

## **A STUDY OF ELEMENTAL MIGRATION FROM POLY (ETHYLENE TEREPHTHALATE) OF FOOD PACKAGINGS TO SIMULATED SOLUTIONS BY RADIOMETRIC METHOD**

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### **ABSTRACT**

Brazilian plastic production for food packagings, in recent years, has grown in the same proportion as food consumption. Considering that the plastic manufacturing involves catalytic processes and the use of additives, when the foods are in direct contact with these materials, the components present in plastics may migrate to the food. The Brazilian Health Surveillance Agency (ANVISA) has established boundary-values of migrants as well as procedures to evaluate migration of elements and substances from plastic packaging to food. In this study elemental composition of poly (ethylene terephthalate) - PET - packaging and results of elemental migration were obtained. Instrumental Neutron Activation Analysis (INAA) was used to determine elemental concentrations in PET packagings and the radiometric method was applied for elemental migration determination. This radiometric method consisted of irradiating the PET samples with neutrons, followed by migration exposition and radioactivity measurement in food-simulated solution. Experimental conditions used for migration were 10 days exposure period at 40°C. Migration was evaluated for soft drink, juice and water PET packaging. The analytical results indicated that PET packagings contain Co and Sb and those elements are transferred to the simulated solutions. However, these migration results were lower than the maximum tolerance values established by ANVISA. The migration detection limits also indicated high sensitivity of the radiometric method.

### **1. INTRODUCTION**

Poly (ethylene terephthalate) - PET is one of the most widely used polymer in the manufacture of packaging for soft drink, edible oils, waters, concentrated juices, alcoholic beverages and others. Bottle grade PET is used to manufacture bottles. In Brazil, about 70% of this PET is used by the soft drink industries and other 20% used for mineral water and oil [1,2]. The plastic manufacturing process involves catalytic processes and the use of additives, which may cause migration and possible food contamination [3].

Toxic elemental determination in food is of great interest and consequently, the regulating agencies have established boundary-values of migrants and methodologies to evaluate the elemental and substance migration from plastic packaging to food.

In conventional migration evaluation methods the sample is immersed into a food simulated solution. Then the elemental contaminants that migrated to the simulant are, in general, measured by atomic absorption spectroscopy, inductively coupled plasma spectroscopy or colorimetric methods, according to the Brazilian Health Surveillance Agency (ANVISA) recommended procedures [4].

In the present study the radiometric method was applied to determine elements that migrated from plastic packaging to simulated solutions. Packaging samples irradiated with neutrons in a nuclear reactor were submitted to the migration test and after, the gamma radioactivity of simulated solution was measured.

## **2. METHODOLOGY**

### **2.1. Cleaning and Preparation of the Samples**

Soft drink, juice and water PET packagings were tested. These packagings were first washed with detergent and water, then cut in approximately 15 cm x 10 cm pieces and again washed using deionized water and dried. Finally they were cleaned with hexane.

### **2.2. Elemental Synthetic Standard Preparation**

Previous qualitative analyses of plastic packaging samples indicated that the elements As, Cd, Co, Cr and Sb may be present in this kind of material. Standard solutions of these elements acquired from Spex Certiprep (US) were used to prepare diluted multielemental standard solutions of these elements. 50  $\mu\text{L}$  of these multielemental standard solutions were pipetted on Whatman filter paper sheets and dried at room temperature. These sheets were folded and placed in polyethylene involucres for irradiation.

### **2.3. Procedure for NAA of Plastic Samples**

To evaluate the elemental concentration in plastic samples, the sample weighed in polyethylene involucres and heat-sealed were irradiated in the IEA-R1 nuclear research reactor for a period of 16 hours and under a thermal neutron flux of  $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ , with elemental synthetic standards. After about five days of decay time, samples and standards were fixed onto stainless steel planchettes for the gamma-ray measurements. The 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 of 0.80 keV for 121.97 keV of  $^{57}\text{Co}$  photopeak and 1.80 keV for 1331.49 keV of  $^{60}\text{Co}$  photopeak. Counting times varied from 6 000 to 50 000 s, depending on the half-lives or activities of the radioisotopes considered. The gamma spectra were processed using VERSAO2 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:  $^{76}\text{As}$  (559.1);  $^{115}\text{Cd}$  (336.2 and 527.9);  $^{60}\text{Co}$  (1173.2 and 1332.2);  $^{51}\text{Cr}$  (320.0) and  $^{122}\text{Sb}$  (564.2) [4]. The elemental concentrations were calculated by comparative method.

