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Table 1: Overview of analysed samples, the number of test specimens for each sample, number of repeated exposures and test conditions.

Sample i.d..	No. of test specimens for each sample	Description of the items tested	No. of repeated exposures	Test conditions	
				(°C)	(hours)
A	3	Plate ^a	3	70	2
B	3	Plate	10	70	2
C	3	Bowl	10	70	2
D	3	Plate	3 ^b	70	2
E	3	Mug	3	70	2
F	1	Jug	3	70	2
G	3	Ladle	3	70	2
H	1	Cup	1	70	2
I	1	Cup	1	70	2
J	1	Cup	1	70	2
K	1	Used cup	1	70	2
L	5	Used cup	1	70	2
K	1	Used cup	1	20	48
L	4	Used cup	1	20	48
M	6	Plate	10	95	0.5

^a Delivered by Food Analysis Performance Assessment Scheme (FAPAS, 2000).

^b One of the test specimens was only analysed once.

Table 2: Migration of formaldehyde after repeated exposures to 3% acetic acid for 2 hours at 70°C.

Melamine migration was below the LOQ except for three exposures (marked test specimens).

Sample id.	Migration of formaldehyde (mg/dm ²) ^a		
	1. test	2. test	3.test
B-1	0.98 ^b	< 0.21	0.50
B-2	0.79	< 0.21	< 0.26
B-3	0.68	< 0.21	0.35
C-1	0.41	< 0.26	< 0.31
C-2	0.22	< 0.26	< 0.31
C-3	0.31	< 0.26	< 0.31
D-1	0.39	< 0.20	< 0.25
D-2	0.91 ^c	0.23	0.50
D-3	0.70	n.a.	n.a.
E-1	1.6	1.0	1.5 ^d
E-2	0.41	0.32	0.35
E-3	0.19	< 0.20	0.32
F	1.2 mg/kg	1.5 mg/kg	1.9 mg/kg
G-1	0.34	< 0.29	< 0.36
G-2	0.23	< 0.29	< 0.36
G-3	0.29	< 0.29	< 0.36
H	< 0.36	n.a.	n.a.
I	< 0.34	n.a.	n.a.
J	< 0.36	n.a.	n.a.

n.a.: not analysed

^a LOQ ranged from 0.14 to 0.36 mg/dm²

^b melamine migration 0.41 mg/dm²

^c melamine migration 0.45 mg/dm²

^d melamine migration 0.28 mg/dm²

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Table 3: Migration of formaldehyde in ten successive tests of three test specimens of sample number B into 3% acetic acid for 2 hours at 70°C.

	Test number									
	1	2	3	4	5	6	7	8	9	10
Test specimen B-1 (mg/dm ²)	0.98	< 0.21	0.50	0.48	< 0.26	0.27	0.26	< 0.26	0.32	<0.26
Test specimen B-2 (mg/dm ²)	0.79	< 0.21	< 0.26	0.27	< 0.26	< 0.26	< 0.26	< 0.26	0.32	0.26
Test specimen B-3 (mg/dm ²)	0.68	< 0.21	0.35	0.44	< 0.26	0.32	< 0.26	< 0.26	0.32	0.27

Table 4: Migration to 3% acetic acid, at two different sets of exposure conditions, of formaldehyde and melamine from melamine-cups K and L used for several years in a day nursery.

Number of test specimens	Test conditions		Migration of formaldehyde (mg/dm ²)	Migration of melamine (mg/dm ²)
	(hours)	(°C)		
6	2	70	0.52, 0.39 and 4 samples < 0.35	0.49, 0.39, 0.35 and 3 samples < 0.25
5	48	20	All samples < 0.35	All samples < 0.25

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Table 5: Migration of formaldehyde and melamine and the molar ratio (CH₂O/MEL ratio) for six test specimens of sample M (a plate) after migration into 3% acetic acid for 30 minutes at 95°C. The number of test specimens (n) where a migration was measured above the LOQ's is given in each case. The number of test specimens (r) with a sufficient migration of both monomers to calculate a CH₂O/MEL ratio is mentioned in each case. Migration measurements were performed after exposure no. 1, 2, 3, 5 and 10.

