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Antimony Assessment in PET Bottles for Soft Drink

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Abstract The aim of this work was to develop a method for the determination of antimony (Sb) in polyethylene terephthalate (PET) bottles and to evaluate its migration into soft drink and simulant. In this context, a new procedure for PET sample preparation, using a high pressure asher (HPA), is presented for the determination of Sb by inductively coupled plasma optical emission spectrometry (ICP-OES). The concentration of Sb in PET bottles ranged between 272 and 650 mg kg^{-1}. The migration of Sb into soft drink after 180 days at 35 °C was below the LOQ, 20 μg L^{-1}. The specific migration of Sb from the bottle into simulant 3% of acetic acid after the contact per 10 days at 40 °C was less than the LOQ, 23.5 μg L^{-1}. The results showed that all packaging evaluated contained Sb, but the maximum permissible migration value for Sb, 40 μg L^{-1}, established by Anvisa and EU, was never exceeded.

Keywords Sample preparation · Soft drink · PET · Migration · Antimony · ICP-OES

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Introduction

Polyethylene terephthalate (PET) is a semi-crystalline polymer belonging to the polyester family. It is one of the most widely produced thermoplastics worldwide achieving, by the end of 2012, a global production capacity of approximately 28 million metric tonnes. The use of PET resin in packaging is widespread, including biaxially oriented and metallized films, bottles obtained by injection-blowing with biaxial orientation for sparkling drinks, mineral water, edible oils, juices and sauces, flasks for pharmaceutical products, nests and transparent blister packaging, and also trays with high thermal stability for use in both conventional and microwave ovens (dual ovenable trays), among others. The widespread use of this material is attributable to its mechanical and thermal properties and low production costs (Romão et al. 2009; Garcia et al. 2008; Bach et al. 2013).

The global PET consumption for 2014 was 197 gigakilograms (Gkg) of which 5.7 Gkg were intended for soft drinks packaging (Swift 2014). In Brazil, approximately 90% of PET resin produced in 2011 was used to manufacture packaging for soft drinks, water, and oils, and the total PET resin consumption was 572,000 metric tonnes, with a forecast consumption of 840,000 metric tonnes for 2016 (ABIPET 2013). The use of PET resin for packaging manufacture in the USA in 2013 amounted to 2.6 million metric tonnes (NAPCOR 2013), while in Europe, the equivalent number was 2.8 million metric tonnes (Welle and Franz 2011).

In order to produce PET resin, inorganic compounds are used as catalysts in the stages of transesterification and polycondensation. Antimony trioxide (Sb$_2$O$_3$) is the most frequently used catalyst. The Sb$_2$O$_3$ offers a high catalytic activity and chemical stability in the presence of phosphorus-based

stabilizers. In addition, antimony catalyst does not engender undesirable colors and has low cost when compared with germanium catalyst (Romão et al. 2009; Thiele 2004; Welle and Franz 2011; Carneado et al. 2015; Bach et al. 2012).

The use of antimony trioxide to produce PET for packaging has been called into question due to the suspicion that it may be carcinogenic and the fact that it is on the list of primary pollutants published by the United States Environmental Protection Agency (USEPA) (Hansen and Pergantis 2006; Carneado et al. 2015). USEPA warns that the constant consumption of water with antimony content well above the maximum permitted level of 6 μg L^{-1} could increase the level of blood cholesterol and reduce the level of sugar (EPA 2009). Germany recommends that the antimony content in the packaging should not exceed 350 mg kg^{-1} (BfR. Recommendation of the Federal Institute of Risk Assessment 2011). In Brazil, RDC Resolution 17/2008 (BRASIL 2008), published by ANVISA, the National Health Surveillance Agency, establishes a positive list of additives for plastic materials intended for the production of packaging and equipment that comes into contact with food and has authorized the use of antimony trioxide in the manufacture of PET resin. It has fixed a specific migration limit for antimony in packaging of 40 μg kg^{-1}, which is the same limit established by the EU regulation EC 10/2011 (EU 2011), while in Japan, the Japan External Trade Organization has established a limit of 50 μg L^{-1} (JETRO 2011). The Food and Drug Administration (FDA) has not specified a migration limit for antimony from PET packaging materials (Welle and Franz 2011).

