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Migration of antimony from polyethylene terephthalate bottles to mineral water: Comparison between test conditions proposed by Brazil and the European Union

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ABSTRACT

This work evaluated the Sb content in polyethylene terephthalate (PET) bottles of mineral water, as well as the migration of Sb, according to the conditions established by Brazilian and European Union (EU) legislation. The total Sb content in the PET bottles was determined by the mineralization of the packaging followed by quantification by inductively coupled plasma optical emission spectrometry (ICP-OES). The migration of Sb from the bottle to the mineral water was carried out after the contact conditions established by Brazilian and EU legislation (40 °C for 10 days and 60 °C for 10 days, respectively). The migrated Sb content was determined directly in the solution, after pre-reduction with L-cysteine, using an ICP-OES coupled with a hydride generator. All evaluated packages showed Sb levels ranging from 173 mg kg^{-1} to 253 mg kg^{-1}. The migration of Sb to the mineral water after 10 days at 40 °C in contact with PET bottles was lower than the limit of quantification and after contact at 60 °C for 10 days it was between 1.59 and 4.42 μg L^{-1}. The highest contact temperature established by the EU favored Sb migration. However, all Sb migration results are within the limits established by Brazilian and EU legislation.

1. Introduction

Brazil is the fourth consumer market for mineral water in the world, considering mineral water sold in packages of up to 10 liters (Datamark, 2017). In 2021, the volume of production sold was 13.2 million liters, an increase of 4.7% compared to 2020. Brazilian per capita consumption in 2021 was 62 liters of mineral water, an increase of 3.9% compared to the previous year (ABIR, 2022). The global bottled water market grew by an average of 6.4% per year from 2012 to 2017. Several factors can be associated with this growth, including population growth, environmental pollution, climate change and the perception of health risks (Cardozo et al., 2021). In this market, packaging is extremely important for the conservation and distribution of the drink. The material most commonly used to produce water bottles is polyethylene terephthalate (PET) (Becerra-Herrera et al., 2022).

Antimony trioxide (Sb_2O_3) is used as a catalyst in the poly condensation stage for the manufacture of bottle grade PET resin (Carneado et al., 2015; Mohammadi and Enayati, 2022; Shotyk and Krachler, 2007). The PET manufacturing process is not able to recover 100% of the catalyst, therefore a residual of antimony (Sb) is retained in the resin and can migrate to food products (Magana-Maldonado et al., 2022; Ozaki et al., 2022). Germany is the only country that has an established limit for Sb in PET packaging, with a maximum limit of 350 mg kg^{-1} PET (BfR, 2011). Some studies, on the evaluation of the total concentration

Abbreviations: EU, European Union; FCMs, food contact materials; FS-FAAS, flame atomization sequential fast atomic absorption spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; HG-AAS, hydride generation atomic absorption spectrometry; HG-AFS, hydride generator atomic fluorescence spectrometry; HG-MP-AES, hydride generator microwave plasma atomic emission spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; LOD, limit of detection; LOQ, limit of quantification; PET, polyethylene terephthalate; Sb, antimony; Sb_2O_3, antimony trioxide.

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of Sb in PET bottles from different countries, have already been conducted and showed variation in the reported values (Filella, 2020). For example, in Spain the concentration of Sb in PET bottles varied between 191 and 268 mg kg^{-1} (Carneado et al., 2015), in China between 104 and 166 mg kg^{-1} (Fan et al., 2014), in Mexico between 73 and 11 mg kg^{-1} (Chapa-Martínez et al., 2016) and in EU countries 224 mg kg^{-1} (Welle and Franz, 2011).