	Exposure number				
	1	2	3	5	10
Formaldehyde migration ± SD (mg/dm ²)	0.28±0.11 (n = 5)	0.77±0.23 (n = 6)	0.25±0.05 (n = 6)	0.22±0.03 (n = 6)	0.40±0.11 (n = 6)
Melamine migration ± SD (mg/dm ²)	0.34 (n = 1)	0.30±0.06 (n = 5)	-	-	0.34±0.09 (n = 6)
Mean of CH ₂ O/MEL ratio ± SD	5 (r = 1)	12±0.8 (r = 5)	-	-	5±0.3 (r = 6)

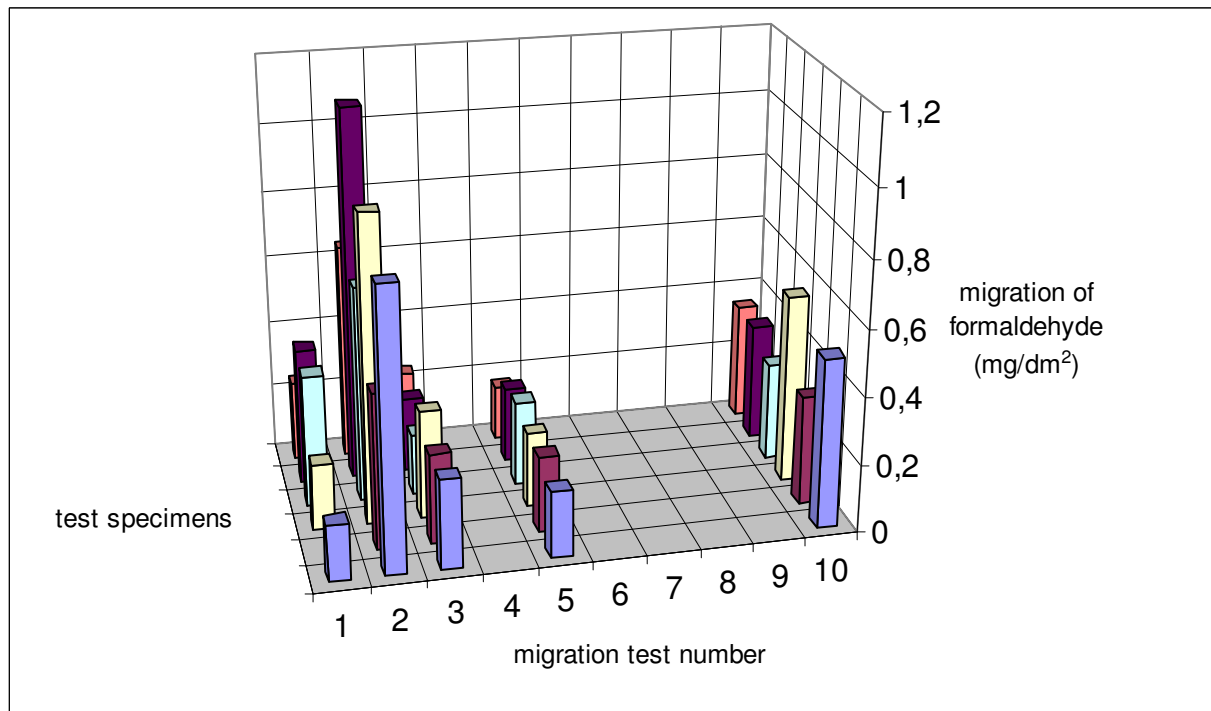


Figure 1: Migration of formaldehyde from 6 individual test specimens of sample M (a plate) after repeated 30 min. exposures to the food simulant 3% acetic acid at 95°C. Migration measurements performed after exposures number 1, 2, 3, 5 and 10.