In order to quantify antimony in the concentration level established by the various legislations, the analytical technique should have a low limit of quantification and good precision and accuracy. The analytical techniques most commonly employed to determine antimony in polymers and in beverages are graphite furnace atomic absorption spectrometry (GFAAS), fast sequential flame atomic absorption spectrometer (FS-FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) with or without hydride generation, and X-ray fluorescence (XRF) (Cadore et al. 2008; Guerra et al. 2011; Shimamoto et al. 2011; Batista et al. 2013; Jesus et al. 2016; Altunay et al. 2016).

Sample preparation is a fundamental step towards good performance in the application of the vast majority of elemental analysis techniques. The mineralization process used to digest polymeric materials is generally similar to that of other organic materials, using nitric acid in closed vessels at high temperatures, or sulfuric acid with an oxidizing agent at high temperatures and atmospheric pressure (Cadore et al. 2008). As an alternative to the microwave digestion, the most commonly used digestion technique, the high pressure asher system, is an alternative used to digest complex samples. The technique has the advantage of attaining a temperature of up to 320 °C in 40 min. Internal digestion pressure is 130 bar (1920 psi), and as a result, a larger sample mass may be digested when compared to the microwave technique, and different samples may be digested simultaneously (White et al. 1998; Kiyataka et al. 2014, 2015).

A number of studies have been published on the quantification of antimony in PET bottles and migration of antimony into water, juice, soft drinks, and into simulants. An overview of these studies can be found in Table 1. The studies showed that the concentration of Sb in PET bottles was in the range of 104 to 323 mg kg^{-1}, but the migration of Sb was below the limit established by Japan, Europe, and Brazil. The migration of Sb to drinking water, when stored at temperatures upper to 60 °C, is accelerated over time. The majority of studies have employed the ICP-MS for Sb determination, a technique which consists of low detection and quantification limits, although maintenance costs are high. None of these studies used the high pressure asher system as an alternative for the preparation of the sample.

Consequently, the aim of this study was to develop and validate a method for quantifying antimony in PET bottles, using a high pressure asher and ICP-OES, and to evaluate the migration into soft drinks and a food simulant (3% acetic acid) using ICP-OES as technique.

Materials and Methods

Instrumentation

All the assessments of Sb were performed using an ICP OES OPTIMA 2000DV model, from PerkinElmer Corporation (Shelton, CT, USA). The axial view, a Mira Mist parallel path pneumatic nebulizer (Burgener Research Inc., Ontario, Canada) and a quartz cyclonic spray chamber were utilized, and the cold recombination area was removed with a shear gas interface. The whole system is controlled by the software WinLab32™ (Perkin Elmer, Shelton, CT, USA). The parameters employed for ICP operation are shown in Table 2. The PET samples were digested in the high pressure asher (HPA) (Anton Paar GmbH, Graz, Austria), equipped with an aluminum rotor and 90-mL reaction vessels. The reaction vessels were placed into a pressure vessel pressurized with nitrogen.

Reagents and Standards

Ultrapure water (resistivity of 18.2 MΩ cm^{-1}) was obtained with a Milli-Q system (Millipore, Bedford, MA, USA). The glassware used in the present study was previously washed with extran detergent (Merck, Darmstadt, Germany),

Table 1 Data in the literature for antimony concentrations in PET bottles, beverages, and to the simulant