## 2.4. Radiometric Procedure for Migration Evaluation

For this study, PET samples with regular surfaces and without risks were selected. The total area of each plastic sample submitted to the migration test was  $0.405 \text{ dm}^2$ . These samples placed in polyethylene involucres and the elemental synthetic standards were irradiated at the IEA-R1 nuclear reactor for 16 hours under a thermal neutron flux of  $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The irradiated samples were immersed into a 30 mL of simulated solution. The migration time of 10 days at temperature of  $40^\circ\text{C}$  and the choice of the simulated solution were based on the ANVISA recommendation [5]. The water simulant was used for water packagings and 3% acetic acid solution (m/v) for soft drink and juice packagings.

After the migration exposure, the plastic samples were removed from the simulants and discarded. The simulant solution was transferred into a polypropylene bottle for gamma-ray measurement. The irradiated synthetic standards of elements were dissolved using nitric acid solution. A carrier solution containing Cd, Cr, Co and Sb was added to avoid loss of the elements during the dissolution. The elemental standard solution was also transferred into a bottle in the same geometry of simulant samples for the measurements.

The gamma-ray activity measurements were carried out using a hyperpure Ge detector coupled to a gamma-ray spectrometer. Gamma-spectra obtained using Canberra S100 software was processed using the VERSAO2 software. The mass of the element that migrated from plastic to simulated solution was calculated by comparative method. The migration detection limit of the elements was evaluated according to CURRIE [6].

## 3. RESULTS AND DISCUSSION

Table 1 shows the results of elemental determination obtained for samples of soft drink, juice and water plastic packagings. As it can be seen in this Table Sb was found in all samples analyzed and Co was not detected in a water packaging. Cd was determined in four samples of water packaging.

Results of elemental migration obtained in soft drink and juice plastic packagings are presented in Table 2. The simulant solution used was 3% acetic acid for these packagings. These migration results are given in terms of elemental mass that migrated per mass of the simulant solution and surface area of plastic exposed to migration ( $\mu\text{g dm}^{-2} \text{ kg}^{-1}$ ). All packagings of soft drink and juice presented Sb and Co migration.

Results of elemental migration obtained for samples of water plastic packagings using water as simulant solutions are presented in Table 3. Four samples of water packagings presented migration of Sb.

**Table 1. Elemental concentrations in samples of soft drink, juice and water plastic packagings, in  $\mu\text{g g}^{-1}$**

Packagings	Elements				
	As	Cd	Co	Cr	Sb
S1 <sup>a</sup>	<sup>d</sup>		1.96±0.03 <sup>e</sup>		185±2
S2			28.4±0.5		230±2
S3	<0.4	<4.0	62.3±0.5	<1.2	243±1
S4			55.9±0.4		244±1
S5	<0.4	<3.8	50.4±0.4	<1.3	247±1
S6	<0.2	<2.9	33.4±0.3	<1.2	218±1
S7			66.4±0.7		248±5
S8			23.7±0.4		227±5
J2 <sup>b</sup>			52.6±0.9		221±6
W1 <sup>c</sup>			52±2		255±2
W2		4.9±0.7	2.17±0.04		231±1
W3		3.1±0.7	58±1		191±1
W5		10±1	48±1		246.9±0.9
W6		19±2	<71.6	<402.7	219.9±0.8

<sup>a</sup> S1 to S8 soft drink packaging samples; <sup>b</sup> J2 juice packaging sample; <sup>c</sup> W1 to W6 water packaging samples <sup>d</sup> Blank space means not detected; <sup>e</sup> Results of one determination and the uncertainty was calculated using statistical counting errors of standard and sample.