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Migration of formaldehyde and melamine monomers from kitchen- and tableware made of melamine plastic

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Abstract

Migration of one or both formaldehyde and/or melamine monomers was found from 7 out of 10 tested melamine samples bought on the Danish market. The samples were a bowl, a jug, a mug, a ladle and different cups and plates. No violation of the EU specific migration limits for melamine (30 mg/kg) and formaldehyde (15 mg/kg) was found after three successive exposures to the food stimulant 3% acetic acid, after two hours at 70°C. To investigate the effects of long-term use, migration tests were performed with two types of cups from a day nursery. Furthermore, medium-term use was studied by 10 successive exposures of a plate to 3% acetic acid for 30 min at 95°C. The results indicated that continuous migration of formaldehyde and melamine takes place during the lifetime of these articles. The molar ratio of released formaldehyde to melamine was seen to decrease from 12 to about 5. This indicates that first the migration of residual monomers is most important but in the long term breakdown of the polymer dominates. Two CEN-methods were used to determine the concentration of monomers; a spectrophotometric method for formaldehyde and a UV-HPLC method for melamine.

Keywords:- formaldehyde, melamine, migration testing, kitchen utensils, tableware

Introduction

The thermoset plastic "melamine" is used for manufacturing of a diversity of food contact articles intended for repeated use. Being almost unbreakable, rather inexpensive and dishwasher friendly, articles made from melamine are present in almost every home and day nursery in Denmark. They are used extensively by children in the form of cups and plates, often printed with popular motifs, and kitchenware such as bowls and ladles. In its native form the polymer is a polycondensation product of the monomers formaldehyde and melamine in a proportion of 2:1 on a molar basis, but amino plastics with a slightly different composition also tend to be sold under the common name "melamine".

Residual monomers can be left in the finished plastic item after manufacturing and their migration to the foodstuffs must be in compliance with the current legislation. Formaldehyde and melamine are both compounds on the positive list for monomers and other starting substances of the EU Plastics Directive having specific migration limits (SML's) of 15 and 30 mg/kg of food or food simulant, respectively. When the volume of food contained in the article is below 500 mL (e.g. a cup) or when the surface to volume ratio in actual use cannot be estimated (e.g. a ladle) the limits are expressed in mg/dm². The corresponding limit for formaldehyde is 2.5 mg/dm² and for melamine 5 mg/dm² (EC, 2002).

Despite the widespread use of melamine articles only few researchers have published studies addressing results from migration testing of the monomers. However, a Japanese group observed a general tendency towards higher migration of the monomers when the food or food simulant is acidic and when the test temperature is high (Ishiwata et al., 1986; Sugita et al., 1990). Moreover, some tarnishing of the surface was reported to take place after repeated testing with acidic food

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simulant (Ishiwata et al., 1986), a physical phenomenon often seen on melamine articles that have been used for some years. The deterioration of the surface has inspired monitoring the development of migration of the monomers from cups used in a cafeteria over several years (Ishiwata et al., 1992), and by up to 20 repeated tests of virgin tableware from the Philippines (Martin et al., 1992). The test conditions with respect to time, temperature and food simulant were in all cases different from what is currently prescribed in the EU legislation.

In none of the above mentioned papers violations of the EU SML's were seen although the test conditions chosen in general were quite severe. Recently, a UK-study of 50 different melamine samples reported formaldehyde migration significantly above the SML in 5 of the samples (10%). In that study, migration of formaldehyde was seen from all samples and migration of melamine monomer was seen from 43 samples (always below 36% of SML in the third exposure) (FSA, 2004, Bradley et al., 2005).

A common tendency in the published work concerned with migration testing of melamine articles seems to be a gradual shift in the molar proportion of formaldehyde (CH_2O) to melamine (MEL) during continuous use towards lower CH_2O /MEL-values. This indicates a relatively high amount of unreacted formaldehyde (or its precursors, e.g. hexamethylenetetramine) being present in the newly manufactured item. It seems also clear that the migration of the monomers continues during the lifetime of melamine articles, but ending up with a "stable" migration with a stable CH_2O /MEL-ratio originating from a gradual breakdown of the polymer. A similar report of migration of bisphenol A, the breakdown product of polycarbonate, from reusable polycarbonate articles during long-term use was published recently (Brede et al., 2003).