Samples investigated	Analytical technique	Results for antimony	References
Migration study in acetic acid in two PET resin samples. The concentration of antimony in Resin A was 160 mg kg^{-1} and in Resin B 230 mg kg^{-1}.	Microwave to digest sample and Sb quantified in ICP-MS	Samples 40 °C/10 days 100 °C/2 h Resin A 2.7 μg L^{-1} 3.9 μg L^{-1} Resin B 1.2 μg L^{-1} 2.6 μg L^{-1}	Fordham et al. 1995
Study of the Sb content in water packed in PET bottles sold in Canada and Europe.	ICP-MS	Sb content in water sold in Canada varied between 112 and 375 ng L^{-1}. The Sb results relating to the samples collected in Europe varied between 6 and 700 ng L^{-1}, the median being 343 ng L^{1}	Shotyk et al. 2006
Study of the Sb content in sparkling and still citric fruit juices packed in PET bottles.	ICP-MS	The Sb concentration present in the samples varied between 0.28 and 1.05 μg L^{-1}.	Hansen and Pergantis 2006
Study of the Sb content in water sold in 28 countries.	ICP-MS	Origin Sb content Japan 9 to 150 ng L^{-1} 16 different Countries 8.9 to 2570 ng L^{-1}	Shotyk and Krachler 2007
Study of the Sb and others elements content in water bottled in various types of packaging, in 132 brands from 28 countries.	ICP-MS	The Sb concentration in the samples ranged from 0.0001 to 2.57 μg L^{-1}.	Krachler and Shotyk 2009
Study of the Sb content in water sold in southwestern USA.	ICP-MS	The Sb concentration present in the samples, stored at 22 °C, varied between 0.095 and 0.521 μg L^{-1}. Through mathematical modeling, it was concluded that exposure temperatures of 65 °C is necessary 38 days of contact to exceed the 6 μg L^{-1} (maximum contaminant level by USEPA) and exposure temperatures of 85 °C is necessary 1.3 days of exposure. The Sb content in the bottles was 213 ± 35 mg kg^{-1}	Westerhoff et al. 2008
Study of the influence of temperature, light and duration of storage on the migration of Sb in sparkling and still mineral water in samples sold in Hungary in PET bottles.	Microwave to digest sample and Sb quantified in ICP-MS	The Sb content in the bottles ranged from 210 to 290 mg kg^{-1} The average content in still water was 0.26 ± 0.16 μg L^{-1} and in sparkling water it was 0.4 ± 0.22 μg L^{-1}. Illumination and increased storage temperature augmented the Sb concentration (reaching 2 ng Sb/mL at 60 °C for 3 days or at 70 °C for 9 h).	Keresztes et al. 2009
Comparative study between mineral water sold in Europe in glass bottles and PET bottles with different color.	ICP-MS	Comparing the same brands of water, the Sb content in a glass bottle was 0.016 μg L^{-1} and in PET bottles it was 0.326 μg L^{-1}. Sb migration increases with dark colored bottles as compared to clear bottles	Reimann et al. 2010
Study of the Sb content in PET bottles sold in Europe and study of the migration of Sb through a mathematical model.	Microwave to digest sample and Sb quantified in ICP-MS	The average Sb concentration value present in PET bottles was 224 ± 32 mg kg^{-1}. Through mathematical modeling it was concluded that in the worst case of contact, Sb migration will be lower than 40 μg L^{-1}	Welle and Franz 2010
Development of a new analytical method and a study of the Sb content in bottled water, sold in three regions of Brazil.	Combined technique of fast sequential flame atomic absorption spectrometry (FS-FAAS) and atomic absorption Spectrometry with hydride generation in continuous flow (CF-HGAAS)	The concentration of Sb present in the samples ranged from 0.14 to 0.61 μg L^{-1}.	Guerra et al. 2011
Study of the influence of temperature on the migration of Sb in mineral water in a sample sold in Europe in a 1.5 L PET bottle, after 7 days of contact.	ICP-MS	Results in μg L^{-1} 2 °C 22 °C 45 °C 60 °C 80 °C Average 0.003 0.012 1.24 2.75 10.9 Maximum 0.023 0.054 1.52 3.32 15.8 Increased storage temperature augmented the Sb concentration.	Reimann et al. 2012
Study of the Sb content in sparkling water, still water and enriched still water, sold in Boston. The still waters were packed in bottles made out of PET, polyethylene (PE), polystyrene (PS) and polycarbonate (PC), while the other types of water were only packed in PET bottles.	ICP-MS	In the samples of sparkling water, the Sb content corresponded to between 55 and 617 ng L^{-1}, having increased 15 to 92% after 60 days of contact. In the samples of non-carbonated and enriched water, the Sb content corresponded to between 77 and 1191 ng L^{-1}, having increased 22 to 105% after 60 days of contact. In the samples of non-carbonated water, the Sb content corresponded to between 0.3 and 473 ng L^{-1}, and after 60 days of contact, the Sb content corresponded to between 4 and 634 ng L^{-1}.	Andra et al. 2012
Study of the Sb content in water and soft drinks sold in Great Britain and Nigeria and the influence of temperature, reuse and the area of contact.	ICP-MS	The Sb concentration present in all the samples ranged from 0.033 to 6.61 μg L^{-1}.	Tukur et al. 2012
Study of the SB concentration in PET bottles and the migration to water simulants, 4% acetic acid and 50% ethanol at temperatures of 25 °C, 40 °C, 55 °C and 70 °C.	Graphite furnace atomic absorption spectrometry (GFAAS)	The migration of Sb was found to increase gradually with storage time and temperature and the 4% acetic acid solution presented the highest migration level.	Rungchang et al. 2013