Still in this context, Sb_2O_3 is on the list of priority pollutants by the USEPA ("United States Environmental Protection Agency") and the EU (Hansen and Pergantis, 2006). Constant consumption of water with a high level of Sb can increase the level of cholesterol and also decrease blood sugar. Sb_2O_3 is classified as a possible human carcinogen by the International Agency for Research on Cancer - IARC (ATSDR, 2017). Therefore, in order to ensure that there is the necessary control over any substance that can be transferred from the packaging to the packaged food, legislation on food contact materials (FCMs) was elaborated and established, such as packaging (Coltro et al., 2023; Marangoni Júnior et al., 2022). These regulations are based on restricting the use of potentially toxic substances in the composition of the material and controlling migration. Such restrictions are usually made through positive lists, with the substances that can be used in the formulation of FCMs and in the definition of a total migration limit. When necessary, based on data concerning the toxicity of certain substances, specific restrictions such as specific migration limit or compositional limit of the substance in the packaging material are established (Padula, 2010).

In Brazil, the Resolution of the Collegiate Board - RDC No. 326/2019 (Brazil, 2019) published by the National Health Surveillance Agency (Anvisa), establishes a positive list of additives for plastic materials intended for the preparation of packaging and equipment in contact with food. The Resolution authorizes the use of Sb_2O_3 in the manufacture of PET resin and establishes a specific Sb migration limit of 40 μg L^{-1}, for all foods and beverages, except for mineral water, which has the limit defined as 5 μg L^{-1} by RDC No. 717/2022 (Brazil, 2022). The same limit is established for the EU in Directive 10/2011 (European--Commission, 2011).

In order to guarantee the analytical quality in the quantification of Sb in mineral water, it is essential to use a technique which has adequate accuracy and precision and limits of detection and quantification, below the maximum limit allowed for Sb by the different countries. The most widely applied techniques for the determination of Sb in water are graphite furnace atomic absorption spectrometry (GF-AAS) or with hydride generation (HG-AAS), inductively coupled plasma mass spectrometry (ICP-MS), hydride generator atomic fluorescence spectrometry (HG-AFS) and flame atomization sequential fast atomic absorption spectrometry (FS-FAAS) (Bach et al., 2013; Guerra et al., 2011; Jesus et al., 2016; Shotyk and Krachler, 2007; Tukur et al., 2012; Zhang et al., 2021).

In addition to these techniques, the use of optical emission spectrometry with inductively coupled plasma (ICP-OES) to quantify Sb in water, at a concentration below 5 μg L^{-1}, is a possibility when performing the generation of antimony hydride (Long et al., 2012; Pohl and Jamroz, 2011). Hydride generation increases selectivity and sensitivity, since almost 100% of the analyte is transported to the plasma and the atomization and excitation steps of the elements are more efficient, because they spend less energy in the desolvation and vaporization processes, because the analyte is in gaseous form. Both pentavalent antimony (Sb^{+5}) and trivalent antimony (Sb^{+3}) form hydride, but the reaction kinetics of Sb^{+5} is slower, so all Sb ions need to be in the trivalent form to react with the reducing agent. To ensure this condition, there is a need to carry out a pre-reduction reaction using a reducing agent. For this purpose, L-Cysteine, thiourea or potassium iodide with ascorbic acid are the most used (Andrade et al., 2017; Long et al., 2012).

In addition to the analytical methods used to quantify Sb, sample preparation conditions must be followed in accordance with applicable legislation. In this sense, to verify the adequacy of the PET packaging in relation to the specific migration of Sb, the packaging must be in contact with the aqueous simulant (water) for 10 days. The temperature used in the tests may vary according to each legislation. In Brazil, RDC No. 51/10 establishes the temperature of 40 ºC (Brazil, 2010) and in Europe, Directive 10/2011 establishes the temperature of 60 ºC (European--Commission, 2011). In this sense, as these legislations present different temperature conditions, it is crucial to carry out a study addressing the different contact conditions to assess the impact of each one on Sb migration.

Thus, to the best of our knowledge, no investigations have been published that used the ICP-OES technique to quantify Sb in mineral water, only to quantify Sb in PET bottles, which is the main novelty of this research. Added to this, it is the first time that the test conditions established by Brazilian and EU legislation are compared in the same research for Sb migration. Therefore, this study aimed to quantify the Sb content present in PET bottles and in migration tests for mineral water sold in Brazil. Therefore, the Sb quantification method in PET bottles and mineral water was performed by ICP-OES with a hydride generator. In addition, Sb migration from PET bottles to mineral water was evaluated using the time and temperature conditions established by Brazilian and EU legislation.