The present study included testing of a selection of virgin melamine articles bought on the Danish market. Moreover, to acquire more knowledge of the effect of long-term use, migration tests were performed on cups, which had been used for several years in a day nursery. Furthermore, the migration pattern for medium term use was illustrated by 10 repeated tests applied to two types of virgin melamine tableware.

Materials and Methods

Sampling

Ten different brands of new melamine plastic kitchenware and tableware were bought in retail shops. When possible at least three test specimens from each brand was bought. No restrictions on use was prescribed by the manufacturers with the exception of that a few of the items, were marked as not recommended for use in the microwave oven. Additionally, a series of used cups (9 red and 2 white test specimens, all of the same brand) from a day nursery was analysed. An overview of all the analysed samples and number of test specimens (replicates) is presented in Table 1.

[Insert table 1 about here]

For each item, transmission infrared spectra were recorded (1725X FT-IR, Perkin Elmer, Beaconsfield, UK) of a tablet pressed from 1-4 mg pulverized sample and KBr. In this way, it was confirmed that all items in Table 1 were made of melamine plastic. Spectra of samples known to be of melamine plastic and the digitalised Hummel polymer library of IR-spectra were used for the identification. In addition to the samples mentioned in Table 1, other samples were purchased. From the appearance and manufacturers information on the packaging it was not always clear if they were

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made of melamine plastic or not. From the IR-spectra, it was possible to distinguish between samples made of melamine plastics and samples made of other plastics.

Chemicals

Glass distilled water was used for the food simulants. The food simulant 3% acetic acid in water (w/v) was made from acetic acid (JT Baker, 100%). The density of the simulants was conventionally set to 1.0 g cm⁻³. Formaldehyde solution (approx. 38%, exact concentration determined by titration [CEN part23, 2005]), pentan-2,4-dione (99%) and melamine (2,4,6-triamino-1,3,5-triazine, 99%) all from Acros. Chromotropic acid (min. 98.5%), starch solution (pro analysi) and iodine solution (0.05 mol/L titrisol) all from Merck. Acetonitrile (HPLC grade S) from Rathburn. Potassium bromide (spectroscopic grade powder) from Graceby Specac Ltd. Sodium hydroxide (99.0%), sulphoric acid (95-97%), sodium dihydrogen phosphate, H₂O (99%), ammonium acetate (98%), sodium thiosulphate, 5H₂O (99.5%) and hydrochloric acid (min 37%, pro analysi) were all from commercial suppliers. All chemicals were used as received.

Exposure of sample to food simulant

Samples were exposed to the food simulant 3% acetic acid as outlined in Table 1; at 70°C for 2 hours, at 95°C for 30 minutes or at 20°C for 2 days. Each article was filled with pre-warmed food simulant up to 0.5 cm from the rim *i.e.* single sided testing [CEN, 2004]. The ladle (sample identity (i.d.) G) was placed in a glass and covered with simulant up to the beginning of the shaft *i.e.* immersion testing. After each exposure period the simulant was removed and combined with additional two times 10 ml (used for washing the article and an eventual migration cell) before analysis of the formaldehyde and melamine concentration.

For each sample the actual surface area in contact with food simulant was measured and when appropriate the concentration of monomer in the volume of food simulant (mg/kg) was converted into migration per exposed surface unit (mg/dm²). Surface to volume ratios from 4,8 dm²/liter to 8,4 dm² /liter were obtained.

Spectrophotometric determination of formaldehyde

Two spectrophotometric CEN methods [CEN part23, 2005] were used for the determination of formaldehyde; called the main method and the verification method. Principle of the main method: Formaldehyde in the food simulant reacts with chromotropic acid in the presence of sulphuric acid to give a violet reaction product, for which the absorbance is measured at a wavelength of 574 nm with spectrophotometer (Perkin Elmer UV/VIS Lambda 10, Beaconsfield, UK). Each sample and each standard were measured twice and the mean absorbance was used for quantification.

