Journal of Food Biosciences and Technology,
Islamic Azad University, Science and Research Branch, Vol. 8, No. 2, 55-60, 2018

Evaluation of the Migration of Antimony from Polyethylene Terephthalate (PET) Plastic Used for Verjuice and Lemon Juice Packaging

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Received: 26 February 2017 Accepted: 15 September 2017

ABSTRACT: The migration of antimony (Sb) from polyethylene terephthalate (PET) bottling for acidic juices have been assessed in this study. Inductively coupled plasma mass spectrometric (ICP-MS) method was chosen for antimony content determination. Experiments were undertaken at different conditions (15, 25, 35, 45days at 25, 50°C for first use bottle, reused bottle). Two different acidic juices (lemon juice and verjuice) were chosen for this experiment. In the first stage of study (15days) the Sb contents in both juices were below the maximum contaminant level of 5 µg/l prescribed by the European Union (EU) regulations. An increase in all the tested samples were observed after 25 days, although the antimony concentrations were below the standard limits. The increase in concentrations continued after 35 days and values were below the standard limit with exception of using reused bottle. In this condition, Sb contents reached to 5.15 and 5.11 µg /L for lemon and verjuices respectively that exceeded the standard limit. Storing at 25°C for 45 day (either for first use or reused bottle) indicated a steady state trend for both juices and as compared to 35 days, significant increases were not observed, whereas, at 50°C, acceleration of antimony migration occurred in all the cases.

Keywords: *Antimony, Migration, Polyethylene Terephthalate*.

Introduction

Due to high application of plastic packaging in food industry, migration of some compounds are undesirable and is the concern of researchers. polyethylene terephthalate (PET) is one of the packaging material because of its desirable properties namely good mechanical properties, moderate moisture and gas barrier, good resistance to grease and oils, good transparency (Lee *et al*., 2008). PET bottles are good alternative for replacing glass and polyvinylchloride bottles (PET resin association, 2015). This polymer is manufactured through polycondensation of dimethyl terephthalate and ethylene glycol, with antimony trioxide in the presence of (Sb_2O_3) as the catalyst (Sax, 2010). Researches approve the remaining of this catalyst in pet bottles between 100 and 300 mg/kg (Rungchang *et al*., 2013). Therefore, the risk of antimony migration to beverages is an undeniable issue since that presence of Sb in PET bottles has been approved by several reports (Bach *et al*., 2012; de Jesus *et al*., 2016).

Regarding to the International Agency for Research on Cancer, there are ample evidence for animal carcinogenicity of Sb_2O_3 that may be applicable to humans (IARC, 1989), therefore, this subject is of importance and concerned by the U.S.

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Environmental Protection Agency. This organization has declared a maximum permitted contaminant level of 6.0 μg L^{-1} Sb for drinking water (USEPA), (USEPA, 1979). The European Union defines a maximum allowable concentration of antimony in drinking water that is 5.0 μ L^{-1} (Commission of the European Communities, 2013), whereas the allowable limit is 20 μg L^{-1}according to the World Health Organization (WHO, 1996).

In addition to water packaging, PET bottles is going to be used for juice packaging like lemon juice, verjuice and some others, especially in household making of these products. Using of reused PET bottle in homemade filling juices raise the issue of probable migration of Sb to juices during storage time. In the present study migration assays were performed by using different acidic foodstuffs in order to reveal the exact Sb concentration in this foodstuff categories. The selection of these food materials is due to the acidic nature and its condition and the effect on Sb migration (Sanchez-Martenez *et al*., 2013). The present study is focused on the key issue regarding the migration of antimony with respect to: i) different acidic foods, ii) different storage time, iii) different temperature and iv) application of reused bottles.

Materials and Methods

All the chemicals and reagents used were of analytical grade. An inductively coupled plasma mass spectrometer (Varian Inc. - Ultramass 700 ICP-MS) fitted with a Meinhard nebulizer and a Peltier cooled sample introduction system was used to measure the total antimony (Fan *et al*., 2014). ICP-MS characteristics are briefed in Table 1.

