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Application of radiometric method for element migration determination from plastic packaging to food

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In the present study, a radiometric method was applied for element migration determination from food plastic packaging to simulating solutions and foodstuffs. This method consisted of irradiating plastics with neutrons, its exposure for migration and radioactivity measurements in the food or food-simulating solutions. The migration was studied for water, juice, soft drinks, acidic fatty food and dairy product plastic packages. The results indicated Co, Cr and Sb migration to the simulating solutions and food. However, the contamination of these elements in food from packaging material was lower than the maximum limit values established by the Brazilian Surveillance Agency (ANVISA) legislation.

Introduction

Plastics have become of increasing importance as packages for foodstuffs and pharmaceutical products. However, plastics may contain toxic elements. These elements originate from catalysts and different types of additives used in order to improve the properties or processing of plastics[1]. Direct contact between plastic packaging and their contents can result in the migration of certain elements. Thus, the evaluation of toxic element migration from food packaging is of great interest for health and food safety.

In order to avoid the use of inadequate packaging material, in Brazil, the National Surveillance Agency (ANVISA) has established boundary-values of migrants and recommended procedures to evaluate migration of elements and substances from plastic packaging into foodstuffs.[2]

These conventional recommended methods consist of element extraction from packaging into food-simulating liquids and its subsequent determination by methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS) and colorimetric methods.[2]

For element migration evaluation, the radiometric method has received much attention[1,3,4] and in this procedure packaging samples irradiated with neutron flux are put in contact with food simulating solutions or the foodstuff itself. The migration is then quantified by carrying out gamma ray spectrometry on the simulants.

In Brazil, data on element migration from plastics to simulant or food are very scarce even though the application of plastic in manufacturing of food packages has increased in the last decades. Besides, in a previous study NOMURA et al.[5] determined several elements in Brazilian plastic materials used for food packages. With the tendency of using recycled plastic for food packaging it becomes ever more important to have a technique such as the radiometric method for the evaluation of element migration in these recycled materials.

Experimental

Plastic packaging samples for migration determination

Plastic packaging of water, juice, soft drinks, acidic fatty food and dairy products were chosen for element migration determination by radiometric method. These packages were washed with water then were cut in pieces of 1.5 cm×4.5 cm. These plastic samples were again washed with purified water, dried and next wiped out using hexane p.a. In each packages, samples with regular surfaces and without scratches were obtained to be used as testing materials. An area of 0.405 dm^2 (from both sides) of each packaging was exposed for migration after irradiation with neutrons.

Preparation of synthetic standards of elements

Certified standard solutions of Cd, Co, Cr and Sb acquired from Spex Certiprep Chemical USA were used to prepare diluted multielemental standard solutions of these elements. An aliquot of 50 μL of these multielemental standard solutions were pipetted on small sheets of Whatman filter paper No. 40 and dried at room temperature inside a dessicator. These paper sheets were folded and placed in polyethylene involucres for irradiation. The quantities of each element in the standards, in μg, were: Cd = 9.985; Co = 0.250; Cr = 2.005 and Sb = 1.004.

Radiometric procedure for migration evaluation

The plastic samples and synthetic element standards placed in polyethylene involucres were irradiated

