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Contamination of Bottled Waters with Antimony Leaching from Polyethylene Terephthalate (PET) Increases upon Storage

WILLIAM SHOTYK* AND
MICHAEL KRACHLER
Institute of Environmental Geochemistry, University of Heidelberg, INF 236, D-69120 Heidelberg, Germany

Antimony concentrations were determined in 132 brands of bottled water from 28 countries. Two of the brands were at or above the maximum allowable Sb concentration for drinking water in Japan (2 μg/L). Elevated concentrations of Sb in bottled waters are due mainly to the Sb_2O_3 used as the catalyst in the manufacture of polyethylene terephthalate (PET(E)). The leaching of Sb from PET(E) bottles shows variable reactivity. In 14 brands of bottled water from Canada, Sb concentrations increased on average 19% during 6 months storage at room temperature, but 48 brands of water from 11 European countries increased on average 90% under identical conditions. A mineral water from France in PET(E), purchased in Germany, yielded 725 ng/L when first tested, but 1510 ng/L when it was stored for 6 months at room temperature; the same brand of water, purchased in Hong Kong, yielded 1990 ng/L Sb. Pristine groundwater containing 1.7 $\pm$ 0.4 ng/L Sb (n = 6) yielded 26.6 $\pm$ 2.3 ng/L Sb (n = 3) after storage in PET(E) bottles from Canada for 6 months versus 281 $\pm$ 38 ng/L Sb (n = 3) in PET(E) bottles from Germany. Tap water bottled commercially in PET(E) in December 2005 contained 450 $\pm$ 56 ng/L Sb (n = 3) versus 70.3 $\pm$ 0.3 ng/L Sb (n = 3) when sampled from a household faucet in the same village (Bammental, Germany), and 25.7 $\pm$ 1.5 ng/L Sb (n = 3) from a local artesian flow.

Introduction

Antimony trioxide (Sb_2O_3) is the single most important catalyst used in the manufacture of polyethylene terephthalate (PET). In a recent study of Sb in bottled waters from Canada and Europe, it was shown that the waters become contaminated during storage because of Sb leaching from PET (*1*). Bottles made using PET typically contain hundreds of mg/kg Sb in the plastic (*2*). In contrast to these concentrations, the abundance of Sb in crustal rocks is on the order of 0.5 mg/kg (*3*) and pristine groundwaters may contain as little as 2 ng/L Sb (*4*). Bottled waters, on the other hand, typically contain several hundred ng/L Sb, with much of this Sb, if not most, apparently due to leaching from PET (*1*).

The intention of the bottled water study (*1*) was to demonstrate to the scientific community that it is not possible to study the natural abundance of Sb in groundwaters by using bottled waters purchased in PET containers. However, the report of Sb in bottled waters was widely disseminated in the popular press, and in many cases the possible significance of the findings for human health may have been overstated. A more balanced summary of the bottled water study (*1*) appeared in the news section of this Journal (*5*). In the intervening period, there have been many inquiries about the possible significance of Sb in bottled waters for human health, from consumers as well as representatives of the plastics, packaging, and drinks industries.

In the previous publication (*1*), little information had been given about the rate of change of Sb concentrations in the bottled waters. To confirm that the extent of contamination of bottled waters increases with time because of Sb leaching from PET, the collection of bottled waters studied earlier (*1*) was evaluated once again, after a period of storage in their original containers. In addition to testing bottled waters which are available commercially, some simple leaching experiments were also undertaken using a pristine groundwater which had been stored for 6 months in PET bottles. Here we also report the measurements of Sb in 69 other brands of bottled waters, from 16 additional countries. Included in this list are bottled waters from Japan where most of the PET is manufactured using a Ti catalyst (*2*).

As PET and PETE are used synonymously, here we refer to them both as PET(E).

Materials and Methods

Bottled Waters from Canada and Europe in Glass, PET(E), and PP. In the previous study, Sb concentrations were determined in 15 brands of bottled water from Canada and 48 from Europe (*1*). The 15 brands of water from Canada included both natural waters and bottled tap water. With respect to the bottled tap water, these products are sold commercially by drinks manufacturers, after treatment by reverse osmosis and deionization. The 48 brands of bottled water from Europe were all natural waters, from Belgium, the Czech Republic, Denmark, Finland, France, Germany, Italy, Poland, Spain, The Netherlands, and Yugoslavia. All bottled waters had been purchased commercially from retail outlets in Canada and Europe, except the natural water from Canada bottled in polypropylene (PP) which was provided by an airline. Three of the brands from Germany were purchased both in glass bottles, and in PET(E). All of these samples had been measured for Sb and other trace metals in November 2005, and the results were reported elsewhere (*1*). Since testing of these bottled waters, they were stored in a Class 10,000 clean lab, at room temperature, for approximately 6 months. During the daytime, the samples were directly exposed to light from both ambient daylight and artificial sources.