- *Leaching experiments*

Leaching experiments were performed according to the European Norm EN 14233 (2002). For this reason, PET colorless bottles were used. The bottles were filled with lemon juice or verjuice. Three bottles were filled with each liquid. Thereafter, they were placed in a bath with controlled temperature (25, 50°C) for given time (15, 25, 35, 45 days). The Sb concentrations in the liquids were then determined.

Table 1. ICP-MS Instrumental Operating Conditions

Forward power	1.2 kW
Plasma gas flow rate	20.0 l/min
Auxiliary gas flow rate	1.0 l/min
Carrier gas flow rate	0.8 l/min
Nebulizer type	Concentric nebulizer C- type
Spray chamber type	Varian 800-MS spray chamber- scott
Isotope monitored	^{121}Sb, ^{123}Sb
Internal standard concentration	^{115}In

- *Reuse migration experiment*

The conditions were the same as for specific migration but, in this case, migration tests were carried out with the application of reused PET bottles.

- *Statistical analysis*

All the data were treated in replicate order and mean values were taken. Data were subjected to one-way analysis of variance (ANOVA) using STATISTICA software. A significance level of $p < 0.05$ was used.

Results and Discussion

According to the results, it is clear that antimony migration take place in all the tested conditions. Among the experiment condition only reused bottle has no significant effect on antimony migration rate (Table 5) but the effect of other parameters (temperature, exposure time and juice variety) were statistically meaningful (Tables 2, 3). Tables 2 and 3, depicted statistical descriptive analysis of different parameters on Sb magnitude.

As presented in Table 3, in the first stage of study (15days) the Sb contents in both

Table 2. Descriptive statistics of different parameters on antimony concentration (µg/l)

Temperature	Juice	Exposure time	Mean ±Std.	N
25ºC	Lemon juice	15 day	0.624333 ±.2074191[(a)]	6
		25 day	1.558000 ±.3341191[(b)]	6
		35 day	2.354167 ±.5249066[(c)]	6
		45 day	2.351167 ±.5095674[(c)]	6
		Total	1.721917 ±.8239022	24
	Verjuice	15 day	0.508000 ±.1380464[(a)]	6
		25 day	1.318500 ±.2244057[(b)]	6
		35 day	2.121667 ±.5429787[(c)]	6
		45 day	2.119667 ±.5433451[(c)]	6
		Total	1.516958 ±.7806128	24
	Total (Regardless of the juice variety)	15 day	0.566167 ±.1786306[(a)]	12
		25 day	1.438250 ±.2987928[(b)]	12
		35 day	2.237917 ±.5234443[(c)]	12
		45 day	2.235417 ±.5165613[(c)]	12
		Total	1.619438 ±.8006916	48

Table 3. Descriptive statistics of different parameters on antimony concentration (µg/l)

Temperature	Juice	Exposure time	Mean ±Std.	N
50ºC	Lemon juice	15 day	2.774500 ±.2627324[(a)]	6
		25 day	3.948167 ±.3452515[(b)]	6
		35 day	5.050333 ±.1157699[(c)]	6
		45 day	5.669667 ±.4327062[(d)]	6
		Total	4.360667 ±1.1646148	24
	Verjuice	15 day	2.726167 ±.2740507[(a)]	6
		25 day	3.824667 ±.4053190[(b)]	6
		35 day	4.928833 ±.2024830[(c)]	6
		45 day	5.564167 ±.3485395[(d)]	6
		Total	4.260958 ±1.1449587	24
	Total(Regardless of the juice variety)	15 day	2.750333 ±.2571997[(a)]	12
		25 day	3.886417 ±.3647125[(b)]	12
		35 day	4.989583 ±.1695708[(c)]	12
		45 day	5.616917 ±.3786295[(d)]	12
		Total	4.310813 ±1.1435874	48

juices were below the admissible level as prescribed by the European Union (EU) regulations (5 µg/l). The results showed that during the 25 days of storage, increases in all the tested samples have been observed but the antimony margins are still below the standard limit. The increasing attitude continued for 35 days whereas values are below the standard limit level with the exception of using reused bottle (5.15 and 5.11 µg /l for lemon juice and verjuice, respectively). Storing at 25°C for 45 days (either for first use or reused bottles) show steady state trends for both juices in relation to antimony leaching and values that are comparable to those of 35 days at 25°Cwhereas, at 50°C, progressive accelerations of antimony migration, have been detected in all the cases.

