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**A comparison of the migration of melamine from melamine-formaldehyde plastics
(‘melaware’) into various food simulants and foods themselves**

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ABSTRACT

A variety of melaware articles have been tested for migration of melamine into the food simulant 3% w/v acetic acid, as a benchmark, and into other food simulants, beverages and foods for comparison. The results indicate that the acidity of the food simulant plays a role in promoting migration but not by as much as might have been anticipated, since 3% acetic acid gave migration values about double those obtained using water under the same time and temperature test conditions. In contrast, migration into the fatty food simulant olive oil was not detectable and at least 20-fold lower than with the aqueous food simulants. This was expected given the solubility properties of melamine and the characteristics of the melaware plastic. Migration levels into hot acidic beverages (apple juice, tomato juice, red-fruit tea and black coffee) were rather similar to the acetic acid simulant when the same time and temperature test conditions are used, e.g. 2 hours at 70°C. However, migration levels into foods that were placed hot into melaware articles and then allowed to cool on standing were much lower (6 to 14-times lower) than if pre-heated food was placed into the articles and then maintained (artificially) at that high temperature in the same way that a controlled time-temperature test using simulants would be conducted. This very strong influence of time and especially temperature was manifest in the effects seen of microwave heating of food or beverage in the melaware articles. Here, despite the short duration of hot contact, migration levels were similar to simulants used for longer periods, e.g. 70°C for 2 hours. This is rationalised in terms of the peak temperature achieved on microwave heating, which may exceed 70°C, counterbalancing the shorter time period held hot. There was also evidence that when using melaware utensils in boiling liquids, as for stove-top use of spatulas, the boiling action of circulating food/simulant can have an additional effect in promoting surface erosion, increasing the plastic decomposition and so elevating the melamine release.

KEYWORDS:

Melamine, melaware, melamine-formaldehyde, plastic, chemical migration, simulants, foods, repeated use.

INTRODUCTION

Melamine (2,4,6-triamino-1,3,5-triazine) is a high production volume chemical that can be used in a variety of food contact materials. Melamine gained notoriety following episodes of the adulteration of food and feed with melamine in 2007 and the adulteration of infant milk and other milk products in 2008, described in [WHO, 2009] and [EFSA 2010]. Melamine, which is rich in nitrogen, had been added with a profit motive to give the appearance of increased protein levels. Both episodes led to sickness and even death in pet animals and infants, mainly from kidney damage caused by crystals or stones in the urinary tract.

Melamine used to make food contact materials and articles

Melamine (M) is reacted with other starting substances, mainly formaldehyde (F) and urea, to make a variety of M-F polymers (Figure 1) used in making food contact materials. These include M-F resins used in paper-making, in adhesives and in can coatings, and MF-plastics used to make durable articles such as cups and plates. In the European Union, melamine is approved for use as a monomer and as an additive in plastics and it has a specific migration limit (SML) of 30 mg/kg food or food simulant [EC 2009]. This SML was derived from the tolerable daily intake (TDI) of 0.5 mg/kg bw/day and the default exposure scenario that is used for plastic FCMs of an intake of 1 kg packaged food per day by a 60 kg bw adult [SCF 1986]. There are no specific EU regulations on melamine used in non-plastics but an SML for plastics is often taken as a presumptive standard. Both the WHO [WHO, 2009] and EFSA [EFSA 2010] have revised the TDI downwards to 0.2 mg/kg bw/day and it seems likely that the EU SML will have to be lowered too.

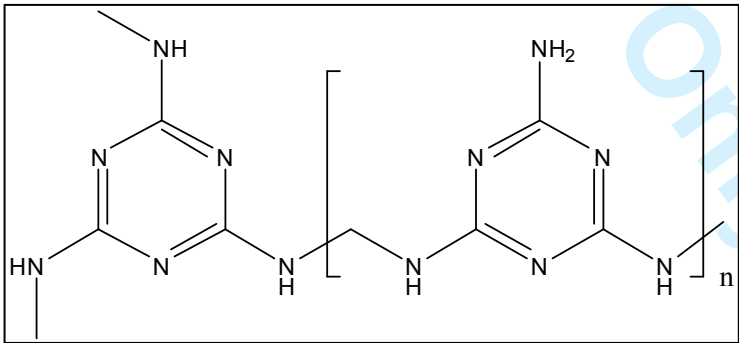


Figure 1: Schematic of a melamine formaldehyde polymer

Melaware articles

The multiple reaction sites of melamine (Figure 1) allow a 3-dimensional polymer matrix to be made into a thermoset M-F plastic. In the recent EFSA risk assessment [EFSA 2010], articles made of this M-F plastic and known colloquially as ‘melaware’ were considered to be

the most important source of exposure to melamine from food contact materials. Typical uses of melaware are children's mugs, bowls, cups, plates and other kitchen utensils. Having some of the attributes of glass or ceramics but being more durable and shatter-proof, and also because it is available with many attractive decorations, melaware could be used on a daily basis for some infants and children. Use by adults is likely to be less frequent, e.g. for picnics, camping and other outdoor-eating occasions. It is important to understand what factors influence migration and the two most recent published studies are outlined below to illustrate some of the characteristics of migration from melaware.