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for 16 hours under a thermal neutron flux of $5.0 \cdot 10^{12}$ n·cm^{-2}·s^{-1} of the IEA-R1 nuclear research reactor to produce radionuclides of the elements present in the plastic. The irradiated plastic samples were then immersed in 30 mL of simulant or food. The experimental condition for plastic sample exposure and types of simulants were selected according to the ANVISA recommendations.[2] The exposition time for migration was 10 days at temperature of 40 °C in an oven. The following simulants were used: water for water packaging and 3% acetic acid solution (w/v) for testing materials of juice, soft drinks, acidic fatty food and dairy product packages. After the end of migration, the plastic testing materials were removed from the simulating solution and discarded. The simulating solution was transferred to a bottle for gamma-ray activity measurements. The irradiated synthetic standards on filter paper sheets were placed in beakers where a carrier solution of the elements Cd, Co, Cr and Sb had been added. The mass of each element used as carrier was 20.0 μg. These standards were dissolved using HNO_3 and water. The resulting solutions were then transferred in plastic bottles to be measured in the same geometry of the simulant. The gamma-ray measurements were carried out using a Canberra system, consisting of a model GX2020 hyperpure Ge detector, which is connected to a Model 1510 Integrated Processor and S100 card. The resolution of the system (FWHM) used was 0.80 keV for 121.97 keV of ^{57}Co photopeak and 1.80 keV for 1331.49 keV of ^{60}Co photopeak. Counting times of 50 000 s for simulants and of 6 000 s for synthetic element standard were used.

The gamma-spectra were processed using an appropriate computer program. The radioisotopes measured were identified according to their half-lives and gamma-ray energies. The radioisotopes and their respective gamma-ray energies (in keV) utilized were: ^{115}Cd (336.2 and 527.9); ^{60}Co (1173.2 and 1332.2); ^{51}Cr (320.0) and ^{122}Sb (564.2).

The mass of the element that migrated from plastic to the simulant was calculated by comparative method. The migration detection limit was evaluated according to CURRIE[6] for the elements not detected in the simulants.

Results and discussion

Table 1 lists the element migration results obtained in packages of soft drinks, juice, acidic fatty food and dairy products using 3% acetic acid or purified water as simulants. These results are given in terms of element mass that migrated per simulant mass and area of plastic material exposed to migration (μg·dm^{-2}·kg^{-1}). All the soft drink packages presented Co and Sb migration. The package of water presented only Sb migration. The juice and acidic fatty food packages presented Co and Sb migration depending on the sample. The high density polyethylene (HDPE) polymer of dairy product packaging presented Co and Cr migration. However, the polypropylene (PP) packaging did not present the expected migration of these two elements. Cd was detected in the analyses of some packages, but its migration was not observed in all samples analyzed.

Table 1. Migration results (in μg·dm^{-2}·kg^{-1}) for soft drink, juice, dairy product and acidic fatty food packagings to simultants

Packaging content	Packaging origin	Packaging polymer	Elements					
			Co		Cr		Sb	
			Mean ± sd[f] (n[g])	Range	Mean ± sd (n)	Range	Mean ± sd (n)	Range
Soft drink[a]	Brazil	PET[c]	0.25 ± 0.13 (22)	0.06–0.61	<0.37	–	0.93 ± 0.35 (22)	0.16–1.58
	Argentine	PET	0.037 ± 0.001[h] (1)	–	<0.30	–	0,78 ± 0.01 (1)	–
	Portugal	PET	0.072 ± 0.001 (1)	–	<0.22	–	0.836 ± 0.01 (1)	–
Juice[a]	Brazil	HDPE[c]	0.101 ± 0.008 (1)	–	<0.39	–	<0.28	–
		PET	0.15 ± 0.04 (3)	0.10–0.19	<0.38	–	0.67 ± 0.13 (3)	0.54–0.80
Acidic fatty food[a]	Brazil	PP[d]	0.110 ± 0.005 (1)	–	<0.75	–	<0.17	–
		PET	0.160 ± 0.004 (1)	–	<0.84	–	0.75 ± 0.01 (1)	–
		HDPE	<0.09	–	<0.66	–	<0.19	–
Dairy products[a]	Brazil	HDPE	0.11 ± 0.03 (3)	0.08–0.13	2.63 ± 0.44 (1)	2.19–3.10	<0.32	–
		PP[e]	<0.08	–	<0.63	–	<0.15	–
Water[b]	Brazil	PET	<0.25	–	<3.84	–	0.56 ± 0.14 (5)	0.42–0.77
	Spain	PET	<0.07	–	<0.51	–	0.63 ± 0.31 (2)	0.41–0.85
	Argentine	PET	<0.05	–	<0.43	–	0.311 ± 0.004 (1)	–

[a] Indicates use of 3% acetic acid as simulant.
[b] Indicates use of distilled water as simulant.
[c] PET = Polyethylene therephthalate.
[d] HDPE = High density polyethylene.
[e] PP = Polypropylene.
[f] sd = Standard deviation.
[g] Number of determinations.
[h] Results of one determination and the standard deviation was calculated using statistical counting errors.

