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**Investigations on the migration behaviour of silicone moulds in contact with different foodstuffs**

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## Investigations on the migration behaviour of silicone moulds in contact with different foodstuffs

### Abstract

Different foodstuffs were prepared in silicone baking moulds and were analyzed for siloxane migration using a previously developed and validated  $^1\text{H-NMR}$  method. Meat loaf was found to be a critical foodstuff which may significantly exceed the overall migration limit of  $60 \text{ mg kg}^{-1}$  ( $10 \text{ mg sdm}^{-1}$ ) in the first as well as in the third experiment. The highest siloxane migration found in a meat loaf after preparation in a commercial mould was  $177 \text{ mg kg}^{-1}$ . In contrast, milk-based food showed only very low or non-detectable migration ( $< 2.4 \text{ mg kg}^{-1}$ ) even if consisting of higher fat amounts. Similar results were achieved when using 50% ethanol as the official simulant for milk-based products as defined in the Plastics Directive 2007/19/EEC. After solvent extraction of the moulds simulating long term usage, no further migration into the food was detectable, indicating that there is no relevant formation of low molecular weight, potentially migrating siloxanes from the elastomer. During repeated usage, the investigated moulds showed a high uptake of fat during the use of up to  $8.0 \text{ g fat per kg elastomer}$ . The proper tempering of the moulds exhibited a major influence on the migration properties of siloxanes into different foodstuffs. Non-tempered moulds with a high level of volatile organic compounds of 1.1 % were shown to give considerably higher migration than the equivalent tempered moulds.

**Keywords:** Silicones, polydimethylsiloxanes,  $^1\text{H-NMR}$ , migration, foodstuffs

### Introduction

During the last decade flexible silicone moulds have achieved significant market share and are widely used in households as well as in commercial food production. Many advantages such as a non-sticky surface, flexible form and low weight as well as the general low toxicity of migrating polysiloxanes led to a broad acceptance of silicone materials in food contact situations (Wacker 2008). On the other hand, silicone elastomers are not very inert when in contact with fatty or oily foodstuffs and may show rather high migration compared to metal moulds (Forrest and Sidwell 2005, Helling et al. 2009).

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3 Different authors have described the interaction between silicone elastomers and foodstuffs.  
4 Earlier studies focused on the amount of volatile organic compounds as an indicator for  
5 potential high migration (Bannister et al. 1981, Lund et al. 2002). A limit of 0.5 % for the  
6 release of volatile organic compounds was introduced to differ between tempered and non-  
7 tempered materials and to avoid excessive migration (BfR recommendation XV). Later on  
8 gravimetric migration studies using the official substitute simulants for olive oil ethanol  
9 (95%), isooctane and Tenax were performed (Forrest and Sidwell 2005, Meuwly et al. 2005).  
10 These studies only gave a first indication of the different temperature profiles in foodstuffs  
11 and simulants and of the different types of diffusion in simulants compared to foodstuffs such  
12 as cake, which change from nearly liquid to solid during the baking process. Using GC-  
13 techniques, linear and cyclic siloxane oligomers were identified as the main constituents of  
14 the migrate. Meuwly et al. (2005) used Tenax to demonstrate the strong temperature  
15 dependence of siloxane migration, and postulated a formation of low molecular weight  
16 oligomers during repeated heating and thus a regeneration of migrating compounds. GC-MS  
17 was discussed as a suitable method to determine the siloxane migration into complex food  
18 such as pizza. However, only a poor recovery of mid and high molecular weight oligomers  
19 (Meuwly et al. 2007, Helling et al. 2009) could be achieved. Until now the only described  
20 method for a reliable quantification of migrating siloxane oligomers in fatty foodstuffs is the  
21  $^1\text{H-NMR}$  spectroscopy (Helling et al. 2009), despite various other methods having been  
22 described for biological samples such as tissues (Čavić-Vlasak et al. 1996, McCamey et al.  
23 1986, Peters et al. 1995, Kennan et al. 1999, Dorn and Skelly 1994, Biggs et al. 1987).

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42 A  $^1\text{H-NMR}$  spectroscopic method was developed and validated for determination of the  
43 migration of organosiloxanes from silicone materials into cake. It was also demonstrated, that  
44 the overall migrate as determined by gravimetric methods consists to more than 90% of  
45 organosiloxanes. Using this method it was shown that the results of migration experiments in  
46 simulants according to the time and temperature conditions as given in the plastics Directive  
47 (82/711/EEC) differ strongly from the siloxane amounts measured in food (Helling et al.  
48 2009). Estimation of the siloxane content in food is essential for the correct assessment of the  
49 individual moulds. Especially for cake the overall migration limit of  $60 \text{ mg kg}^{-1}$  food or  $10 \text{ mg}$   
50  $\text{sdm}^{-1}$ , as defined in the Resolution ResAP (2004) 5 and in the Swiss legislation EDI, was  
51 respected - even in cases where migration experiments with simulants showed migration  
52 results were above the limit. In contrast to the migration studies carried out on simulants, the  
53 migration value in cake after multiple use of the mould tended to be almost constant,  
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3 indicating different migration behaviour compared to the liquid simulants as well as Tenax®.  
4 Moreover all test cakes baked in differently shaped moulds contained similar siloxane  
5 amounts which may result from a somewhat longer baking time needed in case of larger  
6 moulds, and thus equalizing the more advantageous volume/surface ratio (Helling et al. 2009).  
7 Less surprisingly, migration was found to rise with increasing fat content of a comparable  
8 cake or pizza and also with baking time and temperature (Helling et al. 2009, Meuwly et al.  
9 2007).

