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Study on Migration of Melamine from Food Packaging Materials on Markets

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Objectives To study the migration of melamine into foods from plastic food packaging materials and dairy product containers commonly used in China. **Methods** 37 samples were collected from the market. The EU migration testing conditions were adopted with distilled water, 3% acetic acid, n-hexane and 15% ethanol being chosen as the simulating solutions. The HPLC method was used to detect melamine. **Results** No melamine was detected in 15 dairy product containers. Among the 22 plastic samples, 16 of polypropylene, and polycarbonate types had no detectable amount melamine while a low level of melamine was found in 3 of the 6 melamine resin containers. **Conclusion** Migration of melamine from food packaging materials in China market is in line with the requirements of EU.

Key words: Melamine; Migration; Plastic samples; Dairy product containers; China market

INTRODUCTION

A large outbreak of nephrotoxic renal failure attributed to injection of melamine and cyanuric acid-containing pet foods had occurred in dogs and cats in 2007 in USA[1]. In 2008, more than 6 000 infants suffered from kidney stones and renal failure in China as a result of drinking infant formula made from the melamine-contaminated milk[2]. Melamine (2,4,6-triamino-1,3,5-triazine, CAS number 108-78-1) may contaminate foods as it is commonly used as a raw material or additive in the manufacture of melamine-formaldehyde resins, plastic food packaging materials and containers. Its use has a long standing history since it has been commercially available from the late 1930s. Melamine is approved for use as a monomer and other starting substances for food packages in many countries. The European Union Plastics Directive has set up a migration limit of 30 mg/kg for melamine[3].

Information regarding the migration of melamine from food packaging materials and containers into foods is very limited. A Denmark group observed that migration of melamine was found in seven of ten tested melamine samples from the Danish market, including bowl, jug, mug, ladle, cups and plates[4]. A survey on the migration of melamine from containers conducted in UK found that melamine could be migrated from 43 of the 50 samples tested, however, the migration of melamine was much lower than the specific migration limit (SML) set by EU for the monomer[5]. Since no study to date on the migration of melamine from plastic food packaging materials and containers has been conducted in China, the present study was carried out to assess the potential exposure of melamine from packaging materials and containers.

MATERIALS AND METHODS

Chemicals

Citric acid ($C_6H_8O_6$ H_2O), sodium octane sulfonate ($C_8H_{17}NaO_3S$), hydrochloric acid (HCl), n-hexane (C_6H_6), ethanol (CH_3CH_2OH), acetic acid (CH_3COOH) were of analytical grade and purchased from Beijing Chemical Reagents Company (Beijing, China). Acetonitrile (C_2H_3N) of HPLC grade was purchased from J. T. Baker (Phillipsburg, USA). A buffer including10 mmol/L citric acid and 10 mmol/L sodium octane sulfonate, was prepared and adjusted to be pH 3.0. Melamine standard ($C_3H_6N_6$) with a purity 99.0% was purchased from Merck (Darmstadt, Germany).

The melamine stock solution of 1.000 mg/mL

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was prepared by dissolving 0.1000 g melamine in 100 mL methanol and stored at 4 ℃. The working solutions were prepared by diluting the stock solution with 0.1 mol/L HCl and the concentrations of working solutions were 0.50，1.00，2.00，5.00, and 10.0 μg/mL.

Sample of the Food Containers, Utensils and Dairy Products Packages

Samples of the food containers, utensils and dairy products packages were bought from the supermarkets in Beijing, China or provided by dairy companies. They were 13 samples of polypropylene (PP), 3 samples of polycarbonate (PC), 6 samples of melamine resin, and 15 dairy product packages.

Migration Test

Quantification of melamine migration was conducted as previously described[5-6]. In brief, the four simulating solutions including n-hexane, distilled water, 15% ethanol and 3% acetic acid were chosen with a contact time of 2 h at 60 ℃. For food containers and utensils, each sample was filled with the pre-warmed food simulating solutions up to 0.5 cm from the rim. For the dairy product packages, the trilateral of dairy products package was sealed with a sealing machine. The simulating solution was added according to a factor of 2 mL/cm^2. The package was then sealed and heated at 60 ℃.

An aliquot of the resultant simulating solutions was then evaporated to dryness followed by addition of 0.1 mol/L HCl as the final solvent to dissolve the extract. After dilution, the extract was filtered through 0.45 μm filters and the filtrate was subjected to HPLC analysis.

HPLC Analysis

A Water's HPLC system 600E equipped with a PDA detector was used for quantification of melamine. Separations were carried out on a Kromasil KR100-5 C8 column (250 mm×4.6 mm, 5 μm) with an eluting solvent consisting of buffer (10 mmol/L citric acid and 10 mmol/L sodium octane sulfonate): acetonitrile (85:15, vol/vol) and detection at 240nm. The flow-rate was set at 1/mL/min. The injection volume was 20 μL.