Principle of the verification method: Formaldehyde in the food simulant reacts with pentane-2,4-dione to form 3,5-diacetyl-1,4-dihydrolutidine, which is measured at a wavelength of 410 nm with spectrophotometer.

For more details about the two methods consult the CEN standard [CEN part23, 2005].

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HPLC determination of melamine

A HPLC CEN method [CEN part27, 2005] was used for the determination of melamine, see this method for details. A Hewlett-Packard 1100 series HPLC equipped with an autosampler, diode array detector (DAD) and HP ChemStation (ver A.06.01) was used. Column: Lichrosorb NH2 (Merck) 4.6 x 200 mm, particle size 5 µm. Injection volume 20 µL, mobil phase isocratic 75% Acetonitrile and 25% 5mM phosphate buffer, flow 1 mL/min. The absorption at 230 nm was used for quantification. Further all DAD-spectra were qualitatively checked against the spectrum of the melamine standard (max. absorption 205 nm). Retention time of melamine was 3.9 min.

Quality assurance

In each analytical series, 1-3 reagent blanks in glass bottles were included. The reagent blank from each series was used as zero reference for the spectrophotometer before measuring the formaldehyde content of the samples. Melamine was not observed in any reagent blank.

Quantification was carried out using linear calibration curves ($R^2 > 0.996$) ranging from 5 to 60 mg/L (melamine) and 1.5 to 30 mg/L (formaldehyde). It should be noted that for the main formaldehyde method deviations from linearity were seen several times. In those cases the highest point 30 mg/L was omitted from the calibration curve, the highest point then being 20 mg/L.

The limit of quantification (LOQ) in each series was determined from two independent calibration curves as the lowest concentration where the two curves differed less than 5% as required in the CEN standard. The LOQ for formaldehyde using the main method differed between the different series and was between 0.3 and 2.5 mg/kg. Expressed on the basis of exposed food contact area this

corresponds to LOQs between 0.14 and 0.36 mg/dm². The LOQ for melamine was 1.8 mg/kg corresponding to LOQs between 0.24 and 0.38 mg/dm².

The inter-day repeatability of the formaldehyde determination with the main method was better than 2% as determined from the relative standard deviation (RSD) of 17 repeated measurements of a standard with a concentration of 13.1 mg/kg (close to the SML-value). The inter-day repeatability of the melamine determination was found in the same way to be 4% at a level of 5.6 mg/kg (n=8) and 2% at a level of 22.5 mg/kg (n=11).

To demonstrate the trueness of the formaldehyde determination 6 test specimens were analysed using the verification method as well. A satisfactory agreement was seen between the results obtained with the two methods. The trueness of the melamine determination was demonstrated by participation in a FAPAS proficiency test [FAPAS, 2000]. The average concentration of melamine found in a melamine solution in 3% acetic acid by the 11 participating laboratories was 22.9 mg/kg. We reported a concentration of 23.2 mg/kg, which resulted in a z-score of 0.1.

The FAPAS proficiency round included exposure of a melamine plastic plate (sample A) to 3% acetic acid for 2 hours at 70°C followed by measurements of the two monomers in the food simulant. Unfortunately, due to inhomogeneity of the test material, it was not possible for FAPAS to calculate the participants z-scores for formaldehyde as well as for melamine. For both monomers, our results were in the same order of magnitude as the results from the main part of the other laboratories. The median value for formaldehyde of the 14 participating laboratories was 3.9 mg/kg (minimum and maximum-values: 0.1 and 314.7 mg/kg); our laboratory found 6.2 mg/kg (average test result of three plates, standard deviation 0.6 mg/kg). The median of melamine of the 11

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participating laboratories was 2.2 mg/kg (minimum and maximum-values: <0.5 and 14.6 mg/kg); we found 2.6 mg/kg (average test result of three plates, standard deviation 0.5 mg/kg).

Overall, the two CEN methods performed well in our laboratory.