Table 1 (continued)

Samples investigated	Analytical technique	Results for antimony	References
Study on the Sb concentration in a PET bottle and the migration to the simulant distilled water, 3% acetic acid, 10 and 20% ethanol, olive oil and sunflower oil.	Microwave to digest sample and Sb quantified in ICP-MS and HG-AFS	The antimony concentration in PET bottles was between 269 and 276 mg kg^{-1}. The 20% ethanol solution presented the highest migration level, 1.3 µg L^{-1} after 10 days of contact at 40 °C.	Sánchez-Martínez et al. 2013
Study on the effect of temperature on the migration of PET bottle substances to mineral water, both sparkling and still.	ICP-MS	The antimony concentration was 0.5 µg L^{-1} after being stored at 40 °C for 10 days and 3.5 µg L^{-1} after being stored at 60 °C for 10 days observing the influence of temperature on the migration of antimony and the Sb concentration was twice as high in sparkling water, evidencing the influence of carbon dioxide in the migration of Sb.	Bach et al. 2013
Study on the Sb concentration in a PET bottle to mineral water and the influence of time and temperature of the migration of the Sb into water.	Microwave to digest sample and Sb quantified in ICP-MS and HG-AFS	The antimony concentration in PET bottles was between 191 and 268 mg kg^{-1}. The migration of Sb to drinking water, when stored at temperatures of 40 and 60 °C, is accelerated over time. For samples stored at 4 and 20 °C there were no significant differences in Sb concentration in water over time. The 20% ethanol solution presented the highest migration level, 1.3 µg L^{-1} after 10 days of contact at 40 °C.	Carneado et al. 2015
Study on the Sb concentration for 19 brands of mineral water sold in China and the migration of Sb and bisphenol A into mineral water.	ICP-MS	The antimony concentration in PET bottles was between 104 and 166 mg kg^{-1}. The average Sb migration after 1, 2, and 4 week storage at 70 °C was 211, 316, and 448 ng L^{-1}, respectively.	Fan et al. 2014
Study on the Sb concentration in a PET bottle and the migration of Sb into wine, soft drink and acetic acid simulant.	Graphite furnace atomic absorption specphotometer (GFAAS)	The antimony concentration in PET bottles was between 194 to 323 mg kg^{-1}. The media migration of Sb was below the LOD to the different liquids.	Jesus et al. 2016

decontaminated by immersion in a 20% (*v/v*) nitric acid solution for 12 h, and then rinsed with ultrapure water. All chemical reagents were of analytical grade. Nitric, sulfuric, and acetic acids and hydrogen peroxide, obtained from Merck, were used. The calibration solutions of Sb were prepared from dilutions of the stock solution TraceCERT® containing 1000 mg L^{-1} of Sb (Fluka, Switzerland). Certified reference materials (CRM) on low-density polyethylene (LDPE) from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), ERM-EC681k and ERM-EC680k, were also used. To our knowledge, there are no CRMs for antimony in PET, and thus, LDPE was considered the most similar material to PET available.