The amount of melamine migration was calculated by the following formulas.

For the food containers, utensils

$$X = \frac{C \times V_2 \times 1000}{V_1 \times 1000} \quad (1)$$

Where X= content of melamine in samples, mg/L; C= content of melamine found from the standard curves, μg/mL; V_1= the volume of test solution which was absorbed, mL; V_2= final solution volume, mL.

For the dairy product packages

$$X = \frac{C \times V_2 \times 1000}{2S \times V_1 \times 1000} \quad (2)$$

Where X= content of melamine in samples, mg/L; C= content of melamine found from the standard curves, μg/mL; V_1= the volume of test solution which was absorbed, mL; V_2= final solution volume, mL; S= actual measured area to contact with the stimulant, cm^2; 2= solvent milliliters of per square cm area needed.

RESULTS

A UV spectrum in the range of 200-400 nm was obtained using a PDA detector, demonstrating that melamine had a maximum absorption at 235.9 nm. Therefore, 240 nm was selected as a detection wavelength in this study (Fig. 1). A C18 column was found not to be appropriate for the analysis because melamine has a greater polarity. Instead, a C8 column was chosen and the retention time of melamine was found to be 13.5 min (Fig. 2).

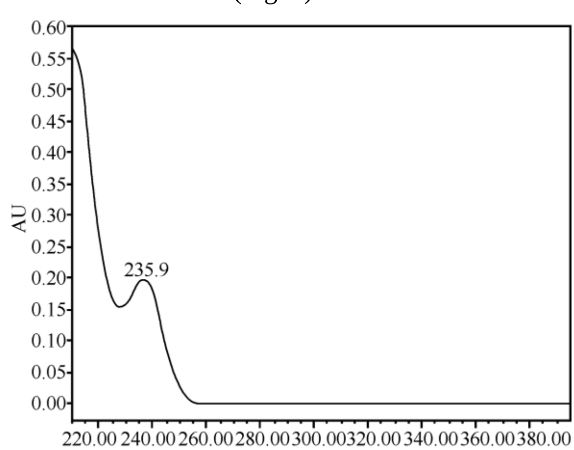

FIG. 1. UV spectrum of melamine.

The calibration graph was linear in a range of 0.592-11.840 μg/mL with a regression equation, y=-10559.6+69042.0x (r=0.9999), where x and y are the injected amount (μg/mL) and peak area, respectively (Fig. 3). The limit of quantification of the method was calculated as 10×SD, where SD is the standard deviation of background noise of the standard diluted. The LOQ was 0.18 mg/kg.

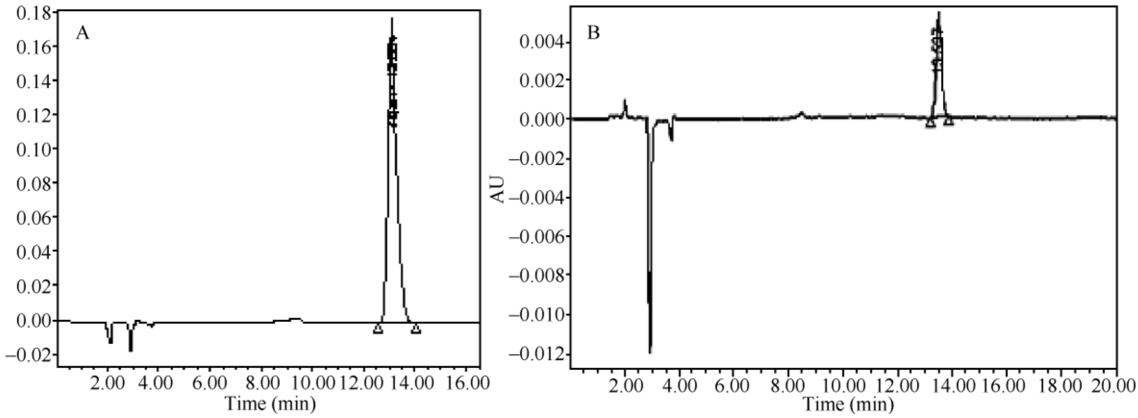

FIG. 2. (A) Standard chromatogram of melamine; (B) separation chromatogram of samples.