**Table 2. Elemental migration from soft drink and juice packagings to simulant solution**  
**Experimental conditions: Simulant solution = 3% acetic acid, Exposure time = 10 days,**  
**Temperature = 40°C.**

Packagings	n <sup>c</sup>	Elements ( $\mu\text{g dm}^{-2} \text{kg}^{-1}$ )	
		Co	Sb
S1 <sup>a</sup>	2	0.08 - 0.09 <sup>d</sup>	0.93 - 1.58
S2	2	0.40 - 0.61	0.16 - 0.20
S3	2	0.09 - 0.21	0.68 - 0.92
S4	2	0.06 - 0.22	1.05 - 1.19
S5	2	0.11 - 0.12	1.19 - 1.24
S6	10	0.24 - 0.36	0.57 - 1.19
S7	1	0.29 ± 0.02	0.67 ± 0.04
S8	1	0.123 ± 0.007	1.27 ± 0.07
J2 <sup>b</sup>	3	0.10 - 0.19	0.54 - 0.80

<sup>a</sup> S1 to S8 soft drink packaging samples; <sup>b</sup> J2 juice packaging sample;  
<sup>c</sup> n = determination number; <sup>d</sup> Range of results.

**Table 3. Sb migration from water packagings to water.**  
**Experimental conditions: Simulant solution = water, Exposition time = 10 days,**  
**Temperature = 40°C.**

Packagings	n <sup>b</sup>	Sb ( $\mu\text{g dm}^{-2} \text{kg}^{-1}$ )
W1 <sup>a</sup>	2	0.48 - 0.63
W2	1	0.77 $\pm$ 0.02
W3	1	<1.69
W5	1	0.49 $\pm$ 0.01
W6	1	0.42 $\pm$ 0.01

<sup>a</sup> W1 to W6 water packaging samples;

<sup>b</sup> n = determination number.

The migration results obtained for Sb and presented in Table 2 and 3, in terms of element mass that migrate per mass of simulated solution and area of plastic, were converted in mass of element that would migrate to mass of “food”. These data obtained for Sb varied from 1.0 to 9.5  $\mu\text{g kg}^{-1}$ , lower than the maximum limit values (200  $\mu\text{g kg}^{-1}$  for soft drink and water and 1000  $\mu\text{g kg}^{-1}$  to juice) established in the legislation [7]. For Co there is no maximum limit value established.

**Table 4. Elemental migration detection limits.**  
**Experimental conditions: Exposition time = 10 days, Temperature = 40°C.**

Packagings	Simulant solution	Migration detection limits $\mu\text{g dm}^{-2} \text{kg}^{-1}$			
		Cd	Co	Cr	Sb
S1 <sup>a</sup>	3% acetic acid	8.11	0.06	0.37	0.10
S2		8.67	0.05	0.35	0.11
S3		8.44	0.02	0.21	0.08
S4		16.44	0.02	0.20	0.10
S5		12.28	0.04	0.28	0.14
S6		14.84	0.04	0.28	0.14
S7		<sup>d</sup>	0.02	0.15	0.06
S8			0.04	0.21	0.09
J2 <sup>b</sup>	3% acetic acid	20.61	0.05	0.35	0.14
W1 <sup>c</sup>	water	13.07	0.09	0.62	0.16
W3		517.7	0.25	3.84	1.69
W6		12.10	0.06	0.57	0.14

<sup>a</sup> S1 to S8 soft drink packaging samples; <sup>b</sup> J2 juice packaging sample; <sup>c</sup> W1 to W6 water packaging samples; <sup>d</sup> Blank space means not determined.

Table 4 presents the migration detection limits for the elements Cd, Co, Cr and Sb obtained using different food-simulant solutions. This limits varied from 0.02 to 20.61  $\mu\text{g dm}^{-2} \text{kg}^{-1}$ , excepting for Cd in a sample of water packaging that showed detection limit of 517.7  $\mu\text{g dm}^{-2} \text{kg}^{-1}$ . Data obtained for detection limits indicate the high sensitivity of this radiometric method.

#### 4. CONCLUSIONS

Results obtained in this study indicated that Co and Sb are present in poly (ethylene terephthalate) of food packagings and these elements migrate to the simulated solutions. The migration detection limit values obtained for these elements indicated high sensitivity of the radiometric method. The advantages of this technique are no necessity of blank analysis and use of high purity simulants and it is possible to evaluate the migration using food sample, instead of simulated solutions. Moreover, there is no contamination during the migration test because the plastic sample to be exposed to the migration test is previously irradiated.

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