Results and discussion

Migration testing of all virgin materials was conducted under test conditions selected from the current EU legislation (EEC 1982, EEC 1985) to be the worst foreseeable use in normal Danish household or day nursery. The foreseeable uses of the melamine articles include contact to acidic foods like juice and stewed apples and the official food simulant 3% acetic acid was chosen. Distilled water is the official food simulant for other aqueous foods like milk, tea and coffee but other studies have shown only a limited migration from melamine plastics to this simulant (Ishiwata, 1986 and Sugita, 1990). When the manufacturer does not deliver any restrictions in service temperature in a user instruction, the current EU-legislation, for enforcement purpose, prescribe testing in three successive four hours test with a new portion of simulant at 100°C with the aqueous food simulants. However, in this case it was decided for each item to simulate a situation considered closer to every-day use. In the majority of cases an exposure period of 2 hour at 70°C was selected: These (so called “hot-fill”) test conditions are prescribed in the current legislation when an article is filled with a hot aqueous liquid and the temperature falls below 70°C within 15 min after filling.

An overview of the analysed samples is given in Table 1 as well as the number of repeated exposures and the test conditions applied. In general, no further testing was performed of samples where none of the three test specimens showed any measurable migration in the first test. Three out

of the ten virgin samples (H, I and J) did not show any migration above the LOQ of either formaldehyde or melamine in the first test (LOQ in mg/dm²: 0.4 for formaldehyde and 0.3 for melamine).

Table 2 contains the results from the six samples exposed to three successive tests at 70°C in 2 hours. Only in one test specimen (E-1), the migration of 1.5 mg formaldehyde/dm² to the food simulant in the third test was close to the SML of 2.5 mg/dm². An interesting observation is that the difference in migration behaviour between individual items of the same brand is quite significant: the difference between test specimens with the highest and lowest migration of formaldehyde is about a factor of 8 (sample E-1 and E-3). This phenomenon, possibly connected to small differences in the manufacturing processes, was observed in other studies as well (FSA, 2004 and FAPAS, 2000). The migration of melamine was limited and only in three test portions a migration above the LOQ was measured.

[Insert Table 2 about here]

All three test specimens of two of the samples in Table 2 (B, a plate and C, a bowl) were exposed in seven additional exposure periods with new portions of food simulant, which were all analysed for both monomers. For one of the samples (C) no migration above the LOQ was seen in these additional tests. For another sample (B), some migration of formaldehyde took place into about half of the test portions but the migration of melamine was, with a few exceptions, below the LOQ. The formaldehyde data are presented in Table 3. The highest formaldehyde migration was seen in the first test. After a general trend towards lower migration during the following tests, apparently the migration becomes stable.

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[Insert Table 3 about here]

In a previous study, a significant increase in the migration of monomers to the food simulant was found when the test temperature was increased from 60 through 80 to 95°C (Sugita et al., 1990). The test conditions giving rise to the highest migration in that study were more severe than the “hot fill”-conditions applied for most of the samples in this study. Therefore, it was decided to use the test conditions: 30 min at 95°C for a virgin sample showing a measurable migration.

In Figure 1, the migration of formaldehyde during 10 successive exposures of sample M is illustrated. Migration measurements were applied for all six test specimens analysing simulant portions from exposures number 1, 2, 3, 5 and 10.

[Insert Figure 1 about here]

Although the migration results obtained from the individual test specimens of sample M are quite different, they follows the same pattern as sample B in table 3. Values for the migration of formaldehyde and melamine at exposures 1, 2, 3, 5 and 10 are seen in Table 5.

A general interpretation of the migration pattern could be the following: The main contribution to the migration in the first and second exposure periods is from residual monomers (migration speed could be dependent on the presence of a surface treatment or not). In the following tests, the monomer migration probably primarily comes from the degradation of the polymer. Others have continued testing for up to 20 exposure periods to investigate the degradation pattern (Martin et al., 1992). However, in this study we decided to analyse samples, which had been used for several years