Food simulants used for testing plastics for migration

Most migration testing of melaware has used 3% (w/v) acetic acid as a food simulant (a simplified model food). Simulants intended to mimic the migration from plastics into foods were introduced in the early-1980's [EC 1982] along with the rules for using simulants such as the time and temperature test conditions to be applied [EC 1985]. For melaware articles - as is the case for other plastic articles used at home - the conditions of use by the consumer are not known exactly and so rather severe test conditions are specified in the legislation [EC 1982; 2002]. This includes the requirement to test using three repeated exposures of the melaware to the simulant to try to indicate migration levels expected during the service-life of the article. Since melamine itself is a basic substance and since migration invariably increases with time and temperature test conditions using acetic acid for 2 hours at 70°C or 100°C are typically employed as the 'worst-case' conditions that are foreseeable for use by the consumer. These test conditions are also recommended by the Community Reference Laboratory [JRC 2009].

Migration from melaware into acidic simulants

In a survey of 50 samples on the UK market [Bradley et al, 2005], migration of formaldehyde into acetic acid simulant was problematic but migration of melamine was always well below the SML of 30 mg/kg food. Each sample was tested three times using 3% acetic acid simulant for 2 hours at 70°C. Results from the first, second and third exposures were variable; for some samples the migration levels remained fairly constant but for other samples the migration increased or decreased. There was a high between-specimen variability which seems to be a feature of migration from melaware. Melamine migration was measurable for 43 of the 50 survey samples. The authors took the result for the third exposure as indicative of migration that may be expected during the service life of such repeat-use articles. Migration was in the range 0.3 to 5.4 mg/kg with a mean of 1.6 mg/kg. For some articles the

melaware was observed to degrade during repeated exposure to simulant. The surface of the plastic became pitted and some samples even cracked and fell to pieces.

[Lund and Petersen, 2006] tested 15 different items of kitchenware using 3% acetic acid. Most of the articles were tested for 2 hours at 70°C under repeated-use conditions. Generally, migration of both melamine (M) and formaldehyde (F) was measurable in the first or second test. In the subsequent tests, the migration most frequently dropped below the limit of quantification (ca. 1-2 mg/kg for each substance) but subsequently increased, so that measurable quantities were released in the tenth test. There was no simple relationship between migration levels and the F:M molar ratio changed from 12 down to 5 on repeated testing. They also tested melaware cups that had been used for several years in a day nursery. Migration of melamine into acetic acid simulant was not detectable for 8 of the samples (LoD ca. 1.5 mg/kg) and was ca. 2 to 3 mg/kg for the other 3 samples. They concluded that continuous migration of formaldehyde and melamine takes place during the lifetime of these articles. They concluded also that the M:F molar ratio indicates that, first, the migration of residual monomers is most important, but in the long-term, chemical breakdown of the polymer dominates.

Migration from melaware into foods

In studies performed in Japan and the Philippines both new [Sugita et al., 1990; Martin et al., 1992] and used melaware samples (collected from canteens after several years of use) [Ishiwata et al. 1986] were examined for migration into simulants and foods. The migration of melamine was in the range 0.5 to 2.2 mg/kg food in certain beverages kept hot in cups. The authors noted that migration levels tended to be higher into acid foods or beverages and also were higher at high contact temperatures. It was noted that for some samples the surface of the plastic seemed to be attacked and suffered deterioration such as roughening and tarnishing, especially when a solution of 3% acetic acid was used as a food simulant.

The aims of this work

The vast majority of melamine migration data come from compliance testing using acetic acid as a food simulant under high-temperature test conditions. The few published studies using foods have been limited in scope and are now quite old. It was of interest therefore to conduct some systematic studies of migration into other food simulants and into foods and beverages themselves. The aim was to address 3 areas of enquiry:

- i) how appropriate is 3% acetic acid and how do other food simulants compare.

ii) how important is the choice of time and temperature test conditions in influencing migration levels, especially into foods

iii) to gather more information on between-specimen variability and migration behaviour on repeated-use, to inform on best approaches to testing.

MATERIALS AND METHODS

Melaware articles

Melaware articles were purchased in 2010 from retail outlets in Germany, The Netherlands and the UK. Before testing the samples were cleaned by hand with warm soapy water and dried, as in domestic use. For repeated testing in contact with foods, samples were wiped clean using laboratory tissue paper between exposures. The ratio of contact surface area to the filling volume or filling mass used is given in the results tables. In the case that simulants or beverages were dispensed by volume, the conventional density value of 1 kg/L was used to express the migration results on a mass (kg) basis.

Tests with hot simulants, beverages and foods

Foods and simulants were preheated before the articles were filled. The articles were left uncovered in the experiments where they were allowed to cool on standing, or they were covered with a glass plate or aluminium foil to minimise evaporative losses where they were then heated in an oven for the duration of the migration test. The internal standard ($^{13}\text{C}_3$ -melamine) was added to a portion of the exposed food/simulant after cooling and the concentration of melamine was determined using LC-MS/MS either with a direct dilute-and-shoot approach or using SPE clean-up and then LC-MS/MS.