2. Materials and methods

2.1. Samples

Nineteen samples of water packed in PET bottles, made with virgin resin, with volumes between 300 and 510 mL were purchased in stores in the city of Campinas, São Paulo, Brazil, as described in Table 1. The products were chosen considering a limit of 25 days since its production date, in order to minimize the influence of the contact time in the specific migration evaluation tests, from different manufacturers in the country. For each sample (brand) of mineral water, 9 units of the same batch were purchased.

2.2. Reagents and instruments

Hydrochloric acid (HCl) 37% (m/m) and analytical grade sodium hydroxide (Merck, Germany), analytical grade sodium borohydride (Vetec) and L-cysteine hydrochloride monohydrate P.A (Synth, Brazil) were used. The solutions were prepared with deionized water with a resistivity of 18.2 MΩ cm^{-1}, purified in Millipore's Milli-Q system (Bedford, USA). The Sb solutions for the calibration curve in the ICP-OES were prepared from dilutions of TraCert stock solutions, containing 1000 mg L^{-1} (Fluka Analytcal, Switzerland). The glassware and flasks used were previously decontaminated in a 20% (v/v) HNO_3 solution,

Table 1
Information about mineral water in PET bottles.

Sample	Manufacturer	PET bottle color	Volumetric Capacity (mL)
S1	X	green	300
S2	Y	colorless	510
S3	Z	colorless	500
S4	K	colorless	510
S5	L	colorless	510
S6	M	colorless	500
S7	N	colorless	510
S8	O	colorless	510
S9	P	colorless	510
S10	M	colorless	350
S11	M	colorless	500
S12	Q	dark blue	510
S13	R	colorless	510
S14	Q	dark blue	510
S15	S	colorless	500
S16	T	blue	500
S17	U	colorless	500
S18	V	dark blue	510
S19	W	light blue	510

leaving them in contact with the acid solution for at least 12 h. After this period, they were washed with purified water in a Millipore Elix system.

All determinations of Sb concentrations were performed using an ICP-OES (Optima 2000DV, Perkin Elmer, Shelton, CT, USA). A Mira Mist nebulizer with a cyclonic chamber was used to quantify Sb in the bottle, and a hydride generator system was coupled to the ICP-OES for Sb analysis in mineral waters. The parameters used for the operation of the ICP-OES are shown in Table 2. The entire system was controlled by the WinLab32™ software (Perkin Elmer, USA).

2.3. Sb quantification in PET bottle

The total Sb content in the PET bottle samples was determined according to the method proposed and validated by (Kiyataka et al., 2018), in which 300 mg of PET sample was mineralized in a high pressure digester (HPA) using 3 mL of HNO_3 and 0.75 mL of H_2SO_4, the mixture was heated to 280 °C and held for 15 min, after this time the mixture was heated to 320 °C and held for 180 min. The sample was diluted to 25 mL with deionized water and Sb quantification was performed on the ICP-OES.

2.4. Migration of Sb from PET bottles to mineral water

2.4.1. Contact conditions

For each sample (brand) of mineral water, three units were used to quantify the initial Sb content in the water. Three other packages were conditioned at 40 ºC for 10 days, equivalent to prolonged contact at temperatures of up to 40 ºC for a period longer than 24 h, as established by Resolution RDC No. 51/2010 (Brazil, 2010). Other three units were stored in a condition which simulates the storage time of over 6 months at room temperature, 60 ºC for 10 days, as established by European Regulation 10/2011 (European-Commission, 2011).

2.4.2. Sb pre-reduction for hydride generation and migration evaluation of Sb PET bottle to mineral water

The use of L-Cysteine in the reduction of pentavalent antimony to trivalent antimony under acidic conditions is well described in the literature (Andrade et al., 2017; Sánchez-Martínez et al., 2013) and was used in the mineral water samples of this study. After the contact time established in item 2.4.1., 1 mL of concentrated hydrochloric acid and 1 mL of 18% L-cysteine (w/v) were added to 10 mL of sample. Subsequently, the mixture was heated at a temperature greater than 90 °C for 15 min. After the sample cooling, the antimony content was quantified directly on the ICP-OES with a hydride generator, using a sodium borohydride solution (1%) in an alkaline medium as the reducing agent.

