22 from the same lot. The high concentration of the photoinitiators and of the amine synergist on the
23 black cups can only be explained with a higher color application in order to achieve a sufficient cover-
24 ing of the cups.
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37 [Insert Table III about here]
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40 *Migration tests with yoghurt*

41 Figure 2 shows the results of the ITX migration into yoghurt depending on the different production and
42 storage conditions for the black cups. These can be considered as a worse case, in comparison with
43 the yellow cups, since the concentration of the photoinitiators is higher and the curing is more difficult.
44 Under the chosen contact conditions, no migration was observed in the printed cups whose insides
45 had no contact with a printed surface (all values below the detection limit of $0.4 \mu\text{g kg}^{-1}$). For the cups
46 whose inside had contact with a printed surface the migration of ITX into the yoghurt was nearly the
47 same under equal conditions, i.e. lamp age and storage time. Furthermore, there was no obvious dif-
48 ference between migration levels in cups with a printed surface and those without. These results
49 clearly indicate that the contamination of the yoghurt with ITX occurred by set-off and not by permea-
50 tion in this experiment. In case of the yellow cups the ITX migration showed the same tendency (data
51 not shown). For MTMP all migration values in yoghurt were below the detection limit ($< 3.8 \mu\text{g kg}^{-1}$),
52 independent of printing ink, stacking method, lamp status and storage time (data not shown). This
53 reveals that MTMP is a photoinitiator which does not migrate as easily as ITX. EDAB, in contrast,
54 showed migration behavior similar to ITX (Figure 3, only data for black cups shown). This supports
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1 the conclusion that under the chosen contact conditions the migration in the yoghurt cups occurred
2 via set-off and not by permeation.
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6 The dependency of the migration level of ITX on (a) the printing inks used, (b) lamp age and (c) stor-
7 age time before filling, is depicted in Figure 4. In this experiment the cups were stacked as in the
8 normal production process. In order to evaluate the influence of the three variables (a-c) on the migra-
9 tion of ITX into yoghurt, analysis of variance (ANOVA) for a three-factor experiment was performed. A
10 comparison of the migration levels after 1 and 21 days' storage time under the same conditions, i.e.
11 ink and lamp, shows that in all cases the migration level after 21 days was higher than after 1 day of
12 storage time ($\alpha < 0.001$). The influence of lamp age can be deduced when controlling for ink and stor-
13 age time. It can be seen that migration is higher for the old lamp ($\alpha < 0.001$). With respect to color of
14 ink, the larger quantity of ITX in the black ink starts to play a role as the lamp gets older. For the yel-
15 low and black cups cured with the new UV lamp, the degree of ITX migration is nearly the same when
16 controlling for storage time, while for the old lamp ITX migration is very different (interaction 'lamp
17 age' x 'color of ink', $\alpha < 0.001$). Due to the lower UV intensity of the old lamp, the extent of polymeri-
18 zation and crosslinking decreases and the diffusion of ITX through the polymer network increases.
19 Furthermore, the effect of storage time on ITX migration is stronger on cups cured with the old lamp
20 than on those cured with the new lamp (interaction 'lamp age' x 'storage time', $\alpha < 0.001$). Thus, all
21 three factors have an influence on the migration level. To simplify the result: the older the lamp and
22 the longer the storage time, the greater the degree of ITX migration into the yoghurt.
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35 For EDAB the migration levels in yoghurt were mainly under or only slightly above the limit of quantifi-
36 cation (see Figure 3). Nevertheless, according to the results for ITX, also for EDAB could be shown
37 that the lamp age clearly influences the migration level: it is higher for the old lamp. However, data for
38 the storage time are not consistent with the findings for ITX.
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43 For the producers of cups and food the results above imply that through an accurate process control,
44 in particular lamp age and storage time of the unfilled printed cups, the migration of substances into
45 foodstuffs can be minimized. Another option for minimization could be using a different cup shape, so
46 that no set-off can take place.
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51 [Insert Figures 2-4 about here]
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56 *Comparison of the migration levels into yoghurt and 50% ethanol*

57 As a result of the widespread detection of ITX in various foodstuffs, it was proven that, contrary to
58 Council Directive (EEC) No 1985/572 (EEC 1985) distilled water was not an adequate simulant for
59 milk and milk products. It was replaced by 50% ethanol, which was found to better simulate the fatty
60 character of these products (Commission Directive (EC) No 2007/19 (EC 2007)). The aim of this part