Microwave heating tests

The food or beverage was placed into the melaware article and then heated in a microwave oven using the conditions described in the tables of results. The filled article was then either left to cool on standing at room temperature or was placed in an oven for a further heating period. The details are given in the tables of results.

Analytical quality control

Each analytical batch contained blank foods or blank food simulants carried through the analytical procedure. Each batch also contained blank samples spiked with known

concentrations of melamine for recovery checks and results were corrected for the analytical recovery.

Analysis by extraction / dilution then direct LC-MS/MS

Juices and simulants. Internal standard $^{13}\text{C}_3$ -melamine was added to a portion of sample (1 mL) to achieve a concentration of 2000 $\mu\text{g/L}$ and then the sample was diluted prior to direct analysis by LC-MS/MS. To give a good measuring range, two dilution regimes were used; (a) dilution 1+9 with acetonitrile (for $\mu\text{g/kg}$ levels); (b) dilution 1+99 with 3% acetic acid followed by 1+9 with acetonitrile (for ca. mg/kg levels). Spiking levels for recovery checks were at 20 or 2000 $\mu\text{g/kg}$ for the two dilution regimes respectively.

Foods (spaghetti with sausages). The food was homogenised using a food blender and internal standard $^{13}\text{C}_3$ -melamine was added to a portion (1 g) to achieve a concentration of 200 $\mu\text{g/kg}$. The sample was extracted with acetonitrile:water (7:3, 50 mL) and, following centrifugation, an aliquot of the supernatant was analysed by LC-MS/MS. Spiking levels for recovery checks were at 20 and 2000 $\mu\text{g/kg}$.

LC-MS/MS analysis. The LC column was an Obelisk N (5 μm , 100Å, 150 x 2.1 mm, SiELC) eluted with 0.25 mL/min 20 mM ammonium acetate + 0.1% (v/v) acetic acid in water (A) and acetonitrile (B) with a gradient A:B of 5:95 up to 50:50 at 5.0 min, held at 50:50 to 9.0 min, equilibrate 6.0 minutes at 0.3 mL/min then reinject. The injection volume was 10 μL and the column was maintained at 30°C. Electrospray ionisation was used in the positive mode with MRM transitions of m/z 127->85 for quantification and 127->68 for confirmation of melamine. The MRM transition of 130->87 was monitored for the labelled internal standard. The LoQ was dependent on the matrix and the dilution regime used.

Analysis by SPE then LC-MS/MS

Sample preparation by SPE. For the acidic beverages in Table 2, sample clean-up used a solid phase extraction cartridge (SPE) packed with a cation-exchange resin (SamplicQ Polymer SCX, 3 mL/60 mg, Agilent). The cartridge was conditioned with 3 mL methanol, equilibrated with 3 mL 1% trichloroacetic acid (TCA) and then 1 mL of sample (simulant or beverage) was loaded after dilution with 2 mL of 1.5% TCA. The cartridge was washed sequentially with 3 mL 1% TCA, 1 mL deionised water, 3 mL methanol and then drawn to dryness. Elution of analyte was with 3 mL of methanol / ammonium hydroxide (made from 4 parts methanol + 1 part 25% ammonium hydroxide solution). The sample was evaporated to

dryness using a centrifugal vacuum evaporator (IR-Dancer, 60°C, 150 mbar, Hettich, Bach, CH) and the residue reconstituted in 1 mL acetonitrile/ammonium hydroxide (95 parts acetonitrile plus 5 parts 25% ammonium hydroxide) with 15 min agitation in an ultrasonic bath.

LC-MS/MS analysis. The LC column was a Luna HILIC (3 µm, 200Å, 150 x 3.0 mm, Phenomenex) eluted with 0.3 mL/min 5 mM ammonium acetate in water (A) and 5 mM ammonium acetate in methanol (B) with a gradient A:B of 5:95 (0-2 min), to 50:50 at 5.7 min (held to 7.0 min), to 5:95 at 8.3 min, equilibrate for 3.2 minutes then reinject. The injection volume was 10 µL and the column was maintained at 40°C. Electrospray ionisation was used in the positive mode with MRM transitions of m/z 127->85 for quantification and 127->68 for confirmation of melamine. The corresponding MRMs of 130->87 and 130->70 were monitored for the labelled internal standard. The LoQ (limit of quantitation) was about 3.5 µg/kg of beverage or food simulant.

RESULTS AND DISCUSSION

Analytical methods used

LC-UV (liquid chromatography with UV detection) has been used in the past for the analysis of samples of low chemical complexity such as the food simulants used in migration testing but LC-UV is not well suited for analysis of foods and beverages. A review of the analytical methods used for melamine and related compounds in foods has been published recently [Tittlemier, 2010] and LC-MS/MS is the method of choice. In this work we have used LC-MS/MS. There were some differences in the exact approach taken, depending on the sample to be analysed and the participating laboratory. The Methods section describes the two basic approaches - LC-MS/MS analysis following extraction/dilution and a more sophisticated approach using SPE clean-up prior to LC-MS/MS. In all cases, isotope-labelled (¹³C₃-) melamine was used as the internal standard. There was significant ion suppression in the case of food analysis because of the limited sample clean-up used and so the injection of co-extractives. By the use of (¹³C₃-) melamine the results are inherently corrected for recovery/suppression. Nevertheless, checks on blanks and analytical recovery were made in each batch. Samples spiked with melamine and carried through the heating procedures used all gave good analytical recovery in the range of 80 to 105% indicating both good analytical recovery and good stability of melamine. The one exception was olive oil where the recovery

was just 16-22%. This was attributed to incompatibility of the olive oil with the spiking solvent used (100 g of simulant was taken and 50 µl of a 1 mg/mL solution of melamine in acetonitrile was added) giving poor mixing, poor homogeneity of the spiked simulant, and possibly physical loss on the glassware.