Sample Description

As described in Table 3, 19 samples of soft drinks from eight different manufacturers and with different capacities, packaged in PET bottles, were collected in supermarkets in Campinas—São Paulo, Brazil. Products with a production date no greater than 20 days were chosen, in order to minimize the influence of the time of contact in the specific migration assays.

Determination of Antimony in PET

The digestion of the samples of PET bottles was performed based on the method proposed by Kiyataka et al. (2014, 2015) in a closed system, using HPA-S. Approximately 3 g of each sample (PET bottles) was cut into small pieces (1 cm × 1 cm, approximately) and rinsed with ultrapure water. A 300-mg portion of each sample was then weighed and introduced into a quartz digestion vessel of the HPA-S equipment.

In order to optimize the digestion parameters, three digestion programs and five different reagent mixtures were tested, resulting in seven procedures, as shown in Table 4. For the initial tests, a green PET sample was used. After digestion, each sample was diluted to a final volume of 25 mL with ultrapure water. To determine the procedure for digestion of PET, the absence of opacity, supernatant, and precipitate after the digestion were ascertained. In addition to the visual analysis of the digested material, the concentration of residual carbon was measured by ICP-OES, in order to ascertain the efficiency of the digestion of the samples, using the method described by Gouveia et al. (2001). We used a standard curve in the range 0.1% up to 1.0% m/v C; the source of carbon was glucose and 193.030 nm wavelength was used.

Table 2 Experimental conditions used on ICP-OES equipment	RF power (W): 1300	Main argon flow rate (L min^{-1}): 15
	Torch configuration: axial	Auxiliary argon flow rate (L min^{-1}): 0.2
	Sample flow (mL min^{-1}): 1.5	Nebulizing flow rate (L min^{-1}): 0.60
	Integration and reading time (s): 10	Wavelength (nm): Sb:217.582

Table 3 Descriptions of the analyzed PET bottles

Samples	Packaging color	Flavor soft drink	Capacity (L)
A	Green	Lemon	2
B	Green	Guarana	3
C	Green	Guarana with tutti-frutti aroma	2
D	Green	Guarana	2
E	Green	Guarana	2
F	Green	Guarana	2
G	Colorless	Orange	2
H	Green	Guarana	2
I	Green	Lemon	2
J	Colorless	Cola	3
K	Green	Guarana	2
L	Green	Apple/grapefruit/orange/lemon	1
M	Green	Guarana	2
N	Green	Lemon	2
O	Colorless	Grape	2
P	Pink	Lemon	1.5
Q	Green	Lemon	2
R	Colorless	Cola	2
S	Green	Guarana	2

Determination of Antimony in Soft Drink

The quantification of antimony in the soft drink was performed at day 0 (the date on which the sample was acquired) and after 180 days of storage at 35 °C ± 3 °C. The soft drink samples were transferred from the PET bottles to polyethylene flasks previously cleaned with 20% nitric acid and maintained for 2 h for degasification in an orbital shaker. After degasification, 5 g of each soft drink sample was weighed and diluted with 5 g of 20% nitric acid (v/v) (FROES et al. 2009).

Migration of Antimony into Simulant (3% Acetic Acid Solution)

The specific migration of Sb into 3% acetic acid solution as food simulant followed the methodology established by norm EN1186-1:2002 (European Committee for Standardization 2002), according to Resolution RDC no. 51/2010 (BRASIL 2010). The packagings were emptied and rinsed with ultrapure water and were kept in contact with a 3% acetic acid solution at 40 °C for 10 days, using a standard ratio of area of material per volume of simulant of 6 $dm^2 kg^{-1}$ (total immersion), and, after contact, an assessment of the Sb was performed directly on the simulant by ICP-OES.