1 of the project was to see whether 50% ethanol would be an adequate simulant for the migration of the
2 two photoinitiators and the amine synergist into yoghurt. Figure 5 illustrates the comparison of the
3 migration of ITX and EDAB into yoghurt with that into 50% ethanol for all cups whose insides had con-
4 tact with printed outsides. In most cases the values for 50% ethanol were above those for yoghurt, i.e.
5 50% ethanol overestimates the migration. This clearly shows that 50% ethanol can be used here as a
6 simulant. Migration of MTMP into 50% ethanol was mainly below either the detection or the quantifica-
7 tion limit, which is in accordance with the findings for yoghurt (data not shown).
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14 [Insert Figure 5 about here]
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17 *Gas phase transfer*

18 Since it was proven that 50% ethanol can be used as a simulant for the migration into yoghurt, this
19 test was only conducted with ethanol. Outside printed cups which had been cured with the old lamp
20 were used, as they can be considered as a worst case in terms of migration. The analytical results in
21 Table IV show that contamination via the gas phase is negligible. Only for MTMP could a value
22 slightly above the detection limit be observed. However, since 50% ethanol overestimates in most
23 cases, it can be concluded that no migration into yoghurt takes place.
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30 [Insert Table IV about here]
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33 *Degree of migration*

34 To determine the degree of migration, the quantities of ITX, MTMP and EDAB on the surface of the
35 cups prior to and after UV irradiation were compared to the quantities migrated into yoghurt (Figures
36 6-8). Here once again the different characteristics of the two photoinitiators and the amine synergist is
37 demonstrated. While, on average, about 22% of the initial quantity of ITX disappeared during the UV
38 curing process, 60% and 54% of MTMP and EDAB, respectively, reacted completely. This means that
39 MTMP and EDAB are more reactive under UV irradiation than ITX. The degree of migration into yo-
40 ghurt was 2% for ITX and about 3% for EDAB while for MTMP no migration could be detected (< 4%)
41 under the chosen conditions.
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50 [Insert Figures 6-8 about here]
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53 **Conclusions**

54 Contamination of yoghurt with the photoinitiator ITX and the amine synergist EDAB occurred under
55 the chosen contact conditions via set-off and not by permeation or by gas phase transfer. Migration
56 of MTMP could not be detected in this study. Exemplary for ITX it was shown that lamp age and stor-
57 age time of the printed cups have an influence on the migration level of the printing ink component:
58 the older the lamp and the longer the storage time, the greater the degree of ITX migration into the
59 yoghurt. However, only 2% and about 3% of the available quantity of ITX and EDAB, respectively, on
60

1 the cups migrated into the yoghurt under the experimental conditions. These results show that by a
2 careful selection of the type of photoinitiators (ITX vs. MTMP) and accurate process control (lamp age
3 and storage time) migration of substances into foodstuffs can be minimized. Another option for mini-
4 mization could be using a different cup shape, so that no set-off can take place. In addition, the suit-
5 ability of 50% ethanol as a simulatant for yoghurt was demonstrated for the three examined substances.
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List of figures with captions for the paper “Study on mass transfer ways of UV printing ink ingredients into foodstuffs”.

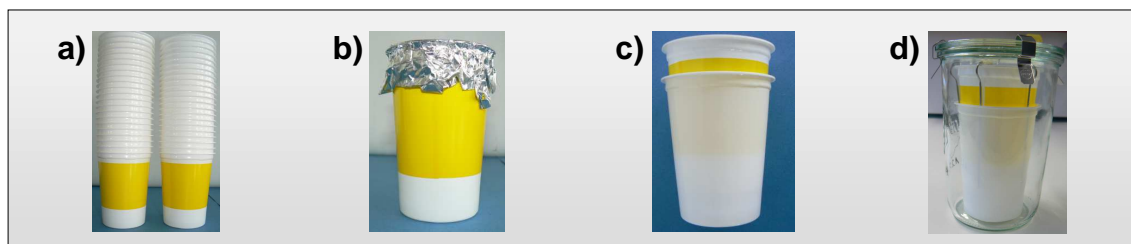


Figure 1. Methods of cup contact

a) printed cups whose insides were in contact with printed outsides (as in normal production process)

b) printed cups whose insides were not in contact with printed outsides

c) unprinted cups whose insides were in contact with printed outsides

d) unprinted cups whose insides were not in direct contact with printed outsides, only via the gas phase