2.5. Analytical control of parameters for quantification of Sb in mineral water

For the evaluate of the Sb quantification method in mineral water, a sample of mineral water was used, packaged in a 510 mL PET container. The parameters evaluated were linearity, limits of detection (LOD) and quantification (LOQ), accuracy and precision (Inmetro, 2020).

Table 2
Experimental conditions used in the ICP OES equipment.

Parameter	Value/Condition
Plasma power	1500 W[(1)] and 1300 W[(2)]
Observation height	15 mm[(1) (2)]
Torch configuration	Axial[(1) (2)]
Main argon flow rate	17 L min^{-1} [(1)] and 15 L min^{-1} [(2)]
Auxiliary argon flow rate	0.2 L min^{-1} [(1) (2)]
Nebulizing flow rate	0.6 mL min^{-1} [(1) (2)]
Wavelength	Sb: 217.582[(1) (2)]

[(1)] ICP-OES conditions with hydride generator
[(2)] ICP-OES conditions with Mira Mist nebulizer

The linearity of the analytical curve was verified using the WinLab32™ software of the ICP-OES equipment, in the concentration range of 1 μg L^{-1} to 15 μg L^{-1} (7 points: 1.0, 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 μg L^{-1}) and a linear calibration function was fitted to the calibration data using the method of least squares, calculated for each analysis performed. The coefficients of correlation (r) of all the curves were 0.999 or greater.

In order to determine the limit of detection, 7 evaluations of the analytical blank were performed, consisting of 10 mL of water, 1 mL of concentrated hydrochloric acid and 1 mL of 18% L-cysteine. The detection limit was calculated according to Equation described in Inmetro (2020).

The standard establishes that the LOD obtained must be confirmed through the analysis of independent samples at the same concentration level. Confirmation of the LOD happened using two concentrations close to the obtained LOD. In this case, the LOD was verified after reading 7 repetitions of a sample of ultra-purified water (obtained in a milli-Q system) fortified with Sb at concentrations of 0.5 μg L^{-1} and 0.6 μg L^{-1}. For all repetitions, the presence of Sb was detected, for the sample fortified with 0.5 μg L^{-1}. For analysts quantification limit at trace level, it is recommended to adopt the limit of quantification (LOQ) as the lowest concentration of the analytical curve, therefore, the smallest point on the analytical curve, 1.0 μg L^{-1}, was adopted as the quantification limit in this study. The accuracy assays of the method for determining Sb in mineral water was verified by performing recovery tests at three concentrations of the Sb standard (2.5, 5.0 and 15.0 μg L^{-1}) and calculated according to Equation described in Inmetro (2020), using the concentration of the analyte in the fortified sample, the concentration of the analyte in the unfortified sample and the concentration of the analyte added to the fortified sample. In this case, the recovery was determined by adding three concentrations of the antimony standard to a sample of mineral water with a concentration of 2.89 μg L^{-1}. The recovery evaluation is a function of the concentration and the objective of the analysis, and establishes for a concentration of 10 μg kg^{-1} an acceptance range of 60–115% of variation (Inmetro, 2020).

The precision of the method for Sb quantification was evaluated through repeatability, fortifying with three different concentrations (2.5, 5.0 and 15.0 μg L^{-1}) of water sample obtained by milli-Q, with concentration lower than the LOD and a sample of mineral water, with a concentration higher than the LOQ. Considering the results, the sample standard deviation was calculated and the repeatability was expressed as a coefficient of variation.

3. Results and discussion

3.1. Determination of Sb in PET bottles

The results obtained for the Sb concentration in PET bottles are presented in Table 3. The maximum Sb content that can migrate to the water was also calculated, in case all the Sb present in the PET bottle migrated to the beverage. For this, the total Sb content was multiplied by the weight of the bottle and divided by the volume of water described on the package label.