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17 Despite the initial data concerning siloxane migration in food, some questions remain: What  
18 could be a worst case scenario for migration into food and are the migration limits still  
19 respected? Are the tempering process and the previously introduced BfR limit for volatile  
20 organic compounds useful and necessary to avoid excessive migration values? Does a  
21 formation of siloxane oligomers happen during repeated and long heating process? How  
22 should silicone moulds for a long term use be assessed from a hygiene point of view? To find  
23 an answer to all these questions and to demonstrate the influence of proper tempering of  
24 silicone materials, more studies on silicone moulds were carried out, using again the <sup>1</sup>H-NMR  
25 spectroscopic method to determine siloxane migration into food. Again, the focus was only on  
26 the overall migration analyzed via the NMR measured siloxane amount which is almost equal  
27 to the overall migration. Meatloaf as well as a milk based dessert (crème brûlée) were chosen  
28 as possible critical foodstuffs and instant baby milk was used for additional testing of teats.  
29 Anthrachinone was introduced as an internal standard to have the opportunity to quantify the  
30 triglyceride content in the multiple used moulds (Malz 2003).  
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## 43 **Materials and Methods**

### 44 *Silicone moulds*

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47 The silicone moulds used from various manufacturers were all bought on the German market  
48 except the moulds for the tempering study, which were provided by Wacker AG, Burghausen  
49 Germany. More detailed investigations concerning different food type experiments were  
50 carried out with a commercial 12 cups muffin silicone mould (volume: 95.8 cm<sup>3</sup>, inner  
51 surface: 0.86 sdm, thickness: 1.0 mm, Pt catalyzed crosslinked) and a box shaped silicone  
52 mould (volume: 1300 cm<sup>3</sup>, inner surface: 5.8 sdm, thickness: 1.2 mm, no information on  
53 crosslinking agents), both bought on the German market as well.  
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3 The tempered / non-tempered moulds had a round shape (volume: 300 cm<sup>3</sup>, inner surface: 2.5  
4 sdm, thickness: 1.5 mm, Pt-catalyst for crosslinking). Teats (tempered and non-tempered, Pt-  
5 catalysed) have been donated by MAPA GmbH (Zeven, Germany).  
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8 All samples were first washed with warm water (45-50°C) and household detergent, as  
9 recommended by the manufacturers.  
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### 12 *Chemicals*

13 All chemicals were obtained from Sigma-Aldrich Germany at analytical grade or higher. All  
14 food ingredients used for the baking studies were of commercial quality.  
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### 18 *Migration into food simulants ethanol 95 % and ethanol 50 %*

19 95 % ethanol and 50 % ethanol were used as substitute simulants. The test conditions  
20 were based on common time-and-temperature conditions used for preparing the relevant  
21 foodstuffs and were selected according to Council Directive 82/711/EEC chapter 3 N<sup>o</sup> 1 and  
22 table 4. As baking moulds are intended for repeated usage, the first, second and third overall  
23 migrate were determined in all cases (Commission Directive 2002/72/EC).  
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32 The tests were carried out as a 2fold determination as described in part 14 of the European  
33 Standard EN 1186:2002: For migration tests with ethanol/water 95/5 or 50/50 (v/v), the intact  
34 samples were brimfully filled with the preheated solvent (60°C). In all cases, only the inside  
35 surface area of the moulds was assumed as contact area. Time measurement was already  
36 started when the samples were put into the oven, although the examination temperature of  
37 60°C was regained later. An exposure time of 75 to 180 min depending of the size of the  
38 moulds was respectively chosen. The solvent was evaporated to determine the overall  
39 migration by the gravimetric standard method (EN 1186:2002).  
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### 49 *Migration into foodstuffs*

50 The studies were performed with creamed cake with 21 % fat (as described previously by  
51 Helling et al. 2009) and meat loaf.  
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#### 54 *Creamed cake, 21 % total fat (Das Backbuch, 1967)*

55 The dough contained 125 g sunflower oil, 100 g egg (homogenized), 125 g sugar, 250 g wheat  
56 flour, 8 g baking powder and 50 g water.  
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#### 59 *Meat loaf, 14 – 19% total fat depending on the meat used*

60 500 g minced meat, 125 g onions, 75 g breadcrumbs, 30 g cheese and 3 g salt were carefully  
mixed.

### *Baking procedure*

The samples were filled to the brim with dough or meat paste and then put into the preheated oven at 175°C. After a suitable baking time (25 min for the small muffin moulds, 35 min for the larger round shaped mould, 40 min for the box shaped mould), the samples were removed from the oven. The cakes or meatloafs (including the leaked water / fat) were removed from the moulds and each one was put into a beaker.

In case of experiments 4, 6 and 8 of the 10 fold baking experiment with meatloaf the leaked sauce (fat and water) was decanted and sauce and meat have been analysed both independently. For the blank samples, the dough or meat paste was filled into a Teflon coated metal baking mould.

### *Crème brûlée (milk-based sweet)*

Ingredients: 395 g cream, 80 g sugar, 70 g egg yolk, 8 g vanilla aromatised sugar.

Vanilla sugar and cream were cooked and added to a mixture of sugar and egg yolk. After intensive mixing, the mixture was poured into the mould and heated in a water bath in an oven at 175°C for 40 min. After half the time of heating the moulds were covered with aluminium foil to avoid excessive browning. After the heating period the moulds were allowed to cool for 2 hours at 7°C.

### *Instant baby milk, 4.0 % fat*

22g commercial instant baby milk powder was dissolved in 135 ml bidistilled water at 50°C.

Teats were incubated in the preheated milk for 6 hours at 40°C. (A longer test time could not be chosen because the instant milk was not stable for a longer time period.)

### *Soxhlet extraction*

The foodstuffs were homogenized and an aliquot (approx. 12 g of the cake, 5 g of the meat loaf and 3 g of the Crème brûlée) was mixed thoroughly with sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) in a mortar (approx. 15 g for cake and meatloaf, approx. 40 g for Crème brûlée and instant milk).