Storage of Pristine Groundwater from Canada in PP and PET(E) Bottles. Bottled waters sold commercially in PET(E) in Canada and Germany were emptied of their contents, then filled with pristine groundwater in Canada, carefully transported to Germany, and stored under the same conditions as described above. Water was obtained from the Old Johnson Farm in Springwater Township, Simcoe County, Ontario, Canada using appropriate clean lab sampling and handling procedures. The average abundance of Ca and Mg in these waters (48 and 18 mg/L, respectively), the carbonate alkalinity (182 mg/L), and the pH (*8*) indicate that the chemical composition of the waters is dominated by reactions between the percolating fluids and carbonate minerals. The natural abundance of Sb in this pristine groundwater is approximately 2 ng/L (*4*). After allowing this artesian well to flow from the sampling faucet for 1 h, water was collected

* Corresponding author e-mail: shotyk@ugc.uni-heidelberg.de; phone: +49 (6221) 54 4803; fax: +49 (6221) 54 5228.

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in triplicate directly into the PET(E) bottles; triplicate samples were also collected directly into PP bottles, for comparison. The bottles were rinsed six times with the pristine groundwater prior to filling. To allow this leaching experiment to take place under realistic conditions, the waters were not acidified. These water samples were each packed individually using three ziploc polyethyene bags and kept refrigerated until they could be transported. They were packed for transport in an insulated plastic box containing freezer packs, and shipped by express courier to Heidelberg; they were still cool when they arrived at the lab. These samples were also stored for 6 months in a Class 10,000 clean lab, under the same conditions as described above.

Household Tap Water from a Faucet versus PET(E) Bottles. A natural artesian flow between Bammental and Heidelberg, in Germany, was sampled on May 30, 2006. The water is derived from reaction between meteoric fluids and Old Red Sandstone, and has a pH of 6. Using appropriate handling techniques (*4*), waters were collected directly into clean LDPE bottles to which 100 μL of nitric acid (purified twice by sub-boiling distillation) had been added. To minimize the risk of contamination, the waters were not filtered. On the same day, tap water was sampled in triplicate from a household in Bammental, after allowing the faucet to run for 60 min. Tap water from this same village had been bottled commercially in PET(E) in December 2005. Twelve bottles of the tap water in PET(E) were stored for 6 months in a Class 10,000 clean lab, under the same conditions as described above.

Bottled Waters Sold Worldwide in PET(E) Containers. Since the previous report of Sb in bottled waters (*1*), we have continued to obtain bottled waters. Additional samples of bottled water were purchased in Canada, as well being sent to us from Australia, Brazil, China, Dominican Republic, England, Hong Kong, Iceland, Israel, Japan, Kenya, Mexico, Peru, Slovenia, Spain, Trinidad, and the United States. These waters were analyzed as is.

Japanese Bottled Waters. Twelve brands of local bottled waters were purchased in Japan on February 1, 2006. These waters were analyzed as is.

Analytical Procedures. All of the water samples described here were measured for Sb and other trace metals in May 2006, using the same clean lab methods and protocols which were used in the previous study (*1*). We add that the lab procedures employed here were designed and successfully employed to determine Sb in arctic snow and ice (*6*).

A sector field ICP−MS (Element2, Thermo Electron, Bremen, Germany) was used for the quantification of Sb in all samples. For analysis, one aliquot of sample was diluted with four aliquots of high-purity water to reduce (1) the concentration of alkaline and earth alkaline elements in the analyte solution which could lead to clogging of the cones or could give rise to detrimental instrument performance, (2) to reduce the amount of dissolved CO_2 which was present in some of the samples, thereby guaranteeing smooth sample introduction into the ICP, and (3) to add the internal standard element. Rhodium (1 μg/L) was used as internal standard to correct for instrumental drifts. The sample introduction system consisted of a tandem spray chamber arrangement (*7*), sapphire injector tube, Ni cones, and a PFA nebulizer operated in the pumping mode (~150 μL/min). Considering the dilution factor of 5, the limit of detection for Sb is 0.35 ng/L in the water samples. The certified water reference material SLRS-4 (National Research Council Canada, Ottawa, Canada) was also diluted 1 + 4 with high-purity water and analyzed at regular intervals during sample analysis. Excellent agreement between the actual Sb concentration determined in the reference material (237 ± 5 ng/L, n = 24) and the certified value of 230 ± 40 ng/L was obtained. The precision of the Sb determinations in the water samples was generally 0.5 to 3%.