The total Sb content present in the analyzed bottles ranged from 173 mg kg^{-1} to 253 mg kg^{-1}. Therefore, all evaluated samples would meet the limit of total Sb in PET of 350 mg kg^{-1}, established by Germany (BfR, 2011). Furthermore, these values are similar to others already reported in studies published in other countries, as shown in Table 4. In the studies, the authors used different analytical techniques, with emphasis on the ICP-MS. Finally, considering that 100% of the Sb migrated to the water, the maximum expected concentration of Sb in mineral water would be 5.1 mg L^{-1} to 11.7 mg L^{-1}, approximately 1000–2300 times higher than the established limit of Sb for mineral water, which is 5 μg L^{-1} defined by RDC No. 717/2022 (Brazil, 2022) and Directive 10/2011 (European-Commission, 2011).

Table 3
Total Sb content present in the PET bottle in mg kg^{-1} and the maximum possible level of Sb migration to the water (1).

Sample	Total Sb content (mg kg^{-1}) (2)	Maximum possible content of Sb migration (mg L^{-1})
S1	253 ± 13	12
S2	253 ± 14	7.0
S3	202 ± 8	6.0
S4	218 ± 6	6.5
S5	220 ± 21	5.2
S6	211 ± 2	5.1
S7	228 ± 28	6.1
S8	216 ± 42	6.5
S9	221 ± 11	5.2
S10	182 ± 8	8.2
S11	236 ± 3	5.7
S12	173 ± 1	5.3
S13	252 ± 1	10
S14	236 ± 2	6.3
S15	234 ± 6	7.3
S16	233 ± 3	7.1
S17	236 ± 6	14
S18	236 ± 9	10
S19	211 ± 7	6.6

(1) Results of two determinations
(2) Mean ± standard deviation

Table 4
Concentration of Sb determined in PET bottle for mineral water evaluated in other countries.

Country	Analytical technique	Sb (mg kg^{-1})	Reference
Hungary	ICP-MS	210–290 (n = 10)	(Keresztes et al., 2009)
Nigeria	ICP-MS	178–287 (n = 14)	(Tukur et al., 2012)
England	ICP-MS	195–241 (n = 18)	(Tukur et al., 2012)
China	ICP-MS	104–166 (n = 16)	(Fan et al., 2014)
Spain	HG-AFS	191–268 (n = 3)	(Carneado et al., 2015)
Mexico	AFS	73–111 (n = 12)	(Chapa-Martínez et al., 2016)
Brazil	GF-ASS	194–323 (n = 12	(Jesus et al., 2016)
Germany	ICP-OES	231–257 (n = 27)	(Alassali et al., 2019)
Mexico	HG-MP-AES	154–279 (n = 4)	(Magana-Maldonado et al., 2022)

ICP- inductively coupled plasma; MS - mass spectrometry; HG - hydride gerenation; AFS - atomic fluorescence spectrometry; GF - graphite furnace; ASS - atomic absorption spectrometry; OES- optical emission spectrometry; MP - microwave plasma; AES - atomic emission spectrometry.

3.2. Analytical control of parameters for quantification of Sb in mineral water

The linearity of the standard curve was verified through the correlation coefficient (r) of the curve and showed a correlation greater than 0.999 in the range of 1.0 μg L^{-1} to 15.0 μg L^{-1}. The limit of detection (LOD) was 0.52 μg L^{-1} (mean = 0.15, standard deviation = 0.12 and t6 = 3.143, analysis on 7 samples). The LOD was calculated as the results between 0.46 μg L^{-1} to 0.61 μg L^{-1} and for the sample fortified with 0.6 μg L^{-1}, the results were between 0.59 μg L^{-1} to 0.75 μg L^{-1}. Therefore, the LOD of the method (0.52 μg L^{-1}) is possible to detect the presence of Sb in the samples.

For LOQ nine solutions with concentration of 1.0 μg L^{-1} were analyzed, and the average result obtained was 1.03 μg L^{-1}, standard deviation of 0.06 μg L^{-1}. Therefore, the method allows to quantify Sb in mineral water in concentration allowed by Brazilian legislation. In the literature, a LOD and LOQ of 0.003 μg L^{-1} and 0.010 μg L^{-1}, respectively, using ICP-MS, more expensive technique, and a LOD of 0.112 μg L^{-1} and a LOQ of 0.375 μg L^{-1} using HG-AFS to quantify Sb in mineral water has been reported (Sánchez-Martínez et al., 2013).