Migration into acidic and non-acidic simulants

The first set of experiments investigated if 3% acetic acid is an appropriate simulant for foods that are not especially acidic. For this, duplicate specimens of thirteen melaware articles were tested - specimen A with 3% acetic acid and specimen B with water - using the same time and temperature conditions. Results in Table 1 are for the first migration exposure.

A detailed comparison of the results point-by-point is not possible because no information is available on the between-specimen variability, which earlier work on melaware indicates can be considerable. However, a comparison of the ratio of the test result into water to the result for the acidic simulant shows that in 11 of the 13 pairs tested the water result is lower, at an average of 38% of the acid result. Taken as a whole and allowing for possible between-specimen inhomogeneity, it seems that 3% acetic acid generally elicits higher migration values than water, but the effect is not dramatic and seems to be on average a factor of about two.

Migration into acidic simulant and acidic beverages

The second set of experiments investigated how the migration into 5 types of beverage compared with migration into the acidic food simulant 3% acetic acid. For this, six large cups and six small cups were tested each with a first, second and third exposure to one of the 6 test liquids. Again, the results (Table 2) should not be over-interpreted because no information is available on the between-specimen variability - these are results for 3 repeat tests on single specimens. Nevertheless it is informative to calculate the migration into the 5 different foodstuffs as a ratio to the migration into the acid simulant (Table 2). Table 2 also shows the pH values measured for the beverages and simulant.

The results for the apple juice, tomato juice, red-fruit tea and coffee seem to be scattered around the results for the acetic acid simulant - some higher and some lower - giving some evidence that the simulant adequately represents low pH beverages when the same time and

temperature test conditions are used. On the other hand, despite the low pH of the cola, being the closest in pH to the acetic acid simulant, the much lower migration into cola suggests a very strong effect of temperature since the cola alone was applied at room temperature whereas the other tests were at 70°C for 2 hours.

Migration into beverages and into a variety of food simulants

A third set of experiments was conducted to expand the comparison by including some additional food simulants in comparison with migration into beverages. Three types of melaware cups were tested with a variety of simulants and foods. The cups were labelled with the advice not to use in microwave ovens. The instruction was embossed permanently in the plastic. To see what would be the migration if the user ignored such instructions, microwave heating was used where the cup was filled with cold food/simulant, brought to boiling using a microwave oven, and then placed in a 40°C oven for 24 hours. For each migration test listed in Table 3 new cups were used and duplicate cups were each exposed three times to food/simulant. The results for the 1st and 3rd exposures are given in Table 3 as the average of the duplicate specimens. Some of the cups could not withstand microwaving three times and they cracked. These are indicated in the table.

It was noted above that for the beverages tested in Table 2 the low pH of the cola was closest in pH to the acetic acid simulant. The results in Table 3 show a very good agreement between 3% acetic acid and cola under test conditions of 24 hrs at 40°C, with results from the third exposure being 279, 201 and 314 into acetic acid and 359, 144 and 326 µg/kg into cola, for cup brands 1 to 3 respectively. The results also confirmed the strong influence of temperature on migration. Migration into 3% acetic acid, water or 50% ethanol was much higher at 70°C than into any of the food or simulants used at 40°C. Migration after microwaving was comparable to the testing with 3% acetic acid for 2 hours at 70°C. There was no detectable migration into the fatty food simulant olive oil even under test conditions of 2 hours at 70°C. In one set of tests the inner surface of the cups was scratched deliberately before testing with 3% acetic acid and microwave heating. Although the melamine migration was higher for the scratched samples, they did survive the three repeated exposures whereas both of the unscratched samples cracked and could not be tested a third time, so a firm conclusion on the effect of surface damage could not be drawn.