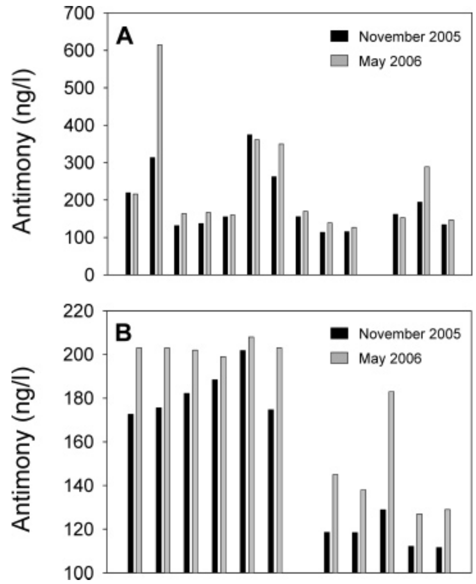

FIGURE 1. (A) Antimony (ng/L) in bottled waters from Canada. The ten samples on the left side are natural waters whereas the three samples on the right side are deionized tap water; all are popular brands, sold commercially. Dark bars represent measurements performed in November 2005, light bars are the data from May 2006. (B) Six bottles of one brand, and five bottles of another brand, measured as replicates.

Results and Discussion

Remeasurement of Bottled Waters from Canada and Europe. All investigated waters were sold in PET(E) containers, except where explicitly mentioned. The bottled waters from Canada, including ten brands of natural water and three brands of bottled tap water, show variable degrees of change in Sb concentrations upon storage (Figure 1a). Two samples increased in concentration 33 and 49%, respectively, upon storage. Another sample increased 96%. Thus, there are no consistent differences upon storage of water in PET(E) bottles. In three brands, there was no significant change in Sb concentrations. Two brands of bottled water purchased in replicates of six and five bottles show that the changes in Sb concentrations are fairly consistent (Figure 1b). Taken together, the average increase in Sb concentrations of all of the bottled waters from Canada was 19% during 6 months of storage.

In contrast to these data, six replicate samples of the natural water from Ontario, Canada which was bottled commercially in PP, yielded much lower as well as stable Sb concentrations: 8.1 ± 0.7 ng/L Sb when measured in November 2005, and 10.0 ± 0.9 ng/L Sb in May 2006.

In contrast to the bottled waters from Canada, the bottled waters from Europe show much greater reactivity (Figure 2a). The average increase in Sb concentrations of all of the bottled waters from Europe was 90%. Analyses of replicate samples of four brands of bottled water from Germany show that the increase in Sb concentrations is reproducible (Figure 2b).

Pristine Groundwater in PP and PET(E) Bottles. The PET(E) bottles filled with pristine groundwater show varying degrees of contamination (Figure 3). Measurements of Sb in this pristine groundwater, collected in triplicate at the Old Johnson Farm on 4/12/06 and 4/13/06 using the methods described previously (*4*), yielded 1.8 ± 0.6 (n = 3) and 1.7 ± 0.1 ng/L Sb (n = 3), respectively. These values are remarkably consistent with the published concentrations of the natural

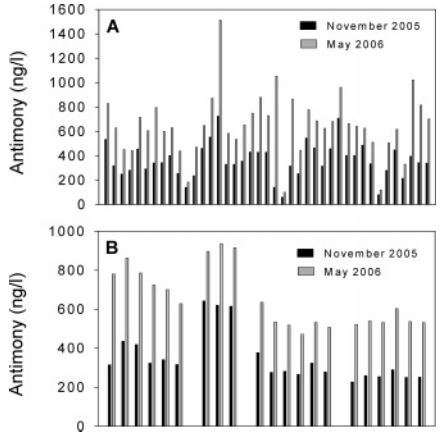

FIGURE 2. (A) Antimony (ng/L) in bottled waters from Europe. (B) Four brands of bottled water, purchased and analyzed in quantities of 6, 3, 6, and 6 bottles, respectively.