Results and Discussion

Antimony in PET

Table 5 presents the results obtained after the digestion procedure assays and the residual carbon content. Procedure 3 (Table 4) was selected for the digestion of the PET samples, as it presented a colorless solution without supernatant and precipitate and carbon content below than 1%. Furthermore, it requires a shorter digestion time and a smaller quantity of sulfuric acid (0.75 mL), compared to the procedures 4, 6, and 7.

The calibration curve was established using Sb aqueous standard solutions, and a linear calibration function was fitted to the calibration data using the method of least squares,

Table 4 Procedures used in the digestion of PET bottles

Procedures	Reagents	Step	Ramp time (min)	Temperature (°C)	Duration (mind)
1	3 mL of HNO_3	1	20	250	10
		2	15	320	200
2	3 mL of HNO_3 + 1 mL of H_2O_2	1	20	250	10
		2	15	320	200
3	3 mL of HNO_3 + 0.75 mL of H_2SO_4	1	25	280	15
		2	20	320	180
4	3 mL of HNO_3 + 1 mL of H_2SO_4	1	25	280	15
		2	20	320	180
5	3 mL of HNO_3 + 0.5 mL of H_2SO_4	1	25	280	15
		2	20	320	210
6	3 mL of HNO_3 + 0.75 mL of H_2SO_4	1	25	280	15
		2	20	320	210
7	3 mL of HNO_3 + 1 mL of H_2SO_4	1	25	280	15
		2	20	320	210

Table 5 Result of PET digestion

Procedure	Aspect	Residual carbon (%)
1	Solution with supernatant and white precipitate	5.5
2	Solution with supernatant and white precipitate	4.9
03	Clear solution and not precipitate	<1.0
4	Clear solution and not precipitate	<1.0
5	Clear solution and not precipitate	2.3
6	Clear solution and not precipitate	<1.0
7	Clear solution and not precipitate	<1.0

calculated using the WinLab32™ software application for each analysis performed. The coefficients of correlation (r) of all the curves were 0.999 or greater in the range 0.1 to 8.0 mg L^{-1}; the analytical curve was prepared in solution of nitric acid 3% (v/v).

In order to determine the limits of detection (LOD) and quantification (LOQ) for Sb in the PET, seven independent readings of the blank were performed. The LOD and LOQ were calculated based on the average (X) and standard deviation (s) of these assessments (LOD = X + 3.1 s and LOQ = X + 10 s) according to INMETRO (2011).

The LOD and LOQ for antimony in PET were 60.0 and 138.1 μg L^{-1}, respectively. The LOQ expressed in milligrams per kilogram of PET, assuming a dilution of 83.3 times, was 11.5 mg kg^{-1}.

The accuracy of the method for determining Sb in the PET packaging was evaluated using two certified reference materials (CRMs), ERM-EC681k and ERM-EC680k, as per the procedure described in INMETRO (2011). The results obtained for Sb, in the two CRMs, were within the confidence intervals of the certified reference materials and had a relative difference lower than 10.9% (Table 6). Therefore, the method showed good accuracy.

The precision of the method for analyzing the packaging was evaluated through repeatability, using two CRMs (ERM-EC681k and ERM-EC680k), according to INMETRO (2011). Precision was assessed by comparing the coefficient of

variation (CV) obtained by CRMs with the values calculated by the Horwitz equation (Horwitz 1982). INMETRO (2011) recommends that the CV of the sample should be lower than the value calculated by the Horwitz equation. The antimony concentration obtained for the two certified reference samples showed lower coefficients of variation than those calculated using the Horwitz equation; for the CRM ERM–EC 681 k, the CV was 1.5% and the value calculated by Horwitz equation was 8.0%, and for the CRM ERM–EC 680 k, the CV was 10.4%, and the value calculated by Horwitz equation was 11.1%. Therefore, the method showed adequate precision.