These results are comparable to other authors' findings. Sanchez-Martenez *et al*. (2013) pointed out that leaching of antimony in PET bottles filled with 3% acetic acid after 10 days storage at 40°C was 0.56±0.02 µg /l. Chapa-Martínez *et al*. (2016) reported the antimony content of drinking water filled in PET bottles reached 5.20µg /l at 75°C after 5 days of storage. Differences in the Sb leaching concentrations from PET in different studies might be due to different raw material and the technology used for PET manufacturing (Sax, 2010).

- *The effect of juice variety on Sb migration*

Both juices show the same order of magnitude in all the cases regarding Sb migration. This could be attributed to the similar acidity and pH values of both tested juices (measured pH of lemon juice and verjuice were the same and equal to 2.8).

According to the results, Sb migration increased between 15 and 35 days at 25°C and then reached a plateau for both juices. Increased rate of migration at 50°C is more noticeable in both juices. (Figure 1).

The results presented in Table 3 confirm that the effect of time, temperature and juice variety are statistically significant. Higher migration of Sb in lemon juice is detected as compared to verjuice that might be presumably due to different chemical composition of the juices. Other researchers have reported different migration rates for different food products (de Jesus *et al*. 2016; Chapa-Martínez*et al*. 2016).

- *The effect of temperature on Sb migration*

Figure 1 presents the results of the analysis of the temperature effects with 95% confidence at different time intervals.

The experiments have approved the effect of temperature on antimony leaching rate. At higher temperature, more antimony leaching has occurred. The worst case in respect to antimony was at 50°C and 45 days storage. Carneado *et al*. (2015) showed that the leaching of Sb from PET bottles at high temperature (60°C) exceeded the maximum allowed by the EU legislations. Reimann *et al*. (2012) reported, Sb leaching take place in all temperatures and is increase at 45°C in PET bottles. Chapa-Martínez *et al*. (2016) illustrated the effect of temperature, pH and time on antimony migration from PET bottles in drinking water. This report confirmed that pH, temperature, and storage time significantly affected the release of Sb, while the temperature had the highest effect among the studied parameters

- *The effect of storage time on Sb migration*

The experiments have shown the obvious effect of storage time on antimony migration (Table 2-4). Sb migration positively correlated with time. The longer the contact time between bottle and juices, the higher the migration.

The analysis has confirmed that leaching of antimony into lemon juice has occurred more rapidly than verjuice. Impact of storage time on antimony concentration is reported by other authors. Fan (2014) pointed out Sb concentration in drinking water explicitly linked to storage condition (storage time and temperature), and the worst case in relation to Sb leaching was at 70°C for 4 weeks. Westerhoff *et al*. (2008) stipulated storage at higher temperatures had a significant effect on the time-dependent release of antimony.

- *The effect of reused bottle on Sb migration*

Since PET bottles could be reused (especially in homemade juices), an experiment accomplished to provide information on the migration over refilling of bottles.

According to Table 4, reused bottle has no unequivocal effect on antimony leaching magnitude than first used bottle (p-value=0.070>α=0.05). This indicates that polymer degradation in both first and reused bottle happened at the same rate. (Takahashi *et al*., 2008). In both first and reused bottles, higher temperature and more storage time resulted in higher antimony leaching.

- *Human risk assessment*

A human health risk assessment was conducted to determine the risk caused by long-term exposure to Sb via tested juices consumption. As Sb migration in lemon juices has the highest rate and since of the lack of report regarding the total verjuice consumption, Chronic daily intake (CDI value) is only calculated based on lemon juice. CDI determination was carried out according to the equation outlined by Fan (2014):

$$CDI=\frac{C\times DI}{BMW}$$

Where:

C = the Sb concentration in the lemon juice (ng/l)

DI= the average daily intake rate of lemon juice (l/day), which is assumed to be 0.1l/day. (Vatanemrooz newspaper, 2013).

BW is body weight (kg), which is assumed to be 72 kg for an adult.