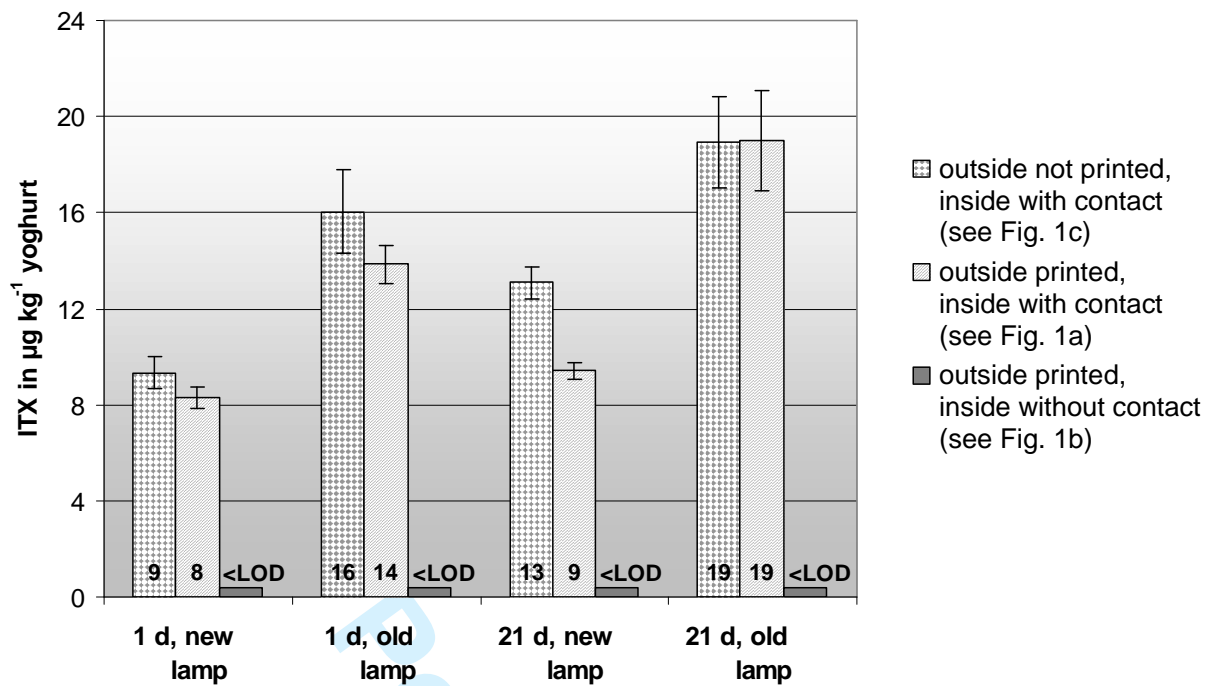


Figure 2. ITX migration into yoghurt filled in black cups (LOD = limit of detection < 0.4 µg kg⁻¹; values corrected by mean recovery rate (92%)).