The dry powder was transferred quantitatively into a Soxhlet cartridge and extracted for 6 h with 150 ml diethyl ether in a Soxhlet extractor to isolate the fat matrix, including the siloxanes. At the end of the extraction, the diethyl ether was removed from the round-bottomed flask by distillation. Before and after extraction, the flask was dried repeatedly for

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3 1h at 103°C until constant weight was reached. The weight of the lipid extract was determined  
4 accurately to 0.1 mg.  
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8 Sodium sulphate had to be annealed for 3 h at 550 °C in a muffle furnace prior to use to  
9 remove siloxane impurities left over from manufacturing. Soxhlet cartridges and filter papers  
10 (used to clean the mortar and pestle and for filtration of the CDCl<sub>3</sub> solution, respectively)  
11 were extracted thoroughly in a Soxhlet extractor with diethyl ether prior to use.  
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17 For recovery experiments instead of the minced meat, tartare was mixed with in total 17 %  
18 lard, containing a known amount of polysiloxanes.  
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### 22 *NMR measurement of fat extracts*

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24 For NMR measurement, 400 mg of the extracted fat were dissolved in 800 µl CDCl<sub>3</sub>, filtered  
25 through silicone free paper and transferred into a NMR tube. The <sup>1</sup>H-NMR spectra were  
26 recorded at 500 MHz on a DRX 500 P NMR spectrometer (Bruker). Parameter settings were  
27 as follows: temperature: 22°C, number of scans: 128, spectral width: 10330 Hz, acquisition  
28 time: 3.17 s, resolution: 0.158 Hz per point, frequency sample rotation: 20 Hz, pulse delay: 1  
29 s, pulse angle: 30°. Tetramethylsilane (TMS) was not added as a position standard for the  
30 chemical shift. Instead of this, the solvent signal ( $\delta(\text{CHCl}_3) = 7.25$  ppm in relation to TMS)  
31 was used to ascertain the position of resonance bands.  
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41 Calculation of the siloxane content using the triglyceride signal as an internal standard was  
42 described previously (Helling et al. 2009).  
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### 45 *Determination of the amount of extractable substances of the box shaped mould*

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47 8 g of the silicone elastomer were cut into small pieces (3 x 3 mm) and extracted with diethyl  
48 ether for 10 hours using a soxhlett unit. The residue was dried at 103°C for 2 hours, weighed  
49 and 200 mg sunflower oil was added as an internal standard. The mixture was dissolved in 1  
50 ml CDCl<sub>3</sub> and used for NMR measurement. The amount of extractable dimethyl siloxanes  
51 was 1.9 %.  
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### 57 *Complete extraction of the intact mould*

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59 The box shaped mould was cleaned after the 10fold baking experiment with meatloaf and  
60 filled completely with ethanol. (Diethyl ether was not used to avoid irreversible swelling of



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3 the mould that would probably influence the following migration experiments.) Incubation  
4 was done at 60°C for 24 hours, evaporated ethanol was subsequently refilled. After 24 hours  
5 an aliquot of 50 ml ethanol was concentrated to 5 ml. To 800 µl of this ethanol extract 100 µl  
6 of internal standard anthracinone (5 mg ml<sup>-1</sup> in CDCl<sub>3</sub>) were added and the amount of  
7 siloxane was calculated using the same principle as described for the triglyceride as an  
8 internal standard. Anthracinone was used according to Malz (2003) because of the  
9 incorporated fat in the mould which required the use of another internal standard.  
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17 The mould was incubated for another 24 hours, and an aliquot was taken again to determine  
18 the siloxane content but no additional extraction could be detected. In total 2.08 g dimethyl  
19 siloxanes were extracted with ethanol from the already used mould. The sum of the ethanol  
20 extracted siloxanes added to the sum of all 10 previously performed migration experiments  
21 with meatloaf is in good accordance with the extract determined from a new mould using  
22 diethyl ether.  
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#### 30 *Determination of the incorporated fat of the silicone elastomer*

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32 Approx. 50 cm<sup>2</sup> of the silicone elastomer were cut into small pieces (3 x 3 mm) and extracted  
33 with diethyl ether for 10 hours using a soxhlett unit. The residue was dried at 103°C for 2  
34 hours, weighted and 100 µl of internal standard anthracinone (5 mg ml<sup>-1</sup> in CDCl<sub>3</sub>) were  
35 added. The mixture was dissolved in 1 ml CDCl<sub>3</sub> and used for NMR measurement.  
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37 Calculation of the amount of triglycerides was done using the protons at C1 and C3 of the  
38 glycerin backbone as described for the determination of siloxanes with triglyceride as an  
39 internal standard.  
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#### 46 *Volatile organic compounds*

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48 To determine the amount of volatile organic compounds 10 g of the elastomer were cut into  
49 pieces of 1 x 2 cm and conditioned over dried CaCl<sub>2</sub> for 48 hours. Afterwards 10 g were  
50 weighted with a precision of 0.1 mg into a glass bowl and heated for 4 hours at 200°C,  
51 conditioned in an exsiccator and weighted again. The loss of weight calculated in percent  
52 gives the amount of volatile organic compounds.  
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### 58 **Results and discussion**

### *Meatloaf*

The method used was validated previously for muffins (Helling et al. 2009) but a sufficient recovery rate was demonstrated again for meatloaf as described in the materials and method part and found to be at  $(103.1 \pm 3.4) \%$ . A blank sample of a meatloaf baked in a coated metal mould amounted to 1.9 mg siloxane per kg. This may result from the foodstuffs used as ingredients. Pork meat can be especially contaminated during industrial processing when exposed to a certain amount of siloxane. All equipment and chemicals used were shown to be almost free of siloxane contamination.

In a first experiment the influence of the baking time was investigated for meatloafs. Three pieces of meatloaf were baked in the same cup-sized mould one after another at a temperature of 175°C for 25 or 45 min. Both foodstuffs differed in the grade of browning but were visually appealing and tasty. In the baking series at 25 min migration tended to increase or stay constant at a level between 55 and 92 mg kg<sup>-1</sup>, whereas the migration experiments at 45 min resulted in a much higher but decreasing migration from 177 to 135 mg kg<sup>-1</sup>. Baking time seems not only to influence the level of migration but also the migration behaviour during multiple use.

