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Migration of Formaldehyde from Melamine-Ware – UK 2008 Survey Results

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Abstract

Fifty melamine-ware articles were tested for the migration of formaldehyde (with hexamethylenetetramine (HMTA) expressed as formaldehyde) to see whether the total Specific Migration Limit SML(T) was being observed. The SML(T), given in European Commission Directive 2002/72/EC as amended is 15 mg/kg. Fourier transform-infrared (FT-IR) spectroscopy was carried out on the articles to confirm the plastic type. Articles were exposed to the food simulant 3% (w/v) aqueous acetic acid under conditions representing their worst foreseeable use. Formaldehyde and HMTA in food simulants was determined by a spectrophotometric derivatisation procedure. Positive samples were confirmed by a second spectrophotometric procedure using an alternative derivatisation agent. As all products purchased were intended for repeat use, three sequential exposures to the simulant were carried out. Formaldehyde was detected in the simulant exposed to 43 samples. Most of the levels found were well below the limits set in law such that 84 per cent of the samples tested were compliant. However, eight samples had formaldehyde levels which were clearly above the legal maximum at 6-65 times the SML(T).

Keywords: formaldehyde, hexamethylenetetramine, melamine, simulant, fourier transform-infrared (FT-IR), migration, survey

Introduction

In 2004 we published a UK survey of 200 samples comprising 50 melamine-ware food contact articles (hereafter called melaware for convenience and to avoid confusion with free melamine as the monomer) and 150 packaged foodstuffs (Food Standards Agency 2004). Formaldehyde migrated from all 50 melaware articles tested. The migration from five of the survey samples exceeded the legal limit by between 8 to 76 times for this monomer. The illegal samples showed discolouration and/or pitting of the surface in contact with the simulant, and cracking. They were withdrawn from the UK market and recalled from consumers who had purchased them. RASFFs (Rapid Alert System for Food and Feed) were issued for all illegal samples.

The Rapid Alert System for Food and Feed (RASFF) was introduced in 1979 to provide control authorities with a tool for exchange of information on measures taken to ensure food safety. In 2004-2008 inclusive there were approximately 35 RASFFs issued for the migration of formaldehyde from melaware, the majority of these products being of Chinese origin.

In 2006 a small survey of melaware samples bought on the Danish market identified migration of one or both formaldehyde and/or melamine monomers from 7 of the 10 tested samples (Lund and Petersen 2006). In all cases the migration levels were less than the SML and SML(T) set for these monomers.

In 2008 we conducted a second survey to ascertain whether the UK market was now free from non-compliant melaware products. This new survey on melaware targeted samples from the Far East in general, rather than one or two specific countries in the Far East,

Materials and Methods

Samples

Fifty melaware samples were obtained, these comprised: 15 bowls: 10 plates: 2 dishes: 20 tumblers/mugs/beakers/glasses: 1 tray: 1 spoon: 1 salad server.

The articles were purchased in March and April 2008 from a range of major and smaller national retail outlets, as well as independent retail outlets and via the internet. The ratio of purchases between major chains and small outlets/internet was approximately 60:40. Nine replicate examples of each melaware article (comprising 1 sample set) were obtained to allow for possible further analysis, after initial testing. FT-IR spectroscopy was carried out on all articles to confirm the plastic type. Each sample set was assigned a unique sample code. Three of the articles were labelled A, B and C and were used for the migration experiments. The remaining six articles were overwrapped in aluminium foil and stored at room temperature. Where appropriate, articles were cleaned before testing by following any accompanying instructions to do so, in accordance with the Comité Européen de Normalisation (CEN) standard EN13130 Section 9 of Part 1 (CEN 2004a).

Test conditions

For articles with a capacity of less than 500 ml or more than 10 litres (L) the specific migration test results should be expressed in units of mg/dm^2 . In these cases the specific migration limits, expressed in mg/kg , are divided by the conventional conversion factor of 6 in order to express them in mg/dm^2 . Thus the SML(T) of 15 mg/kg for formaldehyde (and HMTA expressed as formaldehyde) is equivalent to a limit of 2.5 mg/dm^2 . Similarly when the surface-to-volume ratio in actual use is not known (e.g. forks and spoons) the migration should also be expressed in units of mg/dm^2 . For articles with a capacity equal to or greater than 500 ml but equal to or less than 10 L the migration should be reported as measured, i.e. in units of milligrams of formaldehyde per kilogram of simulant (mg/kg), assuming a density of 1. Melaware may come into contact with all types of foods. In such cases the