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3 310 To give some indication of the between-specimen variability, since the articles listed in Table
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5 311 3 were tested in duplicate, the ratio of the result for specimen a to specimen b was calculated.
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7 312 For Brand A, all migration tests, first exposure, the b/a ratio was 46-548% with an average of
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9 313 the (greater/smaller) values of 222%. For brand A third exposure the range was 46-235%
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11 314 with an average of 148%. For Brand B the corresponding figures were 36-204% (176%) and
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13 315 12-138% (208%). For Brand C the figures were 31-131% (147%) and 46-235% (148%). So
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15 316 there was an up to 8-fold difference between the results for the a and b duplicate specimens
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17 317 and an average of a nearly 2-fold (178%) difference between the two duplicates.
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19 318
20 319 **Migration into foods and food simulants**

21 320 In the fourth set of experiments, melaware articles were exposed successively to simulant,
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23 321 food, simulant (or vice-versa) to eliminate the problem of between-article variability in the
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25 322 interpretation of results. The articles were a bowl and a cup and they were highly decorated
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27 323 as for child's use. There were instructions on a self-adhesive label and embossed
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29 324 permanently into the plastic advising against microwave use. To investigate what the
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31 325 migration would be if the user ignored such instructions, some microwave heating
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33 326 experiments were conducted too. In the hot fill experiments, the food was pre-heated to
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35 327 boiling (in a glass bowl and using a microwave oven) and then poured into the melaware and
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37 328 left to cool on standing at room temperature for 2 hours. In the microwave heating
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39 329 experiments, the food was heated in the melaware article and then left to stand at room
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41 330 temperature for 2 hours. In this way, the hot-fill tests mimicked using the articles to serve and
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43 331 feed a child whereas the microwaving experiments mimicked using the melaware as
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45 332 cookware (for heating) and then as service-ware for feeding.
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47 333
48 334 The results for melamine migration are shown in Table 4. Migration was constant (Bowl 1)
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50 335 or declined (Cup 1) for the 3 successive exposures to hot simulant. Melamine migrated into
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52 336 spaghetti hoops and sausages when the food was microwave-heated in the bowl and the
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54 337 migration level was broadly similar (and perhaps a little lower) to the simulant results (Bowls
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56 338 2 and 3). It seems likely that, although they will have cooled quickly on standing, the peak
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58 339 temperature achieved on microwaving was well above 70°C (they were brought to the boil)
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60 340 and this higher temperature counterbalances the shorter time held hot compared to the 2 hours
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342 at 70°C simulant tests. In contrast, migration was not measurable when the bowl was filled
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344 with hot food (Bowls 4 and 5) and assuming migration was at the LOD (limit of detection,
given in Table 4), the results were thus at least 8 to 14-times lower than the simulant results.

Similarly, melamine migrated into apple juice when microwave-heated to boiling in the cup (Cups 2 and 3) and again at levels comparable (and perhaps a little lower) to the simulant results. When the cup was hot-filled with boiling apple juice, however, migration of melamine was only detectable from the first exposure (Cup 5) and otherwise, using the LOD, the migration was about 6-times lower than into simulant.

Oven and stove-top tests using 3% acetic acid

In the fifth and final set of experiments conducted, because it can be argued that the majority of melamine articles are labelled against microwave heating, it was interesting to see how migration was affected by static high temperature tests compare to stove-top boiling experiments. A small number of kitchen utensils were tested for migration into 3% acetic acid. In the oven tests, the articles were placed into a beaker and brought into contact with 3 % acetic acid preheated to 100°C and then the beaker was placed into an oven set at 100°C. The beaker was not covered because it was not intended to expose the handles of the utensils, and so the handles protruded. The temperature of the simulant (measured using a thermocouple) was 94°C after 30 min and was 91°C after 60 min and this is attributed to evaporative cooling. When duplicate specimens of the same samples were tested by immersion in 3% acetic acid heated to a constant boil on a stove top (hot plate) the migration of melamine was dramatically higher (Table 5). In the first exposure of spatula A the migration was 85 µg/kg heated in the oven for 30 min but migration was 36-times higher at 3030 µg/kg when the duplicate specimen was heated to constant boiling for 30 minutes using a hot plate. A second brand of spatula was tested with three repeat exposures and in the oven the migration was constant at 50, 50 and 50 µg/kg but was 2770, 4810 and 9420 µg/kg with boiling (Table 5), this being 55 to 188-times higher. A third brand was tested in the oven but this time for 60 minutes. The migration was already much higher at 1120, 2160 and 5370 µg/kg for the three successive oven exposures and migration was again significantly higher (but not so dramatically) at 3370, 7530 and 14430 µg/kg when boiled for 30 minutes.

Boiling tests were also conducted on a further 10 brands of spatulas and on 5 brands of spoons and 2 brands of ladle. The results are not shown because no oven testing was done for comparison but the test results were all in a similar range as the stove-top tests reported in Table 5 and this indicates that the samples reported in Table 5 were not atypical.

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3 377 Although the number of experiments is limited and again the between-specimen variability
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5 378 may have some effect, these results suggest three factors come into play. First, they confirm
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7 379 the strong influence of temperature. Classical migration by diffusion does of course always
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9 380 show a dependency on temperature but here, a chemical degradation of the polymer is
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11 381 involved which has a strong temperature-dependency related to the activation energy of the
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13 382 process. Second, they suggest that once the surface starts to be eroded, the decomposition of
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15 383 the plastic leading to melamine release can increase exponentially with time - it was observed
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17 384 that the surface of the melaware samples was attacked in most cases. Third, linked to the
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19 385 surface erosion, it seems likely that the convection currents generated by boiling may help to
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21 386 further accelerate the surface erosion by bringing fresh simulant to the plastic surface and
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23 387 carrying away the decomposition products. By comparison, static heating in an oven could
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25 388 allow a boundary layer to form that may put a partial brake onto the otherwise accelerating
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27 389 process.