“[Insert Figure 1 about here]”

An identical mould was used in a previous study for muffins (Helling et al. 2009). The actual experiment with meatloaf resulted in migration values 5 to 18 fold higher compared to those achieved for muffins and cake in the previous study. It is noticeable that the migration values are much higher for meatloaf, although its fat content is somewhat lower. Since it is not typical to prepare meatloaf in a muffin mould, a box shaped mould with a volume of 1300 ml was used for further experiments. To compare the results again with bakery products a creamed cake was baked twice in an identical box shaped mould and gave migration values in the expected range at both 10.0 mg kg<sup>-1</sup> (1.9 mg sdm<sup>-1</sup>). The overall migration limit was exceeded again when preparing a meatloaf in this mould (87.8 mg kg<sup>-1</sup> and 15.2 mg sdm<sup>-1</sup>). The impressive migration compared to cake may be explained by the leaking fat which extracts siloxane oligomers much more effectively than dough and may also affect a swelling of the silicone material.

“[Insert Figure 2 about here]”

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5 A baking sequence was performed to the 10<sup>th</sup> migrate. For experiment 4, 6 and 8 the leaking  
6 fat was separated from the meatloaf and both analysed separately. The amount of siloxane  
7 oligomers in the liquid fat was at 1330, 1088 and 813 mg kg<sup>-1</sup> and therefore about 30-fold  
8 above the amount measured in the meat (41, 40 and 26 mg kg<sup>-1</sup> ).  
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14 A slight decrease in the migration values was observed from the 1<sup>st</sup> to 10<sup>th</sup> migrate. If judged  
15 according to the 3<sup>rd</sup> migrate as claimed for plastics (Commission Directive 2002/72/EC), the  
16 investigated mould exceeded the overall migration limit as defined in the Resolution ResAP  
17 (2004) 5 on silicones used for food contact applications. On the other hand, rejecting the  
18 leaked fat before consuming the food gives a good opportunity to avoid higher contaminated  
19 meals.  
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26 “[Insert Figure 3 about here]”  
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30 Although migration from 1<sup>st</sup> to 10<sup>th</sup> experiment shows a slight tendency to decrease, there are  
31 much greater variations between successive steps. The main reason is the variation in the fat  
32 content of the used meat, which effects the resulting migration quite strongly. This is difficult  
33 to avoid because minced meat standardized in fat was not available.  
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39 Because there was high migration even in the 10<sup>th</sup> experiment, it was of great interest,  
40 whether the migration would decrease to negligible values or siloxane oligomers would arise  
41 during long term use because of thermal and oxidative stress as described by Meuwly et al  
42 (2005).  
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48 Total extraction of a similar mould with diethyl ether resulted in 1.9% or 2.57 g extractable  
49 siloxanes per mould. The sum of all ten migration experiments yielded 460 mg (18 % of the  
50 totally extractable siloxanes). To shorten the ongoing experiment, further baking was stopped  
51 and the previously used mould was filled with ethanol and incubated at 60°C until no further  
52 siloxanes could be extracted. At the end of this extraction the mould became somewhat rough  
53 and frangible and the original blue colour faded out.  
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59 “[Insert Figure 4 about here]”  
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3 At this point a 2fold baking experiment with the same meatloaf recipe was performed to  
4 demonstrate if siloxane chains were cracked and new oligomers were built and released. In  
5 both cases no migration of siloxanes could be detected (limit of detection  $1 \text{ mg kg}^{-1}$ ).  
6 Compared to the migration values during the first 10 baking cycles, it can be concluded that  
7 no significant formation of low molecular weight and freely available siloxanes occurred.  
8 Furthermore it must be pointed out that during the last baking procedure, the mould became  
9 even more frangible and started leaking. No further use was possible. It can be speculated that  
10 low and mid-size cyclic siloxanes act as plasticizers and are of some importance for the  
11 functionality and the elasticity of the polymer. At least if all those oligomers are migrated the  
12 mould might no longer be useable. Significant new formation of oligomers did not occur.  
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### 23 *Milk products*

24 To assess another kind of food, a milk-based dessert (crème brûlée) was prepared. Again the  
25 recovery rate was proven before and found to be lower than for cake and meatloaf but still to  
26 be analytically suitable (88.5 %). The limit of detection for this dessert was determined at  $2.4$   
27  $\text{mg kg}^{-1}$ .  
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33 It has to be mentioned that the time of preparation for crème brûlée in the moulds is clearly  
34 longer than for the other investigated foodstuffs. But due to the high water content, the  
35 preparation procedure (water bath) and the fat in water emulsion type, the temperature at the  
36 contact surface between mould and food will not rise above  $100^\circ\text{C}$ . There are obviously no  
37 significant amounts of free fat despite the pretty high fat content of 27 % in total.  
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43 A 3 fold determination of each of 5 subsequent migration experiments (one after another) was  
44 done. In all cases, except the 3<sup>rd</sup> migrate, the amount of migrated siloxane was below the limit  
45 of detection ( $2.4 \text{ mg kg}^{-1}$ ). For the 3<sup>rd</sup> migrate, the limit of detection was exceeded slightly but  
46 no reliable quantification could be done.  
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52 Similar results were obtained for silicone teats incubated in instant baby milk for 6 hours at  
53  $40^\circ\text{C}$ . Again no migration above the limit of detection of  $2.4 \text{ mg kg}^{-1}$  could be detected using  
54 the described NMR-method.  
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59 Thus, due to the already investigated foodstuffs muffin and cakes, pizza, meat loaf, milk  
60 based sweets and food (Meuwly et al. 2007, Helling et al. 2009) it can be concluded, that