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3 legislation states that it should be tested in 3 per cent (w/v) acetic acid in
4 aqueous solution, 10 per cent (v/v) ethanol and a fatty food simulant.
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6 However, studies have shown that acetic acid solution is the most aggressive
7 simulant towards melamine plastics (Ishiwata *et al.* 1986) and so this was
8 selected as the food simulant. For articles which may be exposed to
9 temperatures up to 100 °C 'hot-fill' then three articles, labelled A, B and C,
10 were exposed to 3 per cent (w/v) aqueous acetic acid for 2 hours at 70 °C
11 according to CEN methods EN1186 Part 9 for fillable articles and EN1186
12 Part 3 for nonfillable articles (CEN 2004b). Articles which were labelled as 'not
13 for hot food use' or 'do not pour boiling water directly onto the product' etc.,
14 were treated as 'cold-fill' articles and test conditions of 1 hour at 40 °C were
15 used. As all of the products purchased were intended for repeat use, three
16 sequential exposures to the 3 per cent (w/v) aqueous acetic acid simulant
17 were carried out, as described in CEN standard EN13130 Part 1.
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30 *Analysis*

31 All samples of exposed simulant, blank simulant and standards were
32 subjected to a derivatisation procedure with chromotropic acid. The
33 absorption of the resulting complex was measured at 574 nm. Any samples
34 which gave a response at 574 nm outside the calibration range were diluted
35 with 3 per cent (w/v) aqueous acetic acid and re-analysed. Quantification
36 was achieved by means of external standard calibration using 3 per cent (w/v)
37 aqueous acetic acid fortified with known amounts of formaldehyde. The
38 method used was that described in CEN Technical Specification TS 13130
39 Part 23 (CEN 2004c).
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50 *Confirmation criteria*

51 The absorption of the reaction product was measured over the range of 650
52 nm to 450 nm. The presence of formaldehyde in the samples was confirmed
53 by applying the criteria that formaldehyde should have two absorbance peak
54 maxima at 480 and 574 nm.
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Additional confirmation of the presence of formaldehyde was carried out using
a second spectrophotometric method, in which formaldehyde reacts with

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3 pentane-2,4-dione in the presence of ammonium acetate to form 3,5-diacetyl-
4 1,4-dihydrolutidine and the absorbance of the resulting complex was
5 measured at 410 nm.
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10 11 12 **Results and Discussion**

13 14 15 **Quality Assurance**

16 *Accreditation*

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18 The laboratory is accredited to ISO 17025 by the United Kingdom
19 Accreditation Service (UKAS) for a wide range of testing activities. This
20 includes accredited methods for migration testing of materials and articles and
21 these methods were followed for the work reported here. Although the
22 specific determination of formaldehyde is not included in the UKAS schedule,
23 a CEN standard method was used and the testing was preceded by a blind
24 check-sample exercise.
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33 *Method Performance*

34 *'Spiked' samples*

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36 Analysing representative food simulants 'spiked' with appropriate levels of
37 formaldehyde (close to the SML(T)) tested the suitability of both of the
38 analytical methods to determine formaldehyde. See Tables 1 and 2.
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44 Table 1

45 Measurement Method

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49 Table 2

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53 Confirmation Method

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56 A typical batch size ranged from 2 to 4 survey samples, each prepared in
57 triplicate. Each analytical batch also included at least one method blank. The
58 simulant was analysed directly and matrix matched standards were prepared
59 therefore recovery correction was not applicable.
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5 Six food simulant samples were 'spiked' with formaldehyde so that they could
6 be analysed 'blind' as a check of method accuracy. Samples were prepared
7 in by an independent laboratory. For each food simulant sample, aliquots (25
8 ml) of 3 per cent (w/v) aqueous acetic acid were 'spiked' with formaldehyde.
9 Samples were spiked at 0, 6.7 and 24.5 mg/L in duplicate. The samples were
10 then supplied to the testing laboratory for analysis. In all cases the testing
11 laboratory correctly identified the blanks and the 'spiked' samples with a
12 measurement accuracy in the range 85-102%.
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21 Nine of the 50 samples purchased were labelled as 'not for hot food' or similar
22 and therefore they were tested under 'cold-fill' conditions, the results for these
23 are given in Table 3. All results are quoted to 2 significant figures and as
24 mentioned previously the units used are dependant on the capacity of the
25 article and the article type. Formaldehyde migration was not detected from 7
26 out of 9 of these samples; migration from the other 2 samples was within legal
27 limits.
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36 Table 3

37 'Cold Fill' Conditions
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41 Migration was detected from all the 'hot-fill' samples, these results are given in
42 Table 4. Migration was within the limits set in law for 33 out of 41 of these
43 'hot-fill' samples (0.14 – 1.7 mg/dm², or 0.19 – 12 mg/kg). Migration of
44 formaldehyde from 8 of the 'hot-fill' samples was at levels clearly above the
45 legal maximum at between 6 to 65 times the legal limit.
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53 Table 4

54 'Hot Fill' Conditions
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56 Following exposure to simulant, some of the articles became discoloured on
57 the food contact surface, and/or felt rough to the touch (pitted), and in some
58 cases they cracked or even fell apart (see Figure 1).
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Figure 1

Examples of discoloured/pitted/cracked melaware

Although sustained exposure to formaldehyde would probably have been necessary for health to be at risk, formaldehyde is a carcinogen by inhalation if not necessarily from its presence in food. It is also a sensitiser, which may produce allergic dermatitis and transient irritation of the mouth.