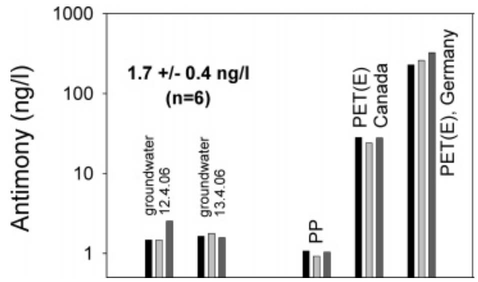

FIGURE 3. Comparison of Sb concentrations (ng/L) in pristine groundwater (Springwater Township, Simcoe County, Ontario, Canada) collected from an artesian flow on 4/12/06 and 4/13/06 versus the same water, but stored for 6 months in PP and PET(E) bottles. The PP bottles were from Canada and the PET(E) bottles were from both Canada and Germany. All experiments were carried out in triplicate. Note the logarithmic concentration scale.

abundance of Sb in these waters (2.2 ± 1.2 ng/L, $n = 34$) established using samples collected from this and other artesian flows in Springwater and Tiny Townships, Simcoe County, Ontario, during 2004 and 2005 (*4*). For comparison, the water collected from this source in PP and stored for 6 months in the clean lab contains 1.0 ± 0.1 ng/L Sb ($n = 3$). In contrast, the same water, collected on the same day and stored for the same length of time, under identical conditions, but in PET(E) bottles purchased in Canada, contains 26.6 ± 2.3 ng/L Sb (Figure 3). The same water, collected on the same day and stored for the same length of time, under identical conditions, but in PET(E) bottles purchased in Germany, contains 281 ± 38 ng/L Sb (Figure 3).

Bammental Tap Water from the Faucet versus PET(E) Bottles. The natural spring between Bammental and Heidelberg was found to contain 25.7 ± 1.5 ng/L Sb (Figure 4). Tap water collected from a household in Bammental, allowed to run for 1 h prior to sampling, contained 70.3 ± 0.3 ng/L Sb (Figure 4). In contrast to these values, tap water in Bammental, bottled commercially in PET(E) and given to inhabitants of the village in December of 2005, contains 450 ± 56 ng/L Sb (Figure 4). The difference in Sb concentrations between the tap water and the tap water bottled in PET(E) is attributed to leaching from the container.

Antimony in Other Brands of Water Bottled Internationally in PET(E). The Sb concentrations in 69 brands of bottled water from 16 countries range from 8.9 to 2570 ng/L, with a median concentration of 216 ng/L (Figure 5). We note that several of these brands of bottled water contain Sb in concentrations at or above the maximum allowable for drinking water in Japan which is 2 μg/L (i.e., 2000 ng/L). The bottled water containing 2570 ng/L Sb is from Peru. Two

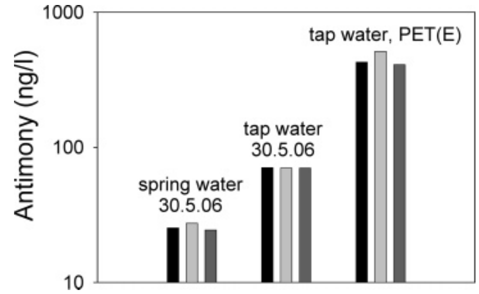

FIGURE 4. Comparison of Sb concentrations (ng/L) in groundwater collected from an artesian flow on 5/30/06 between Heidelberg and Bammental, Germany, versus tap water from Bammental collected on the same day, and tap water from Bammental which had been bottled in PET(E) 6 months earlier. All experiments were carried out in triplicate. Note the logarithmic concentration scale.