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3 exceeding the overall migration limit may only occur in case of foodstuffs with free available  
4 and liquid fat at temperatures well above 100°C as for instance meatloaf and soufflés / gratin.  
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9 To compare once more the situation in food and simulants, it was investigated whether the  
10 very low migration into milk-based food was adequately simulated by the use of an ethanol /  
11 water mixture (50 %) as a simulant for milk as introduced by Directive 2007/19/EEC.  
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13 7 moulds were analyzed gravimetrically using the substitute simulants 95 % ethanol and 50 %  
14 ethanol. Table 1 lists the results: In some cases migration into 50 % ethanol was not  
15 detectable, in other cases only a low migration compared to ethanol 95 % and tenax was  
16 measured. In contrast to the other simulants for fatty foodstuffs, the migration limit of 10 mg  
17  $\text{sdm}^{-1}$  was never reached or exceeded. This accords strongly with the already described study  
18 with instant milk and milk-based sweets and in this special case confirms the suitability of 50  
19 % ethanol as a simulant.  
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28 “[Insert Table 1 about here]”  
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### 31 *Influence of the tempering process on migration properties*

32 Tempered and the corresponding non-tempered silicone moulds were received from Wacker  
33 Chemie AG (Burghausen, Germany) to demonstrate the influence of the tempering on the  
34 overall migration in both cake and meat loaf.  
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39 The amount of volatile organic compounds is often used as a parameter to check adequate  
40 tempering (RASFF) and is regulated within BfR-recommendation XV to a limit of 0.5 %.  
41 This is based on the demand that volatile compounds should be eliminated before use of the  
42 moulds. Otherwise they could both migrate or evaporate and recondensate on the surface of  
43 the food.  
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50 The non-tempered moulds showed an amount of 1.11 % volatile organic compounds, which is  
51 clearly above the BfR limit, whereas the tempered moulds yielded only very low 0.07 %.  
52 Earlier investigation programs of the official food control authority in Saxony demonstrated  
53 that common silicone moulds have in general volatile organic compounds between 0.2 and 0.4  
54 %.  
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60 “[Insert Figure 5 about here]”

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3 Figure 5 shows a comparison of the tempered and non-tempered moulds for cake and  
4 meatloaf. Surprisingly, the overall migration in creamed cake in the non-tempered mould was  
5 for all 3 migration experiments 8 - 9 fold higher than in the tempered mould, resulting in a  
6 first time measured migration well above  $60 \text{ mg kg}^{-1}$  for cake. In contrast to the previous  
7 studies with tempered forms from the market, a decrease of the migration from 1<sup>st</sup> to 3<sup>rd</sup>  
8 experiment was observed also for creamed cake.  
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16 Preparation of meatloaf in the untempered moulds also resulted in very high migration values  
17 up to  $281 \text{ mg kg}^{-1}$  but only 2.5 to 3 fold higher as measured in the tempered moulds.  
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21 Thus, appropriate tempering seems to be essential to achieve low migration values for silicone  
22 baking moulds. Analyzing the amount of volatile organic compounds according to BfR  
23 recommendation XV can give some reliable hints of what migration values should be  
24 expected. But from this single experiment it cannot be stated whether the actual limit of 0.5 %  
25 for volatile organic compounds is low enough to avoid excessive migration or not. As our  
26 results for 201 moulds from the German market (analyzed from 2004 – 2009) indicate, lower  
27 values than 0.5% could be easily achieved.  
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35 “[Insert Figure 6 about here]”  
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### 37 38 *Enrichment of fat in the silicone material*

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40 In all baking experiments migration of fat originating from the food into the silicone polymer  
41 was observed. After some baking cycles fat sweated out, even on the outside of the moulds  
42 used. Moulds which were not used for a while and stored at room temperature for about six  
43 months exhibited a typical and unpleasant odour of oxidised (rancid) fat. As to be expected,  
44 extensive washing and cleaning could not remove the incorporated fat from the moulds. To  
45 estimate what amount of fat was incorporated into the polymer, diethyl ether extraction and  
46 quantification of the fat using again  $^1\text{H-NMR}$  spectroscopy was done for 2 different moulds,  
47 both after repeated preparation of cake or meat loaf.  
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56 The obtained values were in the range from 3.5 to 5.9 g fat per kg elastomer and did not show  
57 a significant difference between the moulds used for cake or meatloaf. Outside this range and  
58 with the highest fat content, the mould used for the long-term baking experiment with  
59 meatloaf (including total extraction of the siloxanes) the following was found:  $8.0 \text{ g kg}^{-1}$  fat  
60 was measured in the polymer. Because all free available substances were extracted with

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3 ethanol before the baking process, it can be assumed that the polymer had more capacity to  
4 swell and incorporate the leaking fat.  
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9 Values of about 0.5 % free fat in used silicone moulds raises the question of the hygiene of  
10 those moulds. Not only do migrating siloxanes need to be given attention but so should the  
11 migrating fat from previously prepared food. A regular change of moulds used seems  
12 advisable. Due to the typical odour of rancid fat, it should be possible to determine the last  
13 time a mould should be used even without any analytical measurement.  
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## 18 19 **Conclusion**

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22 Different types of food were prepared in silicone moulds of different sizes and shapes. The  
23 main result is that the type of food and availability of fat is the most important criteria for the  
24 amount of migration. The total fat content is only of relevance if similar foodstuffs are  
25 compared. In our studies meatloaf with a total fat content of about 17 % was the worst case in  
26 the field of migration and the only food to exceed the overall migration limit as stated in the  
27 Resolution ResAP (2004) 5 on silicones used for food contact applications or in the Swiss  
28 legislation EDI. In contrast creamed cake with a similar baking time and temperature and with  
29 up to 30 % fat or a milk-based dessert (crème brûlée) with even longer heating time and 27 %  
30 fat showed a much lower or even non detectable migration. This applied both for small and  
31 larger moulds with a very different surface / volume ratio.  
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43 Preparing cake or milk-based desserts as well as the use of silicone teats for baby feeding will  
44 typically not lead to an excessive migration of siloxane oligomers, which exceed the overall  
45 migration limit. On the other hand, it must be concluded that most silicone moulds are not  
46 suitable for preparing meatloaf or gratins with larger portions of free available fat if judged  
47 according to the criteria of the Resolution ResAP (2004) 5. Preparation of roasts, gratins and  
48 similar foodstuffs should not be recommended or even better excluded within the declaration  
49 of silicone moulds. Although the overall migration limit will be exceeded in case of the  
50 preparation of those foodstuffs, no toxicological concern exists so far.  
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59 Testing silicone moulds with simulants such as Tenax® instead of foods does not give a  
60 realistic scenario and is not suitable for judging legal compliance. Tests with simulants  
commonly focus on the total fat content of foodstuffs and suggest reducing factors to