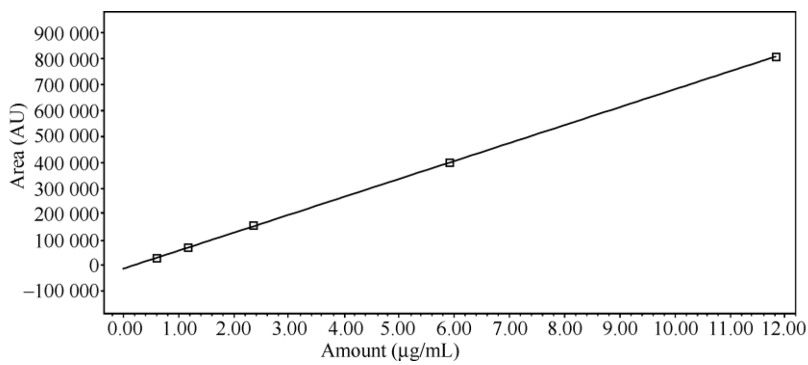

FIG. 3. Calibration curve of melamine.

Melamine was not detectable in the samples of 13 polypropylene and 3 polycarbonate types in all of the four simulating solutions. Melamine migration was confirmed in 3 of the 6 melamine containers with melamine being greater than the detection limit of 0.18 mg/L. It was found that the migration in 15 % (v/v) ethanol aqueous solution and 3 % (w/v) acetic acid aqueous solution was greater than that in the distilled water. No melamine was detected in 15 dairy product containers (Table 1, Table 2, Table 3).

TABLE 1

Migration of Melamine from Food Packaging Materials and Containers

Materials		No. of Samples	No. of Positive Samples	Min (ppm)	Max (ppm)
Polypropylene (PP)		13	0	ND	ND
Polycarbonate (PC)		3	0	ND	ND
Melamine (MA)		6	3	0.18	0.85
Dairy package	Polystyrene (PS)	4	0	ND	ND
	Polyethylene (PE)	1	0	ND	ND
	Polypropylene (PP)	4	0	ND	ND
	PE Complex for Food Packaging Material	6	0	ND	ND

TABLE 2

Migration of Melamine Concentration from Melamine Resin Bowls (mg/L)

	H_2O	3% Acetic Acid	15% Ethanol	Hexane
1	0.19	0.20	0.34	—
2	0.25	0.85	0.40	—
3	—	0.18	—	—

TABLE 3

Dairy Products Packages Tested for Migration of Melamine

No.	Food	Materials	Types of Packaging
1	Yogurt	PS	Plastic Cup
2	Yogurt	PS	Plastic Cup
3	Popsicle	PS	Plastic Cup
4	Ice Cream	PE	Paper Cup
5	Milk Powder	PE Complex for Food Packaging Material	Plastic Bag
6	Yogurt	PS	Plastic Cup
7	Milk Powder	PE Complex for Food Packaging Material	Plastic Bag
8	Cereal Milk	PE Complex for Food Packaging Material	Tetra Pak
9	Milk	PE Complex for Food Packaging Material	Plastic Bag
10	Milk	PE Complex for Food Packaging Material	Tetra Pak
11	Milk Powder	PE Complex for Food Packaging Material	Plastic Bag
12	Ice Cream	PP	Plastic Bag
13	Ice Cream	PP	Plastic Bag
14	Ice Cream	PP	Plastic Bag
15	Ice Cream	PP	Plastic Bag

DISCUSSION

Migration of melamine from food packaging materials and plastic containers and utensils was a concern during the 2008 melamine tainted infant formula crisis. According to the CEN method EN 13130 Part 1, the migration should be tested in distilled water, 3% acetic acid (w/v), 15% ethanol (v/v) and a fatty simulating food. In this study, n-hexane was used as a fatty simulating solution. Since the dairy products were most likely affected during the melamine crisis, various types of dairy product packaging materials including popsicles papers, yogurt cups, fresh milk packages and milk powder packages were purposely tested. The migration conditions for these dairy product packaging materials were the same as those for the plastic food containers and utensils.

It is known that melamine is soluble in methanol, formaldehyde, acetic acid, hot ethylene glycol, glycerin and pyridine but it is slightly soluble in water and hot alcohol. In addition, melamine has a pKb of 9.0, 0.1 mol/L HCl was selected as a solvent in the sample pretreatment to increase the solubility of melamine, because melamine is possibly able to form salt in the acidic conditions.

There have been no national standards on the migration of melamine in food packaging and dairy product packages in China. This study was the first of its kind, finding that melamine was not found in polypropylene and polycarbonate packaging materials and various types of dairy product packages under the current migration conditions. However, 3 out of the 6 melamine resin containers tested were found to have melamine, although the concentrations were low. To be specific, the migration amount in the 3 melamine resin containers was greater than the LOQ of 0.18 mg/L, but it was much lesser than the EU limit of 30 mg/kg (Table 2).

In summary, the present results clearly indicate that the migration of melamine from polypropylene and polycarbonate plastic materials and melamine resin as well as from the dairy product packages is very negligible and should not be of health concern.

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