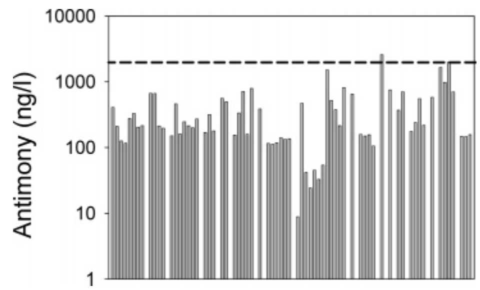

FIGURE 5. Antimony concentrations (ng/L) in 69 brands of bottled waters which had not been tested previously, from 16 additional countries. The dashed horizontal line (2000 ng/L) indicates the maximum allowable Sb concentration in drinking water in Japan.

brands of bottled water from Europe, but purchased in Hong Kong, yielded 1650 and 1990 ng/L Sb. With respect to the latter, this is a bottled water from France in PET(E). In contrast to the Sb concentration found in this brand when it was purchased in Hong Kong (1990 ng/L Sb), we had already tested this same brand of water, also in PET(E), but purchased in Germany; the water contained 725 ng/L when it was first purchased (*1*), but 1510 ng/L when it was stored for 6 months at room temperature in the clean lab (this study). It appears that the Sb concentrations in a given brand of bottled water are predominately a reflection of the rate of leaching of Sb from the bottle, and the duration of storage. Because of transportation distances, European waters bottled in PET(E) but purchased in Asia may have higher Sb concentrations than the same brands sold in Europe, simply because of the additional contamination by the PET(E) bottles during storage.

Antimony in Bottled Waters from Japan. The bottled waters from Japan contain Sb in concentrations ranging from 9 to 1520 ng/L (Figure 6a). The sample containing the highest Sb concentration approaches the maximum allowable for drinking water in Japan which is 2 μg/L Sb. The Japanese bottled waters appear to fall into two groups: those containing a few tens of ng/L Sb (ca. 10 to 50), and those containing hundreds of ng/L Sb (ca. 200 to 1500). According to Nishioka et al. (*8*), some PET(E) bottles used for drinks in Japan contain Sb, but others do not: he found that Sb concentrations in the plastic were either in the range 170−220 mg/kg Sb, or they were below the limit of detection (<0.1 mg/kg).

It has been reported that PET(E) in Japan may be manufactured using a Ti catalyst, with Ge sometimes added to adjust the color of the bottles (*2*). The Ge concentrations in the bottled waters from Japan vary over approximately 3 orders of magnitude (Figure 6b). Although the bottled waters containing the lowest Sb concentrations (Figure 6a) tend to have the most Ge (Figure 6b), there are exceptions. Because these samples were simply collected and measured as is, it

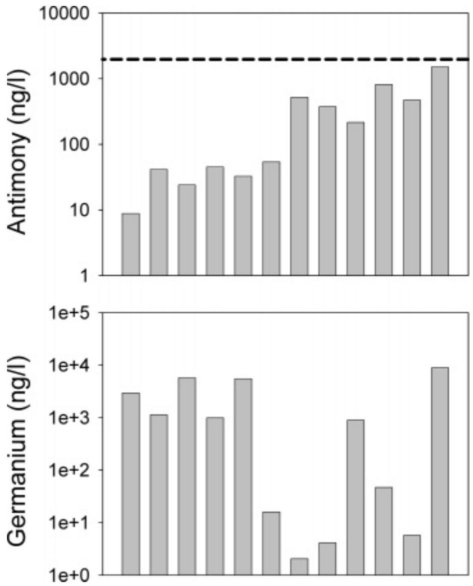

FIGURE 6. Comparison of Sb concentrations (ng/L) in bottled waters from Japan (which had not been tested previously), with concentrations of Ge (ng/L).

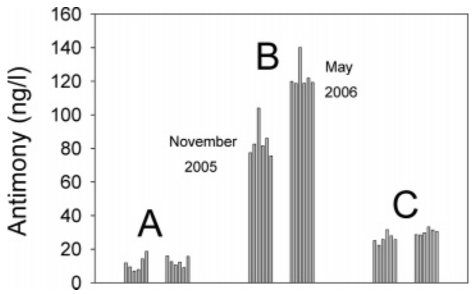

FIGURE 7. Antimony (ng/L) in three brands of bottled waters from Germany, purchased in glass. Six bottles of each brand (A, B, C) were measured in November 2005, then again in May 2006. Notice that the Sb concentrations in Brands A and C did not change, whereas those of Brand B increased significantly.

is not yet possible to distinguish between the inherent, natural abundance of Sb and Ge in these waters, and any possible contamination of the waters by Sb or Ge leaching from the containers.