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3 compensate a lower fat content compared to olive oil or simulants. As shown in this and  
4 previous studies, the total fat content is only one of several parameters to look at and the  
5 amount of the overall migration depends strongly on the type of food, the kind of emulsion  
6 and further aspects. As mentioned in Article 3 of the framework Regulation (EC) 1935/2004,  
7 it is important to assess and overweight the amount of migrating substances in food, but not in  
8 simulants (except if it can be shown, that the simulants reflect the situation in the foodstuffs in  
9 a realistic manner).  
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17 In general, migration from silicone elastomers into food seems to be nearly constant in the  
18 beginning but slightly decreasing with ongoing use. No additional formation of low molecular  
19 weight siloxane oligomers during repeated heating could be observed. This stands in contrast  
20 to the previously published work of Meuwly et al (2005) and requires further investigation.  
21 Eventually the fat incorporated during the preparation of food acts as an oxygen scavenger,  
22 and thus prevents oxidative cleavage of the silicone chains during heating. Further studies that  
23 focus on this particular question are already in progress.  
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32 Adequate tempering was shown to be essential to guarantee a low migration for all types of  
33 food. Analyzing the amount of volatile organic compounds can give a good indication of the  
34 need for further migration studies to examine an individual mould.  
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39 Another critical point of silicone moulds compared to the traditional metal coated ones is the  
40 uptake of food originated fat, which can lead in some cases to organoleptic and hygienic  
41 faults. An exchange of odorous moulds is strongly recommended.  
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50 Chemistry) for doing numerous NMR measurements.  
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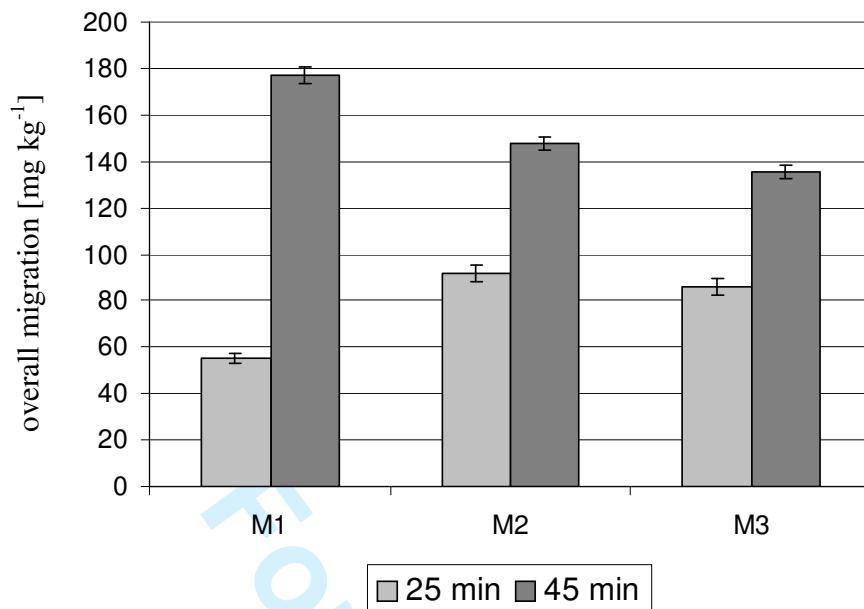
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**Table I.** Determination of the overall migration with ethanol 50% as a simulant for milk compared to ethanol 95% and Tenax as the most common simulants for fatty foodstuffs.

Type	Migration with ethanol 50% [mg dm <sup>-1</sup> ]		Migration with ethanol 95% [mg dm <sup>-1</sup> ]		test conditions for ethanol (t / T)	Migration with Tenax [mg dm <sup>-1</sup> ]		test conditions for Tenax (t / T)
	1st migrate	3rd migrate	1st migrate	3rd migrate		1st migrate	3rd migrate	
large mould for king`s cake A	0,6	0,5	36,5	15,7	180min 60 °C	25,3	15,4	60min 175 °C
large mould for king`s cake B	n.d.	n.d.	30,6	24,9	180min 60 °C	35,0	15,0	60min 175 °C
Madeleine type mould	4,6	3,2	42,0	14,3	75min 60 °C	29,2	15,9	60min 175 °C
muffin mould A (6 cups)	n.d.	n.d.	18,2	22,2	75 min 60 °C	20,0	14,2	25min 175 °C
muffin mould B (6 cups)	3,7	1,2	25,3	8,1	75 min 60 °C	25,8	16,3	25min 175 °C
muffin mould C (6 cups)	1,4	1,3	58,6	25,1	75 min 60 °C	17,5	10,0	25min 175 °C
muffin mould D (8 cups)	n.d.	n.d.	20,4	17,7	75min 60 °C	11,3	5,9	25min 175 °C

n.d. – not detectable (the limit of detection and quantification for the gravimetric method is 0.5 mg dm<sup>-1</sup>).



**Figure 1.** Overall migration in dependence on the baking time of meat loaf prepared in a small round shaped silicone mould. Data given for first (M1), second (M2) and third (M3) baking process. All data are based on a 3fold determination.