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29
30 391 **CONCLUSIONS ON MIGRATION OF MELAMINE FROM MELAWARE**

31 392
32 393 Considering the migration of melamine from melaware, the chemical stability of the plastic
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34 394 must be considered since degradation by e.g. hydrolysis may occur, especially in high
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36 395 temperature applications and possibly accelerated by acid. This was one conclusion from
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38 396 Lund and Peterson 2006 that the migration of residual monomers is important initially, but in
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40 397 the long-term, chemical breakdown of the polymer dominates.

41 398
42 399 *Nature of the food/simulant.* The results found here suggest that the acidity of the food
43
44 400 simulant does play a role in promoting migration but not as large as might have been
45
46 401 anticipated. 3% Acetic acid generally causes higher migration values than water but only by
47
48 402 about a factor of about two. In contrast, migration into the fatty food simulant olive oil was
49
50 403 very much lower than into the aqueous food simulants, being not detectable and at least 20-
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52 404 fold lower. Considering acidic beverages (cola, apple juice, tomato juice, red-fruit tea and
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54 405 coffee) the results were rather similar to the acetic acid simulant when the same time and
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56 406 temperature test conditions are used.

57 407
58 408 *Time and temperature of contact.* The results do illustrate that the most important effect is
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60 409 that of time and temperature. Thus, despite the low pH of cola, migration was very low when
410 410 room temperature test conditions were used. Similarly, migration levels into foods that were

placed hot into melaware articles and then allowed to cool on standing were much lower (6 to 14-times lower) than if pre-heated food was placed in the articles and then maintained at that high temperature using an oven in the same way that a controlled time-temperature test using simulants would be conducted. If the simulant was held boiling, as would be the case for utensils used at high temperature on a stove-top, the action of circulating food/simulant can have an additional effect in promoting surface erosion and giving high melamine release.

Microwave heating. Finally, the effect of microwave heating was the most dramatic, where, despite the short time of hot contact, migration levels were comparable to simulants used for longer periods. It seems likely that although they will have cooled quickly on standing, the peak temperature achieved on microwaving counterbalances the shorter time period held hot.

The need for well-described test procedures

Visual inspection of melaware articles in the shops reveals that some have a glossy and seemingly hard surface whilst others have a matt appearance that seems to be softer. Some brands are labelled with instructions advising against microwave oven use and washing in automatic dishwashers whereas other brands can be found in the shops that lack one or both of these instructions, or the instructions are not permanently embossed in the article but are on the packaging or on a label that can be lost and the instructions forgotten by the user. According to [Bradley et al 2005] melaware articles are made by compression moulding of melamine-formaldehyde resin from powder or granular form. The heat and the pressure of the moulding process cures the resin to provide a thermoset plastic. Most moulding powders contain additives such as cellulosic fibres, pigments and fillers. It can be anticipated that poor formulations (inadequate formaldehyde to melamine ratio, presence of fillers) and/or poor process conditions (inadequate time and pressure of moulding) may yield articles showing high migration values.

Migration of melamine from melaware is characterised by a high between-specimen variability for some samples and by inconsistent behaviour on repeated contact with food or simulants - with migration levels falling for some samples but rising for others. A further complication is that the articles can have a long service life during which time the surface may become scratched. Migration clearly depends on the time and temperature conditions of use along with the characteristics of the food - acidic, aqueous, fatty and (although not studied here) dry.

It will be a challenge to better define standard test procedures that can ‘predict’ adequately the migration levels to be expected over a long and varied service life of melaware. It seems likely therefore that the migration test procedures using simulants will need to be re-examined and set conservatively to take this extra uncertainty into account. The high migration of melamine from cookware can be quite dramatic. If this cannot be simulated adequately using test procedures, then it may be that using melaware for cooking applications should be forbidden in regulations.

Future research needs

In related work on melamine-formaldehyde containing resins used as can coatings, a similar strong dependency on the temperature rather than the acidity of the simulant (food) was found (unpublished). It would be interesting to understand which structures in a M-F resin are the most labile towards hydrolysis, so that synthesis of the resins could be optimised to minimise the hydrolysis and subsequent release of melamine under high temperature conditions of use.

REFERENCES

Bradley, E. L., Boughtflower, V., Smith, T. L., Speck, D. R., and Castle, L. (2005). Survey of the migration of melamine and formaldehyde from melamine food contact articles available on the UK market. *Food Additives & Contaminants*, 22, 597-606.

EC 1982. European Commission Directive 82/711/EEC of 18th October 1982 laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs. Official Journal of the European Communities (1982) L297.

EC 1985. European Commission Directive 85/572/EEC of 19th December 1985 laying down the list of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. Official Journal of the European Communities (1985) L372.

EC 2002. European Commission Directive 2002/72/EC of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs. Unofficial consolidated version

including 2002/72/EC, 2004/1/EC, 2004/19/EC, 2005/79/EC, 2007/19/EC, 2008/39/EC. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2002L0072:20091109:EN:PDF>.