Table 7 shows the results of the total quantification of Sb in the various samples of PET bottles. In the 19 samples of PET bottles studied, the Sb content varied from 272.2 to 640.5 mg kg^{-1}. According to Welle and Franz (2011), the average Sb content of 67 PET bottle samples from Europe was 224± 32 mg kg^{-1}. Jesus et al. (2016) analyzed six PET bottle samples from Brazil, and the Sb content varied between 194 and 323 mg kg^{-1} of Sb.

The results obtained in this study displayed concentrations higher than those observed by the before mentioned authors and six among analyzed samples contained Sb over than 350 mg kg^{-1}, which is the limit recommended by BfR (2011). All samples were of green color, which may indicate that the masterbatch used may be another source of Sb.

Shimamoto et al. (2011) analyzed a PET bottle of water and soft drinks obtained in the region of Campinas using the X-ray fluorescence technique by energy dispersion (EDX-RF) and found concentration of Sb varying between 2.4 and 11 mg kg^{-1}, lower than the values detected in the present study. Besides the differences in the samples, these variations may be explained by the occurrence of interference of the standard used in the calibration curve for the quantification of Sb by the EDX-RF technique.

Migration of Antimony into the Soft Drink and Simulant

The calibration curve was established using Sb aqueous standard solutions. Coefficients of correlation (r) of all the curves were 0.999 or greater in the range 10.0 to 60.0 μg L^{-1}. Sb migration into acetic acid 3% was determined using an

Table 6 Certified values and values obtained and relative error in the measurements of Sb in the reference materials: ERM-EC681k and ERM-EC680k

Reference material	Certified value (mg kg^{-1})[a]	Value obtained (mg kg^{-1})[b]	Relative difference (%)
ERM-EC681k	99 ± 6	99.6 ± 1.5	0.6
ERM-EC680k	10.1 ± 1.6	11.2 ± 1.2	10.9

The average value plus standard deviation for ten replicate measurements

[a] Average ± expanded uncertainty

[b] Average ± standard deviation

Table 7   Levels of Sb in the PET bottles in mg kg^{-1}

Samples/packaging color/flavor	Sb (mg kg^{-1})
A/green/lemon	640.5 ± 9.5
B/green/guarana	637.7 ± 7.5
C/green/guarana with tutti-frutti aroma	624.3 ± 24.9
D/green/guarana	620.9 ± 10.3
E/green/guarana	605.5 ± 3.1
F/green/guarana	561.4 ± 2.3
G/colorless/orange	317.2 ± 14.9
H/green/guarana	315.0 ± 13.7
I/green/lemon	311.3 ± 2.1
J/colorless/cola	308.8 ± 5.5
K/green/guarana	308.4 ± 2.9
L/green/apple/grapefruit and orange and lemon	301.8 ± 0.7
M/green/guarana	300.4 ± 0.1
N/green/lemon	294.2 ± 0.0
O/colorless/grape	283.0 ± 9.7
P/pink/lemon	279.4 ± 5.7
Q/green/lemon	275.6 ± 0.1
R/colorless/cola	273.7 ± 0.5
S/green/guarana	272.2 ± 0.9

The average value plus standard deviation for two replicate measurements

Average ± standard deviation

Table 8   Recovery of Sb in soft drink and in 3% acetic acid solution

Added concentration (µg L^{-1})	Recovery in softy drink (%)[a]	Recovery in 3% acetic acid (%)[a]
30	100.5 ± 4.1	101.4 ± 3.6
40	97.2 ± 0.4	96.6 ± 4.1
50	96.1 ± 1.5	101.0 ± 0.8

The average value plus standard deviation for three replicate measurements

[a] Average ± standard deviation

analytical curve prepared in solution of acetic acid 3%, and the quantification of Sb in soft drinks was assayed using an analytical curve prepared in solution of nitric acid 3% (v/v).