**Deleted:** The meat loafs showed different browning but were of good quality.

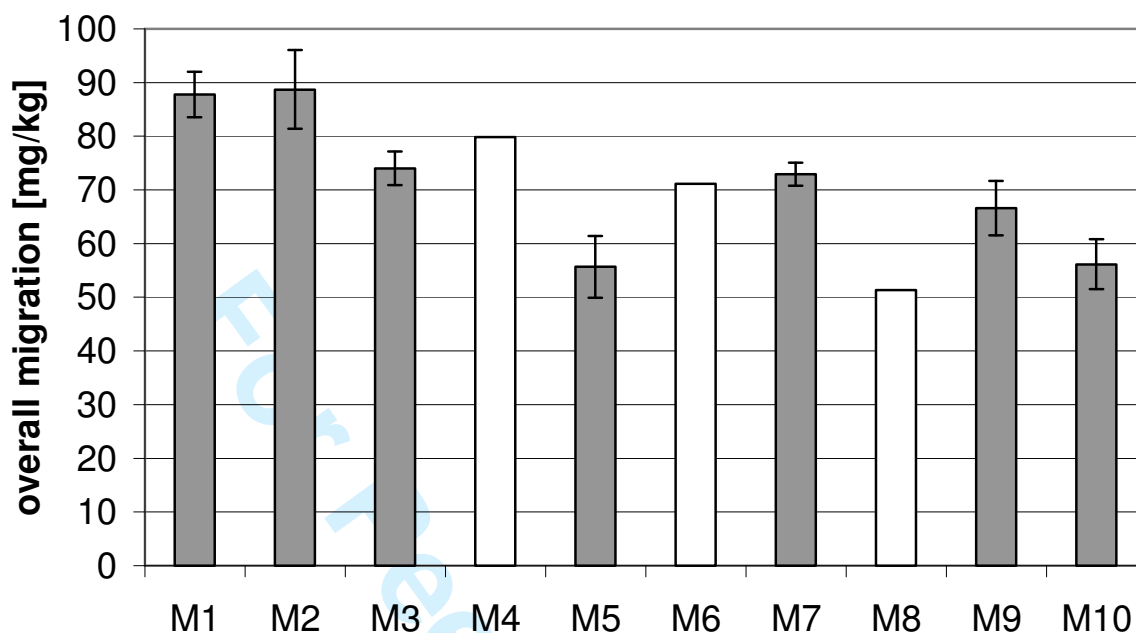


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18 **Figure 2.** Picture of a typical meat loaf prepared in a box shaped silicone mould as done 10  
19 times one after another for repeated migration studies.

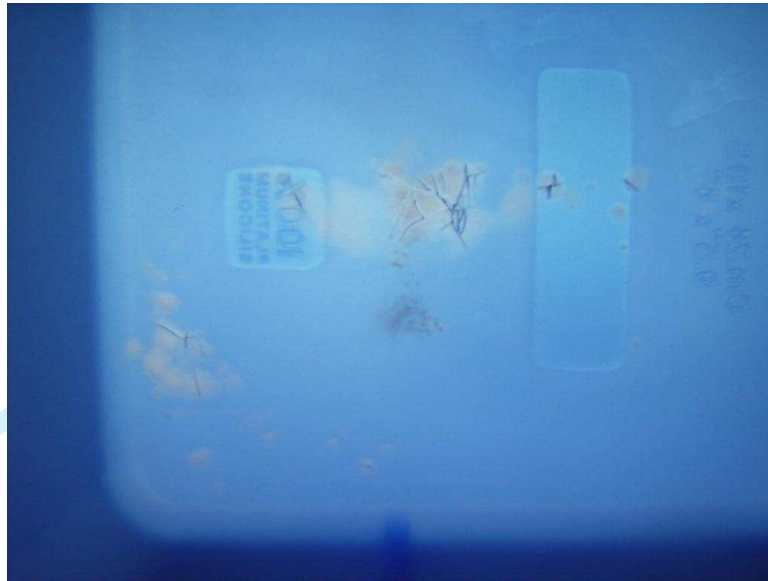
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**Deleted:** Both meat and sauce together or in some cases separated were homogenized and analyzed for migrating polysiloxanes via  $^1\text{H-NMR}$ .