EC 2009. Substances listed in EU Directives on plastics in contact with food. Update version as of 20 October 2009. Available from: <http://ec.europa.eu/food/food/chemicalsafety/foodcontact/>

EFSA 2010. Scientific Opinion on Melamine in Food and Feed. *EFSA Journal* 2010; 8(4):1573.

Ishiwata, H., Inoue, T., and Tanimura, A. (1986). Migration of melamine and formaldehyde from tableware made of melamine resin. *Food Additives & Contaminants*, 3, 63-69.

JRC 2009. Guidelines on testing conditions for articles in contact with foodstuffs (with a focus on kitchenware). A CRL-NRL-FCM Publication. 1st Edition. EUR 23814 EN 2009. Available as http://crl-fcm.jrc.it/files/guidelines%20test%20conditions_final_ed2009.pdf (accessed 13th May 2010)

Lund, K. H., and Petersen, J. H. (2006). Migration of formaldehyde and melamine monomers from kitchen- and tableware made of melamine plastic. *Food Additives & Contaminants*, 23, 948-955.

Martin, R.E. , Hizo, C.B. , Ong, A.M. , Alba, O.M. and Ishiwata, H. (1992) Release of formaldehyde and melamine from melamine tableware manufactured in Philippines. *Journal of Food Protection* 55:632-635.

SCF 1986. Report of the Scientific Committee for Food on certain monomers of other starting substances to be used in the manufacture of plastic materials and articles intended to come into contact with foodstuffs. Seventeenth series. Opinion expressed on 14 December 1984. Available at URL. http://ec.europa.eu/food/fs/sc/scf/reports/scf_reports_17.pdf.

Sugita, T., Ishiwata, H., and Yoshihira, K. (1990). Release of formaldehyde and melamine from tableware made of melamine-formaldehyde resin. *Food Additives & Contaminants*, 7, 21-27.

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56
57
58
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60

513
514 Tittlemier, S. A. (2010). Methods for the analysis of melamine and related compounds in
515 foods: a review. *Food Additives & Contaminants, Part A*, 27, 129-145.
516
517 WHO 2009. Report of a WHO Expert Meeting held 1–4 December 2008 in collaboration
518 with FAO and supported by Health Canada. ISBN 978 92 4 159795 1.
519 http://whqlibdoc.who.int/publications/2009/9789241597951_eng.pdf
520

Table 1. Migration of melamine ($\mu\text{g/kg}$) from melaware articles into water in comparison with 3% acetic acid

Sample	Test conditions	SA:V ratio $\text{dm}^2:\text{kg}$	Water $\mu\text{g/kg}$	Acetic acid $\mu\text{g/kg}$	Ratio Water/Acetic
child's plate	30 min 40°C	8.20	20	160	0.13
salad article	30 min 40°C	4.60	50	13	3.85
spatula	10 min 70°C	1.70	80	138	0.58
kitchen aid	10 min 70°C	3.20	6	10	0.60
spoon	10 min 70°C	4.31	28	103	0.27
whisk	10min 70°C	undefined	35	76	0.46
bowl	30 min 70°C	5.67	183	926	0.20
box	30 min 70°C	5.56	82	276	0.30
plate	30 min 70°C	24.1	70	160	0.44
plate	30 min 70°C	19.3	70	190	0.37
plate	120 min 70°C	16.0	65	52	1.25
spoon	10 min 100°C	2.40	90	740	0.12
spoon	10 min 100°C	2.44	650	880	0.74

Table 2. Migration of melamine (µg/kg) into acidic beverages and the ratio (%) of that migration compared to 3% acetic acid

	3% acidic acid	apple juice	tomato juice	tea made of red fruits	black coffee	cola drink
test conditions	2 h/70°C	2 h/70°C	2 h/70°C	2 h/70°C	2 h/70°C	2 h/20°C ¹
pH	2.56	3.43	4.22	3.58	5.03	2.61
<u>Large cups (500 mL, inner surface area: 2.8 dm²)</u>						
1st (µg/kg, ratio)	35	12 , 35%	60 , 174%	17.6 , 51%	44 , 127%	2.4 , 7%
2nd (µg/kg, ratio)	92	24 , 26%	168 , 183%	24 , 26%	23 , 25%	0.23 , <1%
3rd (µg/kg, ratio)	112	20 , 17%	195 , 174%	18 , 160%	21 , 18%	0.8 , <1%
<u>Small cups (200 mL, inner surface area: 1.6 dm²)</u>						
1st (µg/kg, ratio)	631	467 , 74%	439 , 70%	121 , 19%	707 , 112%	2.2 , <1%
2nd (µg/kg, ratio)	836	1132 , 135%	843 , 101%	172 , 21%	658 , 79%	1.3 , <1%
3rd (µg/kg, ratio)	559	1192 , 213%	865 , 155%	155 , 28%	458 , 82%	0.7 , <1%

1: nominal temperature of 20°C, stored at ambient (room) temperature

Table 3. Migration of melamine ($\mu\text{g/kg}$) from melaware cups into beverages and into a variety of food simulants