For recovery the results and the added concentrations are described in Table 5. The method presented accuracy, considering that the Sb recovery was in the range between 89.4% and 96.1%. For the precision of the method, two water samples were fortified. The Sample A Sb concentration was below the LOD and for sample B the water concentration was 2.89 μg L^{-1}. The variation coefficients results obtained are also described in Table 5. The acceptance criterion for repeatability, considering a concentration of 10 μg kg^{-1}, represents a maximum CV of 21% (Inmetro, 2020). Thus, the method presented precision, considering that the coefficients of variation of the repeatability test were below 4.8% for both fortified samples.

3.3. Migration of Sb from PET bottles to mineral water

The results obtained for the concentration of Sb in the mineral water samples, after zero day of contact (day of purchase), 10 days at 40 °C (Brazil, 2010) and 10 days at 60 °C (European-Commission, 2011), are presented in Table 6. In all the evaluated samples, the values obtained for the Sb concentration in the condition of zero day (day of purchase) and in the samples after conditioning for 10 days at 40 °C, were below the quantification limit of 1.0 μg L^{-1}. On the other hand, in 10 of the 19 samples submitted to 60 °C for 10 days (a condition established by the European regulation), the Sb migration value was in the range of 1.59–4.42 μg L^{-1}, below the maximum limit of 5.0 μg L^{-1} established by Anvisa legislation and the European (Brazil, 2022; European-Commission, 2011). The results obtained were similar to those found in the literature, with an average Sb concentration of 3.5 μg L^{-1} after storage at 60 °C for 10 days and 0.5 μg L^{-1} after 40 °C for 10 days (Bach et al., 2013).

Published studies have shown that temperature is the main factor for Sb migration (Al-Otoum et al., 2017; Carneado et al., 2015; Chapa-Martínez et al., 2016; Fan et al., 2014). The temperature influences the diffusion of Sb because with the increase in temperature, the mobility of the migrant and the polymer chain increase (Catalá and Gavara, 2002; Marangoni et al., 2020; Welle and Franz, 2011). In the literature, it was confirmed that the diffusion of Sb in PET increased with higher temperature (Haldimann et al., 2013; Magana-Maldonado et al., 2022; Welle and Franz, 2011).

In respect to the 9 samples that did not present Sb migration above 1 μg L^{-1} after 10 days of contact at 60 °C, considering that all PET bottles analyzed presented Sb content above 170 mg kg^{-1}, it is believed that there is variability among PET bottles regarding the quality of the raw material, technology used in the manufacture of bottles, bottle designs and the different formulations used by PET manufacturers (Al-Otoum et al., 2017; Pinto and Reali, 2009). The degree of crystallinity is also an important factor to explain the difference in Sb migration at the same temperature, since semicrystalline polymers, such as PET, contain amorphous and crystalline morphological regions. In bottles with a

Table 5
Result of the recovery test and evaluation of the repeatability of the Sb determination method in mineral water (1).

Added Sb concentration (μg L^{-1})	Recovery (%)	CV of sample A (%) (2)	CV of sample B (%) (3)
2.5	89.4 ± 3.1	3.6	1.5
5.0	96.1 ± 3.8	4.8	2.4
15.0	96.1 ± 2.3	3.4	2.0

(1) Mean of 7 determinations ± standard deviation
(2) Sample A: Initial concentration lower than LOD.
(3) Sample B: Initial concentration of 2.89 μg L^{-1}

Table 6
Results of antimony migration from PET bottle to mineral water in μg L^{-1}[(1)].