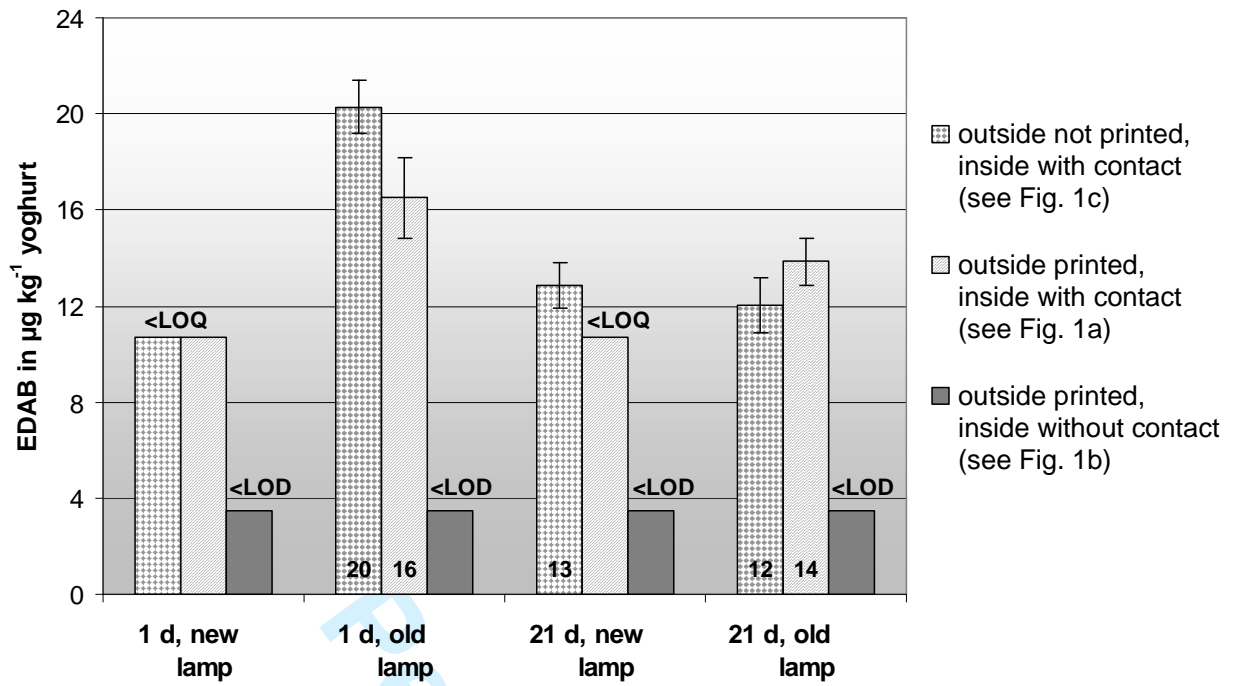


Figure 3. EDAB migration into yoghurt filled in black cups (LOD = limit of detection < 3.5 µg kg⁻¹; LOQ = limit of quantification < 10.7 µg kg⁻¹; values corrected by mean recovery rate (89%)).