The Food Standards Agency took immediate action to stop the sale of illegal melaware and encourage its return by the public to retailers. As part of the follow-up investigation on failed products, the Agency's Incidents Branch contacted all relevant Local Authorities (LA's) where the products were purchased. The LA's then investigated on behalf of the Food Standards Agency to establish traceability details for the products in question. As part of the investigation the LA's visited premises to ensure affected products had been removed from sale and suitable arrangements made for their disposal. The EU Commission informed all Member States of the breaches via the RASFF system to ensure consistent enforcement action was taken across the EU.

During the course of this survey, it materialised that, in good faith, some of the companies had had 'hot-fill' articles tested for compliance, but the tests used were those described in the British Standard BS EN ISO 4614. This standard is produced by the CEN Technical Committee (TC) for plastics, TC 249, entitled: 'Plastics – melamine formaldehyde mouldings – determination of extractable formaldehyde' (BS 2000). In the scope and field of application it states that this is a method for determining formaldehyde in melamine-formaldehyde mouldings intended for use in contact with food and beverages. There is no reference in this standard to Commission Directive 2002/72/EC as amended; Directive 82/711/EEC as amended, which describes test conditions for food contact plastics; or Directive 85/572/EEC as amended, which lays down the simulants to be used for such testing (EC 1982, 1985 and 2002). The time and temperature given in BS EN ISO 4614:2000 (single exposure of

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3 the article for 30 min at 80°C) are not combinations that are listed in Directive
4 82/711/EEC as amended, as suitable for hot-fill repeat use articles.
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9 The Plastic Materials and Articles in Contact with Food (England) Regulations
10 2008 implement the provisions of the various Commission and Council
11 Directives governing food contact plastics (Plastic Materials and Articles in
12 Contact with Food (England) Regulations 2008). These Regulations therefore
13 lay down the requirements that goods should comply with when placed on the
14 market, and the testing conditions that should be used to ensure their
15 compliance. In doing so, the Schedules to the England Regulations are
16 explicit in laying down the basic rules, the selection of food simulants and the
17 migration test conditions that must be observed to ensure compliance with the
18 overall and specific migration limits laid down in the Regulations. Tests
19 carried out that do not follow the requirements of the Regulations are
20 therefore not valid in assessing the compliance of a food contact plastic
21 material or article with the Regulations. The tests carried out for this survey
22 follow a CEN standard explicitly designed to meet the requirements laid down
23 in the EC measures on food contact plastic materials and articles, as
24 implemented by the England Regulations. Results from those tests confirm or
25 deny the compliance of a particular plastic material or article with the
26 Regulations. Any tests carried out to a different standard that lays down
27 different test conditions, however based, does not reflect the requirements
28 laid down in the Regulations and cannot therefore be taken to prove or
29 disprove compliance with the Regulations.
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48 The European Commission and the Community Reference Laboratory for
49 food contact materials (Joint Research Centre, Ispra) were informed of the
50 unsatisfactory situation vis a vis the inappropriate EN ISO 4614 standard.
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formaldehyde remains unchanged).

Table 1

Measurement Method

Matrix	LOD	LOQ	Recovery Range %	RSD %	Accreditation Yes/No
Spiked simulant	0.46 mg/l	1.40 mg/l	85-102	1.6 (n=8)	No
Reference solution	0.46 mg/l	1.40 mg/l		4.6 (n=2x24)	No

For Peer Review Only

Table 2

Confirmation Method

Matrix	LOD	LOQ	Recovery Range %	RSD %	Accreditation Yes/No
Spiked simulant	0.46 mg/l	1.40 mg/l	94-97	1.6 (n=8)	No

For Peer Review Only

Table 3

'Cold Fill' Conditions

Sample Matrix	Numbers of samples in the range (mg/dm ²)			
	< LOD (LOD <0.1)	< LOD (LOD = 0.1 - 0.5)	0.5 - 2.5	2.5 +
Not for 'Hot-fill'	5	1	2	0
	2 plates 1 bowl 1 mug 1 salad server	1 glass	2 tumblers	
	Numbers of samples in the range (mg/kg)			
	< LOD (LOD <0.1)	< LOD (LOD = 0.1 - 0.5)	0.5 - 2.5	2.5 +
-	1	-	-	
	1 bowl			

Table 4

'Hot Fill' Conditions

Sample Matrix	Numbers of samples in the range mg/dm ²					
	<0.1	0.1 - 0.5	0.5 - 2.5	15 - 35	65 -70	120-160
'Hot fill'	0	16	13	2	1	4
		7 plates 4 bowls 3 mugs 1 spoon 1 tumbler	5 bowls 3 mugs 2 tumblers 1 beaker 1 plate 1 tray	1 dish 1 mug	1 tumbler	3 mugs 1 tumbler
	Numbers of samples in the range mg/kg					
	<0.1	0.1 – 0.5	0.5 – 2.5	2.5 - 4.5	4.5 -1 2.5	450+
-	-	-	2	2	1	
			2 bowls	2 bowls	1 dish	

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Figure 1
Examples of discoloured/pitted/cracked melaware