LOD and LOQ for migration of antimony into solution of acetic acid 3% were 9.0 and 23.5 µg L^{-1}, respectively. They were calculated based on the average (X) and standard deviation (s) of these assessments (LOD = X + 3.1 s and LOQ = X + 10 s) according to INMETRO (2011).

For the determination of Sb migrating into the soft drink, the LOQ was obtained from the value of the first point of the analytical curve (10 µg L^{-1}) multiplied by the dilution of sample factor (2), resulting in an LOQ of 20 µg L^{-1} (INMETRO 2011).

The LOQ determined in this study, both for the specific migration of Sb to the solution of 3% acetic acid and to the soft drink, were higher than those in some of the studies already published (Shotyk et al. 2006; Welle and Franz 2011; Guerra et al. 2011). However, they met the proposed objectives as they were lower than the limit of 40 µg kg^{-1} established by European Regulation 10/2011 (EC 2011) and Brazilian Resolution 17/2008 (BRASIL 2008).

A recovery study by adding three standard concentrations to the solution of 3% acetic acid and to the cola-flavored soft drink was also performed before the ICP OES analyses, aiming to the evaluation of the method accuracy (AOAC

2013). According to AOAC International (2013), for a concentration of 10 µg kg^{-1} of analyte, there is an acceptable variation range between 70 and 125%. Therefore, the method utilized was acceptable, given that the recovery of the Sb in the soft drink and 3% acetic acid varied from 96.1 to 101.4% (Table 8).

For all samples evaluated, the concentrations of Sb on day 0 were below the LOQ. After 180 days of storage at 35 °C, no migration from the PET bottles into soft drinks above the LOQ was detected. Therefore, the Sb present in all analyzed PET bottles did not migrate into the soft drinks.

The results obtained in the study of the Sb migration into 3% acetic acid solution were below than the LOQ (23.5 µg L^{-1}). In this way, it can be seen that, despite the presence of Sb in the packaging studied, migration did not occur above the LOQ for the solution of 3% acetic acid after 10 days of contact at 40 °C. These results are in agreement with the studies reported by several authors, shown in Table 1, which shows Sb migration to water, juice, and soft drink below 20 µg L^{-1}.

According to ABIPET (2013), 57.1% of materials manufactured using PET resin in Brazil are recycled. Given that in 2011, consumption in the country of PET packaging for water, soft drinks, and edible oils was 515,000 kg and the average concentration of Sb in the 19 samples studied was 396.4 mg kg^{-1}, it can be estimated that approximately 87,579 kg of antimony from PET packaging are disposed every year in Brazil, and this could lead to environmental damage.

Conclusions

The method of PET packaging decomposition in a closed high pressure system (HPA) and quantification by ICP OES was duly validated and seen to be adequate for the determination of Sb. This enabled the quantification of the element by a simple, relatively inexpensive method in comparison with the ICP-MS. All of the packaging analyzed presented Sb content above the LOQ and several samples presented high quantities of the element. This may be explained by the use of the antimony trioxide catalyst in the manufacture process of the samples studied. All the samples complied with the limit of

specific migration for Sb established by both Brazilian and European legislation for food contact materials. Migration of Sb into soft drinks was found below the quantification limit of the used method. As its limit of quantification is quite inferior to the Sb specific migration maximum limit established by the legislation, there is no risk for the consumers. On the other hand, considering the quantity of Sb present in PET packaging, it is possible that environmental damage ensues if these packages are not adequately recycled or are disposed of in the environment.

Compliance with Ethical Standards

Conflict of Interest Paulo Henrique M. Kiyataka declares that he has no conflict of interest. Sílvia T. Dantas declares that she has no conflict of interest. Aline Cristina Albino declares that she has no conflict of interest. Juliana Azevedo Lima Pallone declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Informed consent was obtained from all individual participants included in the study.

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