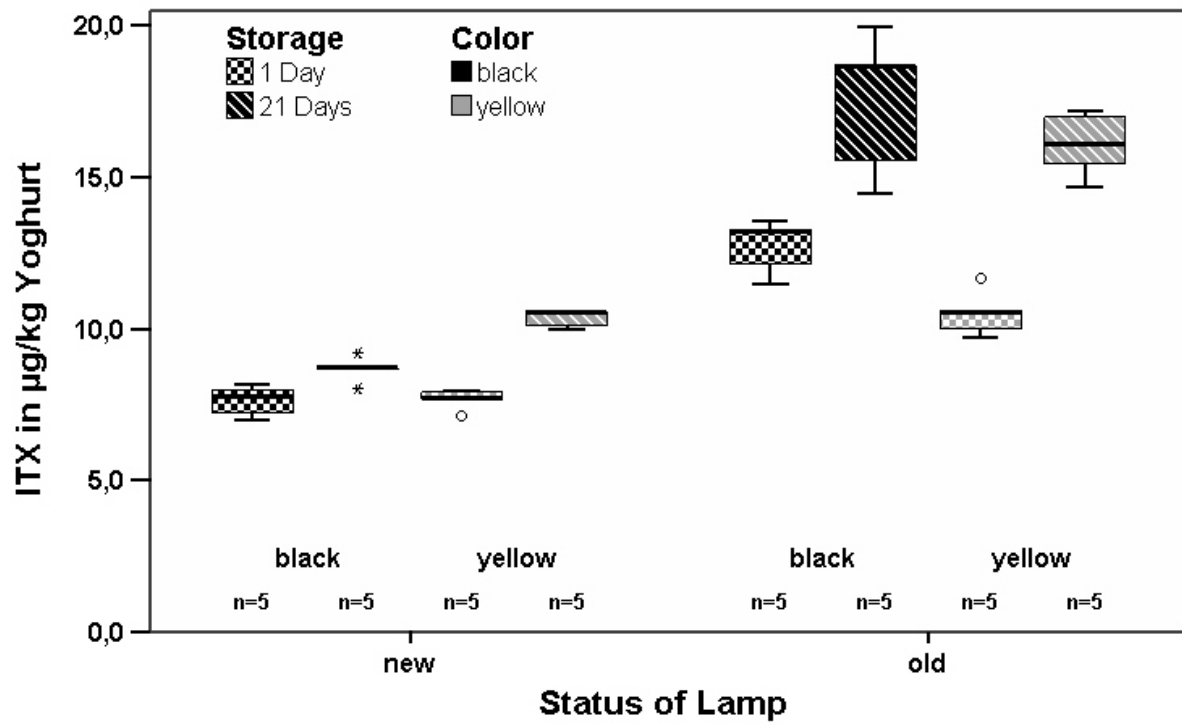


Figure 4. Influence of the lamp age and storage time on the ITX migration level in yoghurt (cups outside printed and inside in contact with printed outsides (see Fig. 1a).

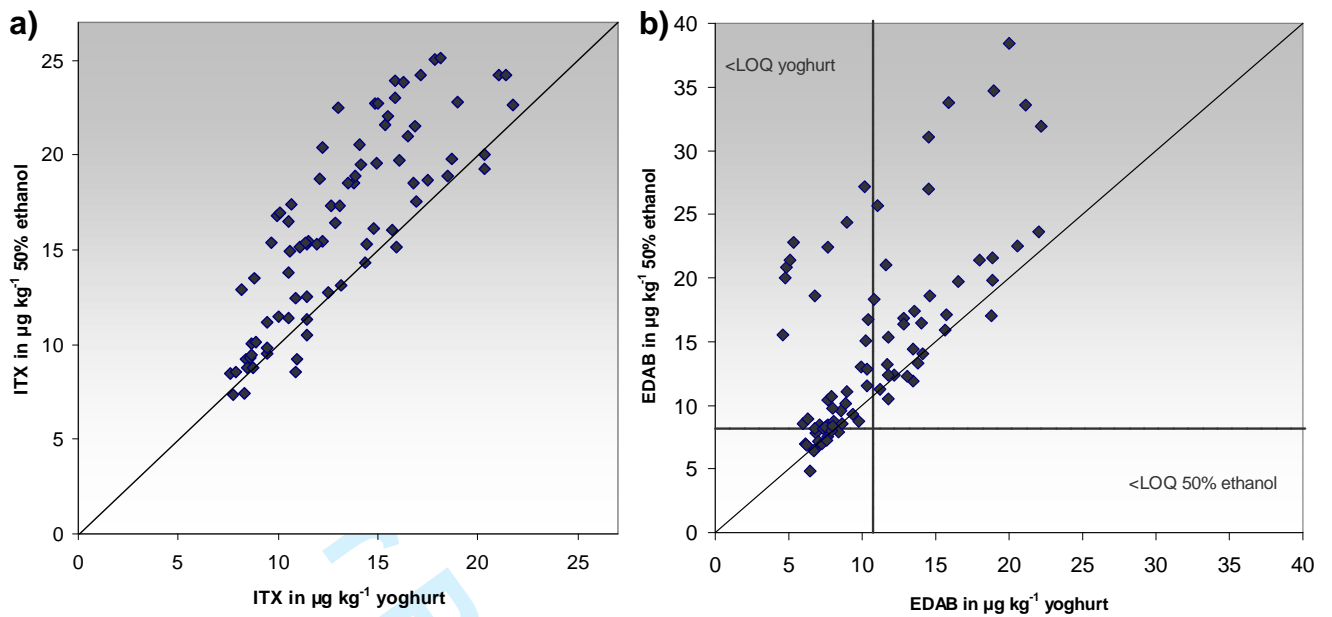


Figure 5. Comparison of the quantities of ITX (a) and EDAB (b) migrated into yoghurt and 50% ethanol (values corrected by mean recovery rates (see Table I+II)). Limits of quantification (LOQ) for EDAB are $10.7 \mu\text{g kg}^{-1}$ for yoghurt and $8.2 \mu\text{g kg}^{-1}$ for 50% ethanol. Analyzed values below the LOQ are only rough estimations of the expected value, but nevertheless support the applicability of 50% ethanol as a simulant.