Table 2. Migration results in $\mu g \cdot dm^{-2} \cdot kg^{-1}$ from Brazilian plastic packaging to proper food

Packaging content	Packaging polymer	Elements					
		Co		Cr		Sb	
		Mean ± sd[d] (n[e])	Range	Mean ± sd (n)	Range	Mean ± sd (n)	Range
Soft drink	PET	0.33 ± 0.02 (5)	0.32–0.35	<0.27	–	0.9 ± 0.2 (5)	0.60–1.11
Juice	PET	0.212 ± 0.003 (2)	0.209–0.214	<0.28	–	1.78 ± 0.52 (2)	1.41–2.15
Dairy product	HDPE	0.107 ± 0.002 (1)	–	2.17 ± 0.09 (1)	–	<0.09	–
Water	PET	<0.04	–	<0.36	–	0.67 ± 0.02 (1)	–

Table 3. Migration detection limit results in $\mu g \cdot dm^{-2} \cdot kg^{-1}$

Packaging content	Packaging polymer	Migration detection limits			
		Cd	Co	Cr	Sb
Water	PET	22.3	0.25	3.84	1.69
Soft drink	PET	16.4	0.06	0.37	0.14
Juice	HDPE	–	0.08	0.39	0.28
	PET	21.8	0.05	0.38	0.16
Acidic fatty food	PP	17.9	0.11	0.75	0.17
	PET	17.7	0.10	0.84	0.19
Dairy products	HDPE	3.4	0.09	0.66	0.19
	HDPE	57.1	0.09	0.89	0.32
	PP	19.5	0.08	0.63	0.15

Simulants: Water for packaging of water and 3% acetic acid solution for the others.

Table 2 presents the element migration results obtained for soft drinks, juice, water and dairy products packages to food. These packages presented migration of Co, Cr and Sb.

From the migration results presented in Tables 1 and 2, the total mass of each element that migrated to food was calculated. These results for Cr and Sb indicated that the contamination in food from packaging material is lower than the maximum limit values established in the legislation.[7] These limit values are 100 $\mu g \cdot kg^{-1}$ for Cr and 2000 $\mu g \cdot kg^{-1}$ for Sb. There is no limit value established in Brazilian legislation for Co.

Table 3 shows the migration detection limits obtained for Co, Cr and Sb and they were lower than 3.84 $\mu g \cdot dm^{-2} \cdot kg^{-1}$ indicating the high sensitivity of the radiometric method. In the case of Cd the detection limits obtained were lower than 57.05 $\mu g \cdot dm^{-2} \cdot kg^{-1}$. The sensitivity for radiometric determination of Cd is not so good since this element does not present appropriate nuclear characteristics for neutron activation.

Conclusions

Results obtained in this study indicated that the elements Co, Cr and Sb migrated from plastic packaging samples to simulants or food. However, the contamination in food from packaging material is lower than the maximum limit values established in the Brazilian legislation. The radiometric method presents several advantages over traditional methods used for element migration determination e.g., no need of blank analysis and the possibility to evaluate the migration to the food itself instead of the simulant. The migration detection limit values obtained indicated high sensitivity of the radiometric method. However, this method is not appropriate for migration evaluation of elements presenting short half lives due to migration exposure time. Furthermore future studies should be undertaken to study the influence of neutron irradiation on element migration from plastics.

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