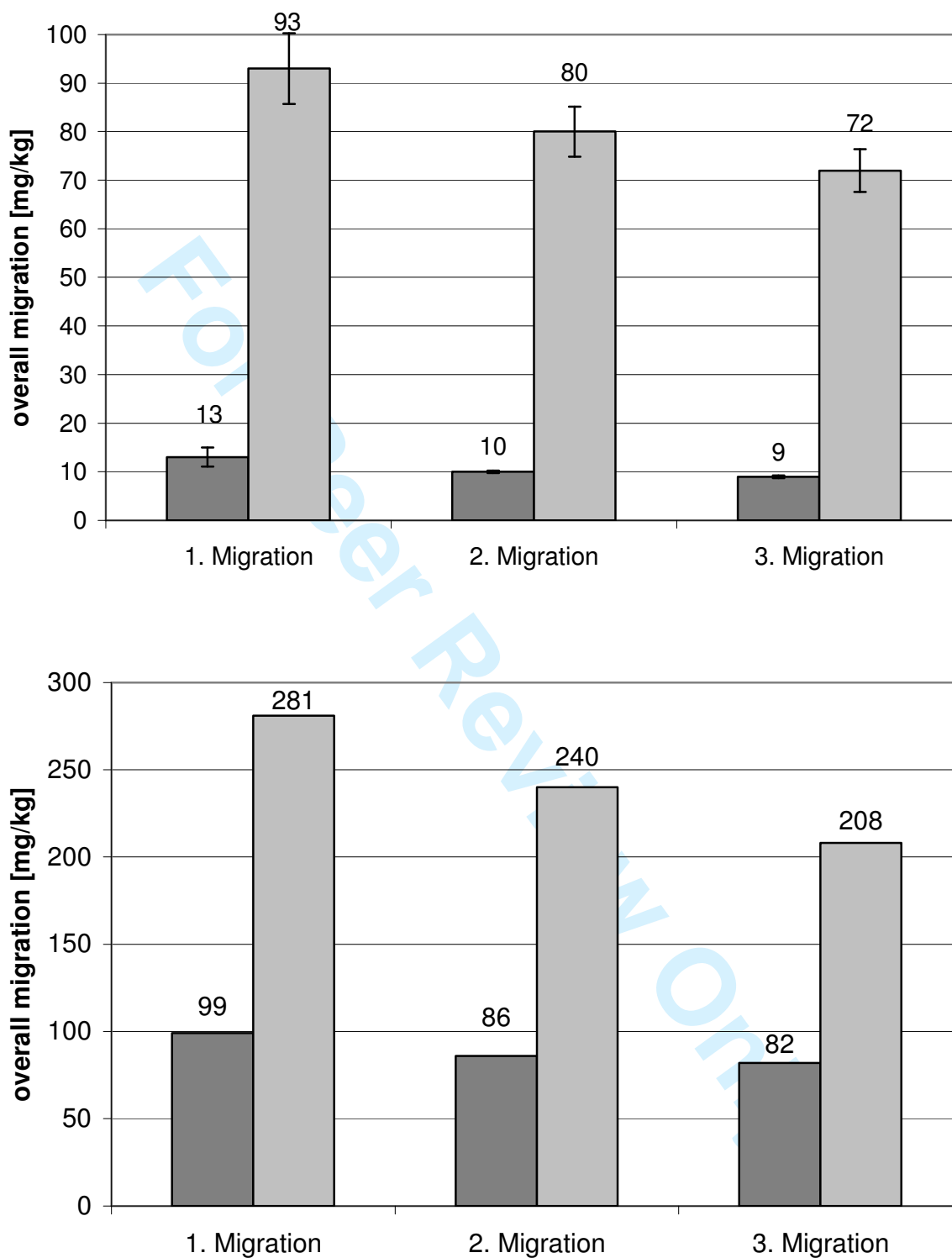




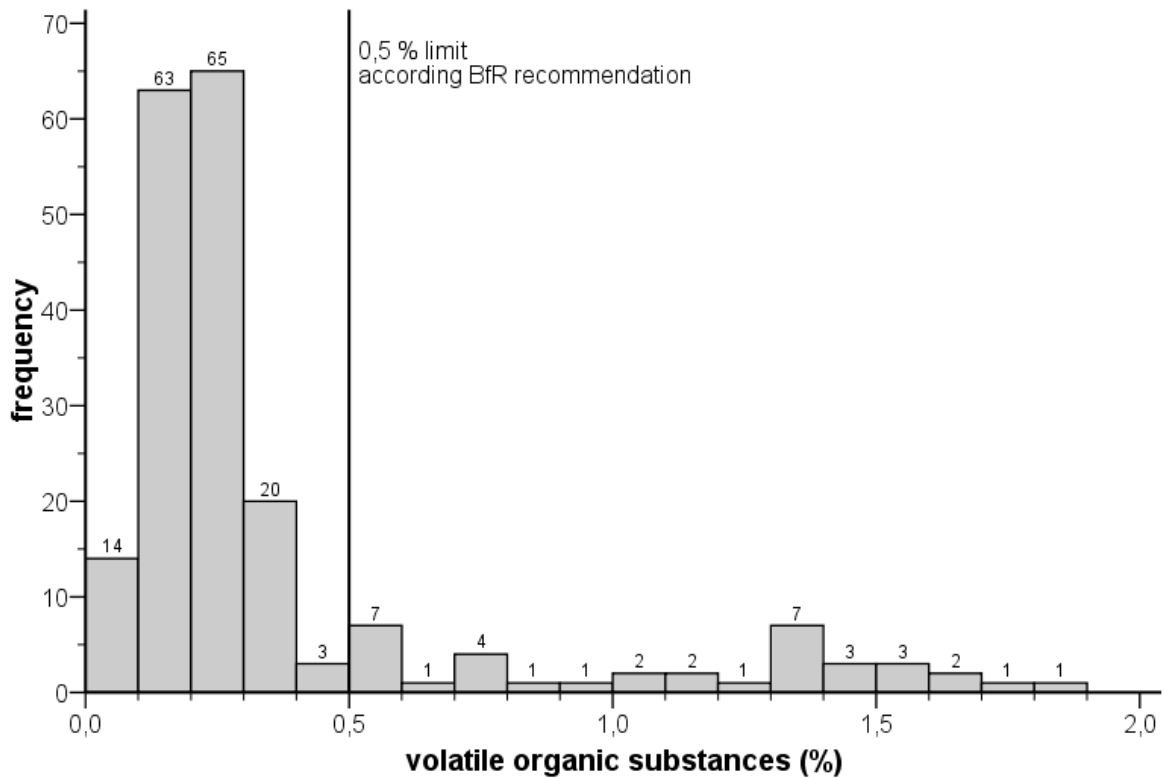
**Figure 3.** Overall migration of meat loaf prepared 10 times (M 1- 10) in a box shaped silicone mould. Differences in the overall migration occurred partly due to differences in the fat content of the meat used (14 – 19 % fat). M 5 was the foodstuffs lowest in fat. For samples M 4, M 6 and M 8 sauce and meat loaf were analyzed separately and the sum used for calculation of the overall migration. For these, 20 g of sauce contained as much siloxanes as approx. 640 g meat loaf. All together 0,46 g siloxanes were extracted with those 10 experiments.



**Figure 4.** Picture of the bottom of the box shaped silicone mould after 10 migration experiments with meat loaf, complete extraction of remaining unbound siloxanes with ethanol and another baking procedure. The elastomers colour faded out, the elastomer itself became rough and frangible. During the next experiment the mould started leaking and could not be used further.



**Figure 5 a)** Migration in creamed cake (21 % fat) **b)** Migration in meat loaf (aprox. 17 % fat); both 1<sup>st</sup> – 3<sup>rd</sup> migration shown: dark columns represent the tempered moulds whereas the lighter columns stand for the untempered moulds



**Figure 6.** Volatile organic compounds in % in silicone elastomers for food contact. Data of 201 samples from the German market, analyzed from the official food control authority of Saxony in the years 2004 - 2009. In total 18% of the samples exceeded the limit of 0.5% as defined in BfR recommendation XV. 68% contained only 0.3% or less volatile organic compounds.