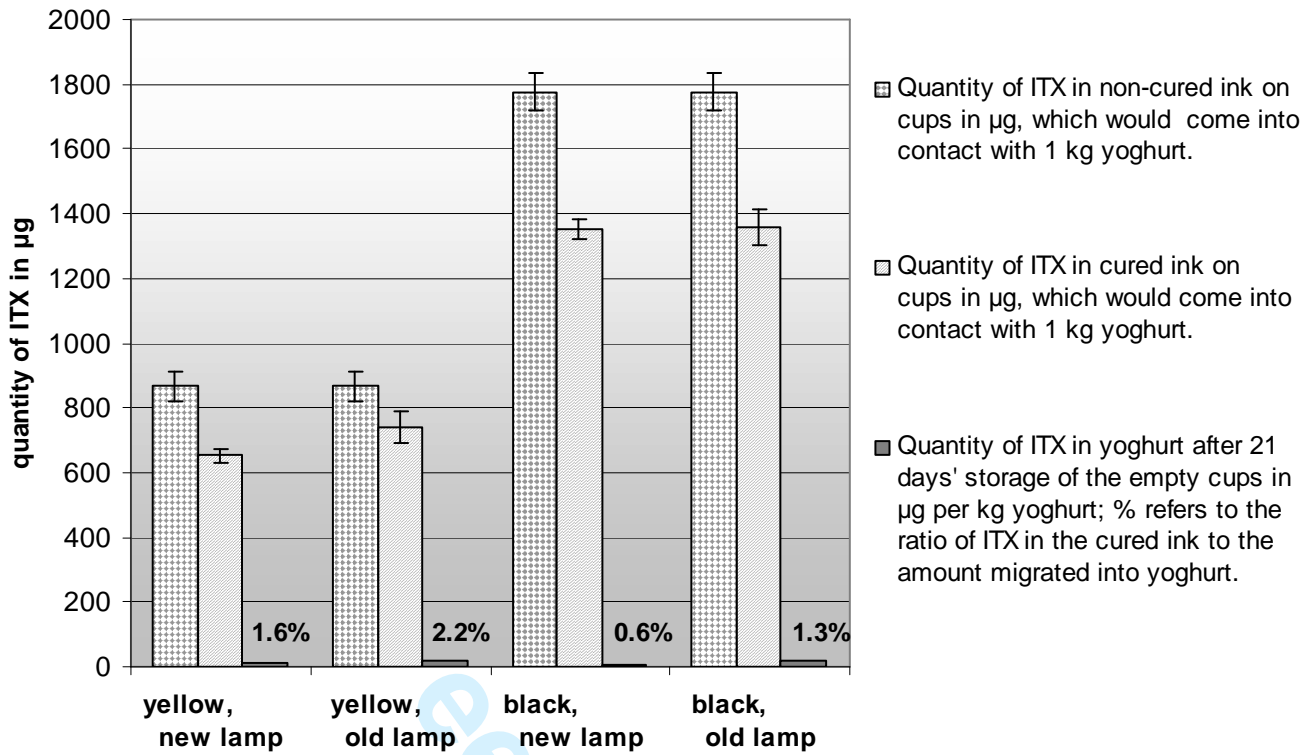


Figure 6. Comparison of the quantity of ITX on the outside of the cups with quantity of ITX migrated into the yoghurt (cups printed outside and insides in contact with printed outsides (see Fig. 1a)).