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4 in a day nursery. Such cups have been exposed to acidic foods like juice and also to high
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6 temperature and an acidic environment when frequently cleaned in the dishwasher. The cups were
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8 exposed to the acidic food simulant for only one exposure period at “hot-fill” conditions or one
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10 period at 2 days at 20°C. The results of the testing are presented in Table 4.
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16 [Insert Table 4 about here]
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21 It was obvious from the rather rugged surface that the cups from the day nursery were well used. At
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23 the lower test temperature migration of the monomers was always below the LOQ. At hot-fill
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25 conditions, two of the six test specimens showed a measurable migration of formaldehyde and three
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27 of the test specimens showed a measurable migration of melamine. The levels of formaldehyde
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29 migration from these old cups are comparable to the level seen for other melamine articles after
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31 only 10 exposures (see Table 3).
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37 As mentioned in the introduction, a certain shift in the molar proportion between formaldehyde and
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39 melamine could be expected when the samples are tested (or used) several times. Others have
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41 shown that the molar proportion of formaldehyde to melamine (the CH₂O/MEL-ratio) in repeated
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43 testing of a plate exposed to 4% acetic acid at 95°C in 30 min decreases from about 15 to about 1.8
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45 after 12 exposures (Sugita, 1990). In a recent UK survey, 50 samples were exposed for 3 successive
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47 test periods to 3% acetic acid at 2 hours at 70°C. Calculation of the CH₂O/MEL-ratio in the third test
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49 for 43 of the samples from this study gave a ratio of 14 (range 7-32) (Bradley et. al.2005). In Table
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52 5, the change in CH₂O/MEL-ratio obtained with plate M in the present study is presented.
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58 [Insert Table 5 about here]
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The CH₂O/MEL-ratio of 12 obtained in the 2nd exposure are reasonably in line with the values found by others and a decrease in the ratio can be seen towards the 10th exposure. The lower CH₂O/MEL –value obtained in the first exposure period could be due to a surface treatment (see discussion above).

The CH₂O/MEL-ratio found in the well-used cups from a day nursery was close to 3 for the only test specimen where a calculation was possible. This is in line with or slightly higher than other reported values from long term use studies (Ishiwata et al. 1986, Sugita et al., 1990 and Martin et al. 1992)

Until recently the EU Scientific Committee for Food (SCF) performed evaluations of the health aspect of chemicals migrating from food contact materials, a function which is now transferred to the European Food Safety Agency (EFSA). SCF did evaluate melamine in 1987 and the tolerable daily intake (TDI) for melamine was established at 0.5 mg/kg bodyweight/day (SCF, 1987). This value leads to the current SML-value of 30 mg/kg food using the conventional procedure of the EU-Commission taking in consideration a “standard EU-citizen” with a bodyweight of 60 kg consuming one kg of food per day. However, small infants and young children are a major group of users of melamine tableware and consume several times more food per kg bodyweight than a 60 kg person (Petersen and Lund 2003). Anyway, due to the rather low migration of melamine found in this survey there cannot in all probability be an intake above the tolerable daily intake from the melamine plastics alone.

For formaldehyde, neither SCF nor EFSA did yet agree upon a TDI but the EU-Commission has established a SML of 15 mg/kg food. The SML could be compared to a reported naturally occurring

formaldehyde concentration of 17 mg/kg in apples and of 60 mg/kg in pears (WHO, 1989). Again the migration values from melamine plastics like those found in this study could not alone result in children intake of excessive amounts of formaldehyde.

Conclusions

In general, at low test temperatures, the migration of formaldehyde and melamine was negligible while being measurable at higher test temperatures. Only in one sample a migration of 1.5 mg/dm² of the monomer formaldehyde came close to the specific EU migration limit of 2.5 mg/dm² when exposed to the food simulant 3% acetic acid.

The results of this study confirm what has been demonstrated in the few other studies published; a continuing migration of monomers especially to hot acidic foods takes place from melamine plastics during the whole lifetime of the product. This phenomenon must be attributed to a gradual breakdown of the polymer, which potentially could have adverse effects on the foreseeable users of such articles, namely children. Fortunately, the migration was low compared to the current restrictions for the articles included in this limited study.

It could be worth paying more attention to consumer exposure related to breakdown products from used table and kitchenware, an aspect normally remaining unnoticed in exposure assessments.

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