Antimony uptake through lemon juice consumption could account for 2.1% of recommended uptake that is 400 ng/kg/day (Drinking Water Standards and Health Advisories, 2012) (Table 5). Due to the fact that these juices are acidic and have a long shelf life, therefore the concentration of antimony might increase during storage and reach an unacceptable concentration.

Conclusion

According to the findings concerned with this research, antimony migration in two tested juices (lemon juice and verjuice) of the first used bottle for 15 and 25 days are lower than the standard limit (5 µg/l) but in the case of

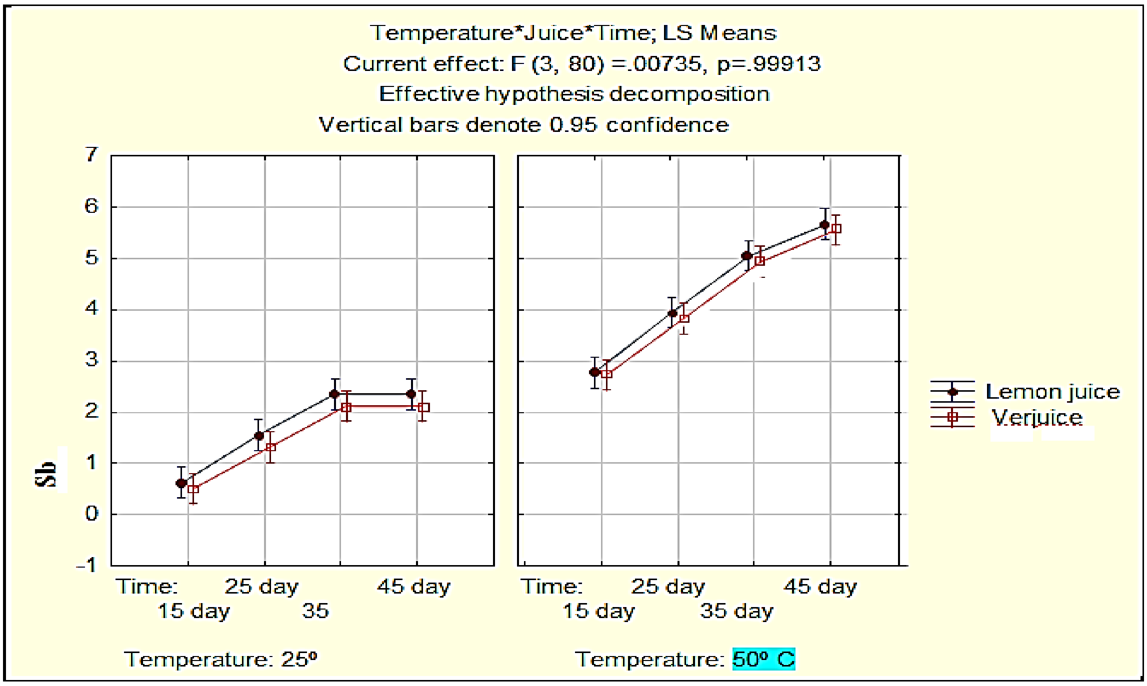

Fig. 1. The effect of time and temperature on antimony concentration (µg/l) of lemon juice and verjuice.

Table 4. Descriptive statistic of first used or reused bottles on antimony migration magnitude

Parameter	Groups	Descriptive Statistics			*t-test*	*P-value*
		Sample size (n)	Mean ($\bar{X}_i$)	Standard deviation (S_i)		
Response	First use bottle	48	2.6564	1.64866	-1.832	.070
	Reused bottle	48	3.2739	1.65375		

Table 5. Chronic daily intake (CDI, ng/kg/day) for Sb via consumption lemon juice based on the Sb concentration released from PET bottles in circumstances that exceeded the standard level of limit.

Sample	Chronic daily intake (ng/kg/day)
50°C, 45 days, first used bottle	8.021
50°C, 35 days, reused bottle	7.152
50°C, 45 days, reused bottle	8.41

reused bottle for 35 days, antimony content was higher than the critical level. Similarly, preservation at 25°C caused antimony migration lower the standard limitation but at 50 °C it exceeded the limitation.

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