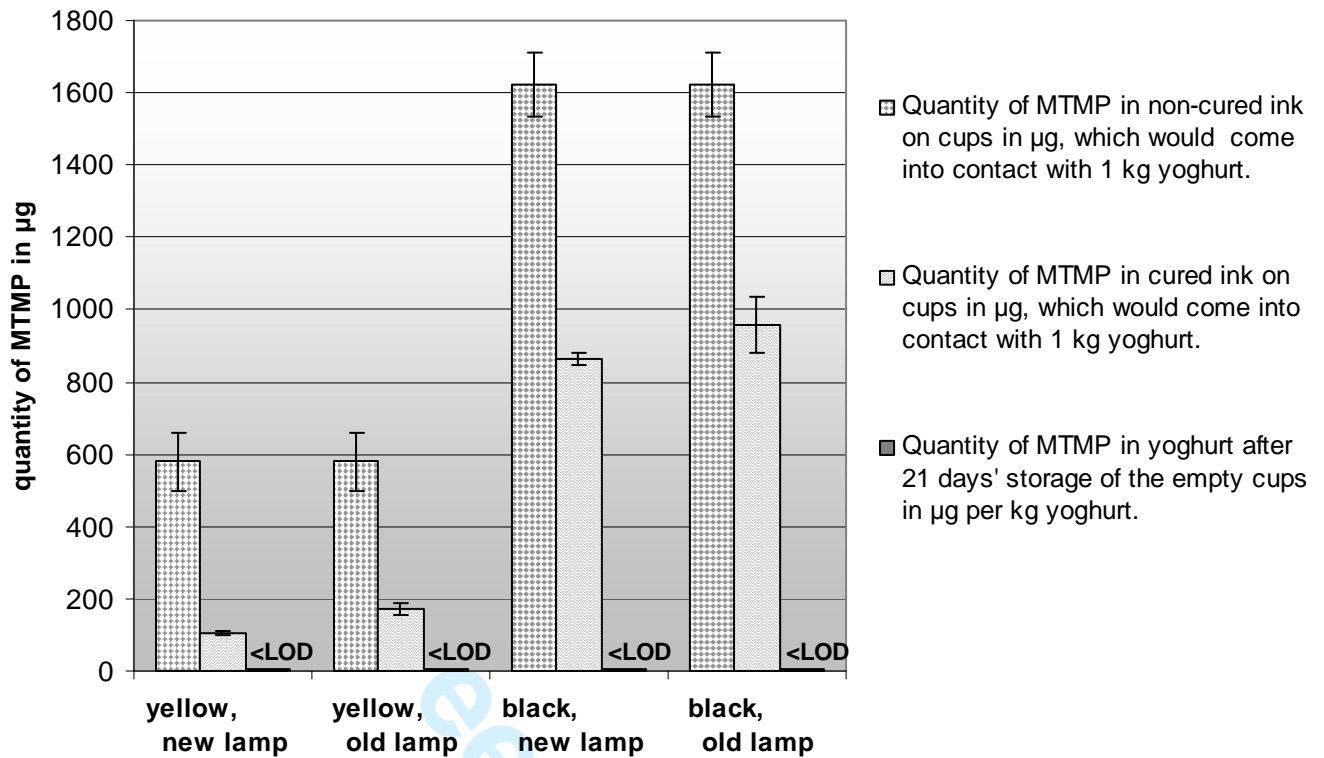
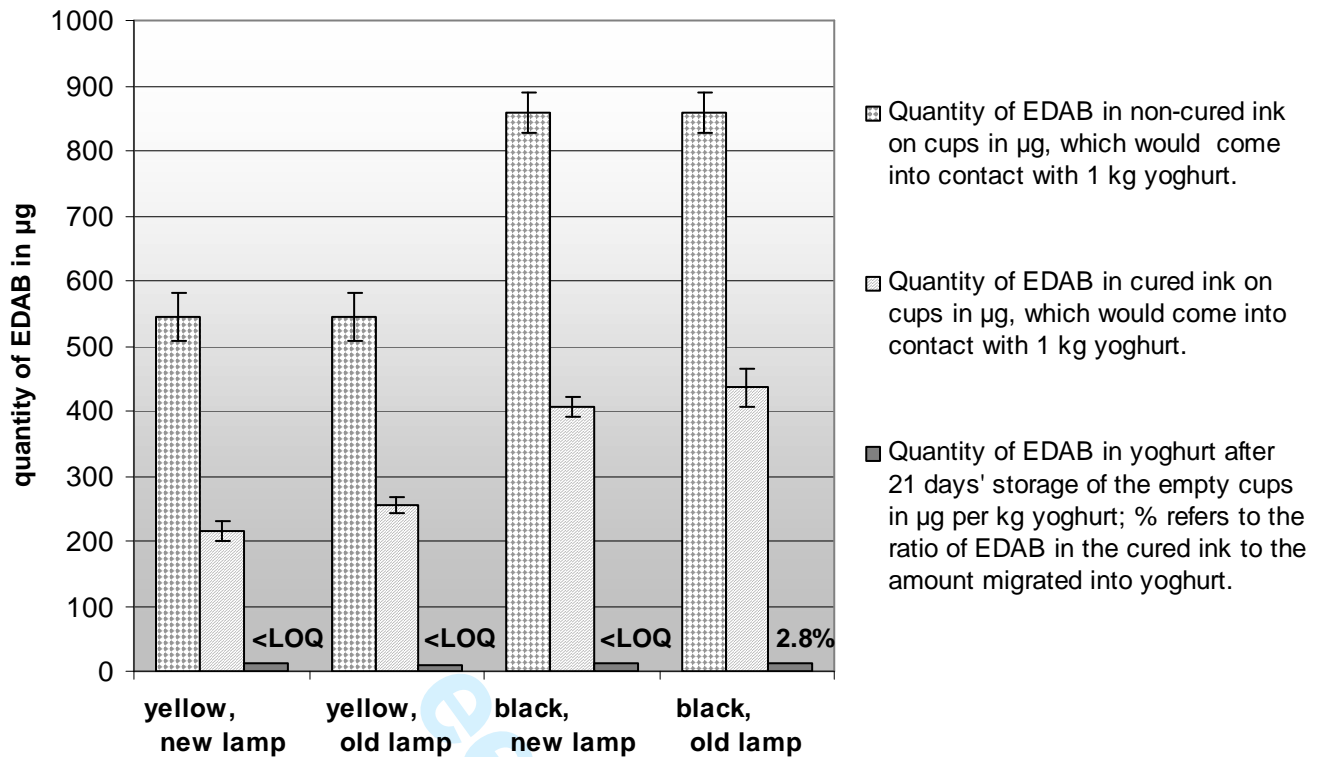