Antimony in Natural Waters Bottled in Glass. Six replicate samples of three brands of glass-bottled water from Germany which had already been studied (*1*) were also stored at room temperature in the clean lab for 6 months, and remeasured (Figure 7). In Brand A and Brand C, there was no measurable change in Sb concentrations (ng/L): 11.5 ± 4.4 and 26.4 ± 3.1 in November 2005 versus 12.7 ± 2.8 and 30.3 ± 1.8 in May 2006 ($n = 6$). However, the source water from Brand A had also been tested (*1*), and was found to contain only 3.8 ± 0.9 ng/L Sb ($n = 6$). Thus, there is a detectable amount of Sb contamination of bottled waters caused by leaching from glass, and this has already been reported (*1*).

In contrast to Brands A and C, here we report that in Brand B there was a measurable change during storage in the clean lab: 84.5 ± 10.2 ng/L Sb in November 2005, compared with 123.1 ± 8.4 ng/L Sb in May 2006 ($n = 6$). It was noted previously that antimony trioxide is used as an opacifier in the manufacture of glass, and that measurements of Sb in glass using instrumental neutron activation (INAA) revealed concentrations on the order of 7−10 mg/kg (*1*). The observation that Sb concentrations increased significantly over time in one of the brands stored in glass bottles shows that glass bottles, like their PET(E) counterparts, show variable reactivity. The extent of the contamination of bottled waters caused by leaching from glass, however, appears generally to be dwarfed by the extent of leaching of Sb from PET(E).

Comparison of Bottled Water Values with Drinking Water Standards. All of the bottled waters measured in our lab to date were found to contain Sb in concentrations well below the guidelines recommended for drinking water by the WHO (20 μg/L), U.S. EPA, Health Canada, and the Ontario Ministry of Environment (6 μg/L), as well as the German Federal Ministry of Environment (5 μg/L). For the first time, however, we report concentrations of Sb in bottled waters which exceed the Japanese drinking water standard of 2 μg/L.

Factors Affecting Sb Release from PET(E) Containers to the Fluids. The extent of contamination of bottled waters by leaching of Sb from PET(E) increases with duration of storage in the containers. However, the reactivities of the bottles are variable, for reasons which are not apparent. Analytical advances recently applied to the chemical speciation of Sb in beverages (*9*, *10*) should allow detailed studies of the rates and mechanisms of the leaching process.

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Literature Cited

(1) Shotyk, W.; Krachler, M.; Chen, B. Contamination of Canadian and European bottled waters with antimony leaching from PET containers. *J. Environ. Monit.* **2006**, *8*, 288−292.

(2) Thiele, U. K. Quo vadis polyester catalyst? *Chem. Fibres Int.* **2004**, *54*, 162−163.

(3) Wedepohl, K. H. The composition of the continental crust. *Geochim. Cosmochim. Acta.* **1995**, *59*, 1217−1232.

(4) Shotyk, W.; Krachler, M.; Chen, B.; Zheng, J. Natural abundance of Sb and Sc in pristine groundwater, Springwater Township, Ontario, Canada, and implications for tracing contamination from landfill leachates. *J. Environ. Monit.* **2005**, *7*, 1238−1244.

(5) Christen, K. Bottled antimony. *Environ. Sci. Technol.* **2006**, March 22 (Online News story: http://pubs.acs.org/subscribe/journals/esthag-w/2006/mar/science/kc_antimony.html).

(6) Krachler, M.; Zheng, J.; Zdanowicz, C.; Koerner, R.; Fisher, D.; Shotyk, W. Increasing enrichments of antimony in the arctic atmosphere. *J. Environ. Monit.* **2005**, *7*, 1169−1176.

(7) Krachler, M.; Rausch, N.; Feuerbacher, H.; Klemens, P. A new HF-resistant tandem spray chamber for improved determination of trace elements and Pb isotopes using inductively coupled plasma-mass spectrometry. *Spectrochim. Acta, B* **2005**, *60*, 865−869.

(8) Nishioka, K.; Hirahara, A.; Iwamoto, E. Determination of antimony in polyethylene terephthalate bottles by graphite furnace atomic absorption spectrometry using microwave sample preparation. *Bull. Inst. Life Sci. Hiroshima Prefectural Women's Univ.* **2002**, *8*, 35−42.

(9) Hansen, H. R.; Pergantis, S. A. Detection of antimony species in citrus juices and drinking water stored in PET containers. *J. Anal. At. Spectrom.* **2006**, *21*, 731−733.

(10) Hansen, H. R.; Pergantis, S. A. Investigating the formation of an Sb(V)citrate complex by HPLC-ICP-MS and HPLC-ES-MS(/MS). *J. Anal. At. Spectrom.* **2006**, *21*, 1240−1248.

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