Food/simulant	Test condition	Brand 1		Brand 2		Brand 3	
		1st $\mu\text{g/kg}$	3rd $\mu\text{g/kg}$	1st $\mu\text{g/kg}$	3rd $\mu\text{g/kg}$	1st $\mu\text{g/kg}$	3rd $\mu\text{g/kg}$
3% acetic acid	2h at 70°C	1686	1599	385	331	1095	638
50% ethanol	2h at 70°C	371	989	129	56	166	61
olive oil	2h at 70°C	< 26	< 26	< 26	< 26	< 26	< 26
3% acetic acid	24 h at 40°C	< 51	279	< 51	201	82	314
50% ethanol	24 h at 40°C	40	32	< 26	< 26	48	37
olive oil	24 h at 40°C	< 26	< 26	< 26	< 26	< 26	< 26
water	24 h at 40°C	27	31	78	89	43	28
milk	24 h at 40°C	30	53	< 26	34	116	74
cola	24 h at 40°C	56	359	55	144	120	326
orange juice	24 h at 40°C	< 26	28	< 26	< 26	48	33
3% acetic acid	Microwave + 24h/40°C	1966	4194	664	cracked	1475	cracked
orange juice	Microwave + 24h/40°C	1062	1449	257	547	1020	cracked
milk	Microwave + 24h/40°C	no test	no test	406	812	no test	no test
3% acetic acid	Microwave +24h/40°C (pre-scratched cup)	no test	no test	1024	1308	no test	no test

Cup brand 1 had a 200 mL capacity and 1.90 dm² contact area. Cup brand 2 had a 250 mL capacity and 1.85 dm². Cup brand 3 had a 200 mL capacity and 1.83 dm². Microwave heating used a 750W nominal output and heating until the boiling temperature was reached.

Table 4. Melamine migration ($\mu\text{g/kg}$) into foods and simulants from melaware articles exposed in sequence

Article	Exposure	Food or simulant and conditions used	$\mu\text{g/kg}$
Bowl 1	1st	3% acetic acid, 2 hrs/70°C	1860
	2nd	3% acetic acid, 2 hrs/70°C	1430
	3rd	3% acetic acid, 2 hrs/70°C	1750
Bowl 2	1st	3% acetic acid, 2 hrs/70°C	1720
	2nd	Spaghetti & sausages in tomato sauce, microwaved	1210
	3rd	3% acetic acid, 2 hrs/70°C	1820
Bowl 3	1st	Spaghetti & sausages in tomato sauce, microwaved	1930
	2nd	3% acetic acid, 2 hrs/70°C	2710
	3rd	Spaghetti & sausages in tomato sauce, microwaved	510
Bowl 4	1st	3% acetic acid, 2 hrs/70°C	2020
	2nd	Spaghetti & sausages in tomato sauce, hot filled	<140
	3rd	3% acetic acid, 2 hrs/70°C	1900
Bowl 5	1st	Spaghetti & sausages in tomato sauce, hot filled	<140
	2nd	3% acetic acid, 2 hrs/70°C	1100
	3rd	Spaghetti & sausages in tomato sauce, hot filled	<140
Cup 1	1st	3% acetic acid, 2 hrs/70°C	4600
	2nd	3% acetic acid, 2 hrs/70°C	2630
	3rd	3% acetic acid, 2 hrs/70°C	2560
Cup 2	1st	3% acetic acid, 2 hrs/70°C	2390
	2nd	Apple juice, microwaved	1270
	3rd	3% acetic acid, 2 hrs/70°C	1910
Cup 3	1st	Apple juice, microwaved	2000
	2nd	3% acetic acid, 2 hrs/70°C	1880
	3rd	Apple juice, microwaved	1070
Cup 4	1st	3% acetic acid, 2 hrs/70°C	2420
	2nd	Apple juice, hot filled	<340
	3rd	3% acetic acid, 2 hrs/70°C	1660
Cup 5	1st	Apple juice, hot filled	2770
	2nd	3% acetic acid, 2 hrs/70°C	1580
	3rd	Apple juice, hot filled	<340

For filling with liquids (simulant and juice) the bowls required 220 mL and cups required 250 mL, and the contact areas were 1.52 dm² and 1.98 dm² respectively. For filling with food, 163 g was placed in the bowls and the surface area covered was 1.22 dm². Microwave heating used a 600W nominal output oven for 2 min (spaghetti & sausages) and 3.3 min (juice) to bring each to the boil.

Table 5. Migration of melamine ($\mu\text{g}/\text{kg}$) from melaware kitchen utensils into 3 % acetic acid, testing in an oven compared to boiling on a hot plate

Sample	Oven 30 min / * °C	Oven 60 min / * °C	Boiling 30 min
Spatula A			
1st exposure	85		3030
Spatula B			
1st exposure	50		2770
2nd exposure	50		4810
3rd exposure	50		9420
Spatula C			
1st exposure		1120	3370
2nd exposure		2160	7530
3rd exposure		5370	14430

* See text. The temperature of the simulant was 94°C after 30 min and was 91°C after 60 min.

Migration was determined experimentally on an area-related basis ($\mu\text{g}/\text{dm}^2$) and the results have been recalculated into units of $\mu\text{g}/\text{kg}$ using a ratio of surface area to simulant of 1.7 dm^2/kg for spatulas, taken from Table 1.