Figure 7. Comparison of the quantity of MTMP on the outside of the cups with quantity of MTMP migrated into the yoghurt (cups printed outside and insides in contact with printed outsides (see Fig. 1a); LOD = limit of detection <math>< 3.8 \mu\text{g kg}^{-1}</math>).



29 Figure 8. Comparison of the quantity of EDAB on the outside of the cups with quantity of EDAB migrated into
30 the yoghurt (cups printed outside and insides in contact with printed outsides (see Fig. 1a); LOQ = limit of quan-
31 tification $< 10.7 \mu\text{g kg}^{-1}$).
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List of tables with captions for the paper “Study on mass transfer ways of UV printing ink ingredients into foodstuffs”.

Table I. Mean recovery rates and relative standard derivations (RSD) for the two photoinitiators and the amine synergist in yoghurt (n = 5). The bracketed data are the absolute mean recovery rates and RSD without internal standard correction.

Fortification levels ($\mu\text{g kg}^{-1}$)	ITX		MTMP		EDAB	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
10	91	2	88	11	102	4
30	93	4	93	3	91	10
50	92	3	87	5	76	4
70	93	2	87	7	91	3
90	91	3	90	6	85	4
Mean	92 <u>(80)</u>	3 <u>(3)</u>	89 <u>(79)</u>	7 <u>(9)</u>	89 <u>(79)</u>	11 <u>(11)</u>

Table II. Mean recovery rates and relative standard derivations (RSD) for the two photoinitiators and the amine synergist in 50% ethanol (n = 5). The bracketed data are the absolute mean recovery rates and RSD without internal standard correction.

Fortification levels ($\mu\text{g kg}^{-1}$)	ITX		MTMP		EDAB	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
10	97	3	89	3	78	6
20	100	1	91	2	77	4
40	101	2	93	4	79	8
60	101	3	92	3	81	9
80	96	8	91	2	84	6
100	83	9	89	3	97	10
Mean	96 <u>(66)</u>	8 <u>(9)</u>	91	3	82 <u>(48)</u>	6 <u>(8)</u>

Table III. Concentrations of the two photoinitiators and the amine synergist in the model printing inks and on yoghurt cups before curing

	Concentration in the ink (%)		Concentration on a yoghurt cup before curing (μg per cup)	
	Yellow	Black	Yellow	Black
ITX	3.3	4.3	217	444
MTMP	3.5	6.4	145	406
EDAB	3.4	2.6	136	215

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Table IV. Gas phase transfer of the two photoinitiators and the amine synergist from cups printed with the old lamp (see Fig. 1d): migration into 50% ethanol (* = limit of detection, # = limit of quantification)

	Migration into 50% ethanol ($\mu\text{g kg}^{-1}$)	
	Yellow cups	Black cups
ITX	< 1.4*	< 1.4*
MTMP	< 1.6*	< 5.4#
EDAB	< 2.5*	< 2.5*

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