Sample	Sb (μg L^{-1})		
	Initial time	40 °C / 10 days	60 °C / 10 days
S1	≤ LOQ	≤ LOQ	3.54 ± 0.15[(2)]
S2	≤ LOQ	≤ LOQ	≤ LOQ
S3	≤ LOQ	≤ LOQ	3.05 ± 0.10[(2)]
S4	≤ LOQ	≤ LOQ	2.03 ± 0.03[(2)]
S5	≤ LOQ	≤ LOQ	2.97 ± 0.24[(2)]
S6	≤ LOQ	≤ LOQ	2.43 ± 0.08[(2)]
S7	≤ LOQ	≤ LOQ	≤ LOQ
S8	≤ LOQ	≤ LOQ	1.59 ± 0.65[(2)]
S9	≤ LOQ	≤ LOQ	≤ LOQ
S10	≤ LOQ	≤ LOQ	3.46 ± 0.12[(2)]
S11	≤ LOQ	≤ LOQ	2.74 ± 0.05[(2)]
S12	≤ LOQ	≤ LOQ	≤ LOQ
S13	≤ LOQ	≤ LOQ	≤ LOQ
S14	≤ LOQ	≤ LOQ	≤ LOQ
S15	≤ LOQ	≤ LOQ	≤ LOQ
S16	≤ LOQ	≤ LOQ	3.67 ± 0.19[(2)]
S17	≤ LOQ	≤ LOQ	≤ LOQ
S18	≤ LOQ	≤ LOQ	≤ LOQ
S19	≤ LOQ	≤ LOQ	4.42 ± 0.16[(2)]

LOQ = Limit of Quantification (1 μg L^{-1})
[(1)] Mean of three units of bottles determined in triplicate.
[(2)] Mean ± standard deviation

higher degree of crystallinity, the diffusion of Sb in the polymer will be lower, since the crystalline regions are impermeable and act as "knots" between the polymer chains, restricting its movement and consequently the mobility of the migrant (Catalá and Gavara, 2002). Another factor is the degree of orientation of the PET molecules after the bottle manufacturing process, because the greater the orientation of the PET molecules, the smaller the diffusion of Sb in the polymer (Haldimann et al., 2013). Consequently, the crystallinity in combination with the orientation of the PET chains in the packaging may explain the differences in Sb migration results between the analyzed bottles.

Finally, based on the results obtained, Sb migration was greater when the samples were conditioned in the test condition established by the European regulation, compared to the milder condition established by the Brazilian legislation (Anvisa). Therefore, the test conditions used in the migration imply important differences in the results obtained. Considering the Brazilian tropical climate, in which in some regions the temperature is above 40 ºC, it is recommended to review the condition of the specific migration test, proposed by Anvisa. It is suggested that new studies be carried out in order to verify which factors are associated with PET, such as resin formulation, preform and packaging manufacturing parameters, degree of crystallinity, binding of Sb to PET, among others and/ or to the composition of mineral water, inhibit or accelerate the migration of Sb to water.

4. Conclusions

The PET bottles, made with virgin resin, used for packaging mineral water, contained relevant concentrations of Sb, with the possibility of migration in concentrations above the values allowed by Brazilian and European legislation. For the determination of antimony content at trace levels, the ICP-OES technique with hydride generation was evalueted and proved to be efficient and effective in meeting the migration limit required by Brazilian and European legislation for bottled mineral water. Sb trioxide, which is used as a catalyst in the manufacture of PET resin, can migrate to mineral water. In this work, based on the results obtained, using different conditions for the Sb migration tests for mineral water, it was verified that the contact condition established by the European Regulation (60 ºC for 10 days) presented a superior antimony migration in relation to the condition of contact established by Anvisa (40 ºC for 10 days). In both contact conditions, all evaluated samples showed antimony concentrations below the maximum migration limit established by Anvisa and the European regulation.

CRediT authorship contribution statement

Paulo Henrique Massaharu Kiyataka: Conceptualization, Validation, Formal analysis, Methodology, Investigation, Data curation, Formal analysis, Resources, Funding acquisition, Writing – original draft. **Luís Marangoni Júnior:** Data curation, Formal analysis, Writing - review & editing. **Aline Cristina Albino Brito:** Investigation, Data curation. **Juliana Azevedo Lima Pallone:** Conceptualization, Validation, Formal analysis, Methodology, Supervision, Data curation, Resources, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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