

## Speciation of Antimony in PET Bottles Produced in Japan and China by X-Ray Absorption Fine Structure Spectroscopy

Antimony (Sb) has been frequently used as a catalyst of polycondensation reaction to produce polyethylene terephthalate (PET). As a result, Sb is incorporated into some PET bottles used for beverages at concentrations of 100 to 300 mg/kg. Considering its high toxicity [1], the possible leaching of Sb into beverages is of great concern, which has motivated various studies of Sb content in PET bottles and Sb leaching into beverages [1]. In addition, the effects of pH, water temperature, elapsed time, and other factors on Sb leaching have also been examined [1,2]. In addition, the effect of beverage type in PET bottles has been studied especially in terms of the complexation effect of Sb with ligands in the liquid (such as citrus juice or acetic acid) that may enhance Sb leaching. However, there have been no studies dealing with the direct characterization of Sb species in PET so far, such as the oxidation state and local structural environment around Sb, which can be associated with its leaching into the liquid, as seen from the Sb behavior in the natural environment [3]. Since Sb is initially added as Sb<sub>2</sub>O<sub>3</sub> in the production of PET, the possible oxidation of Sb(III) should be verified considering that the leaching behavior of Sb may depend on its oxidation state.

Considering the relatively scarce knowledge of the chemical state of Sb in PET, this study employed X-ray absorption fine structure (XAFS) to obtain Sb atomic scale information [4]. XAFS spectroscopy consisting of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) give

independent information such as the oxidation state and local structure of Sb (= coordination number and bond lengths to neighboring atoms), respectively. Although XAFS has been employed in various environmental studies [3,5], its application to the speciation of Sb in PET has not yet been reported. Thus, PET bottles collected in China and Japan have been used for XAFS measurement. In addition, leaching experiments have been done to investigate the possible relationship between the difference in the chemical state of Sb in PET and Sb leachability in water.

Prior to XAFS, Sb concentration has been determined in 105 and 72 brands of PET bottles sold in Japan and China, respectively. A relatively high content of Sb (170 – 220 mg/kg) has been reported for PET bottles in Japan; this has not been documented for those in China. It was also found that 30.5% and 100% of Japanese and Chinese PET bottles, respectively, contained more than 10 mg/kg of Sb (Fig. 1(a)). Generally, PET bottles can be classified into five to six types depending on their use: (A) bottles for aseptic cold filling mainly used for noncarbonated cold drinks; (B) pressure-tight bottles for carbonated drinks; (C) heat-resistant and pressure-tight bottles for semi-sparkling drinks; (D) heat-resistant bottles for hot filling like those hot tea; and (E) bottles for freezing. When the results were confined to Japanese PET bottles, it was found that most of the PET bottles categorized into types A and B contained Sb at more than 150 mg/kg (Fig. 1(b)). In addition, about half of the type C bottles also contained large amounts of Sb.

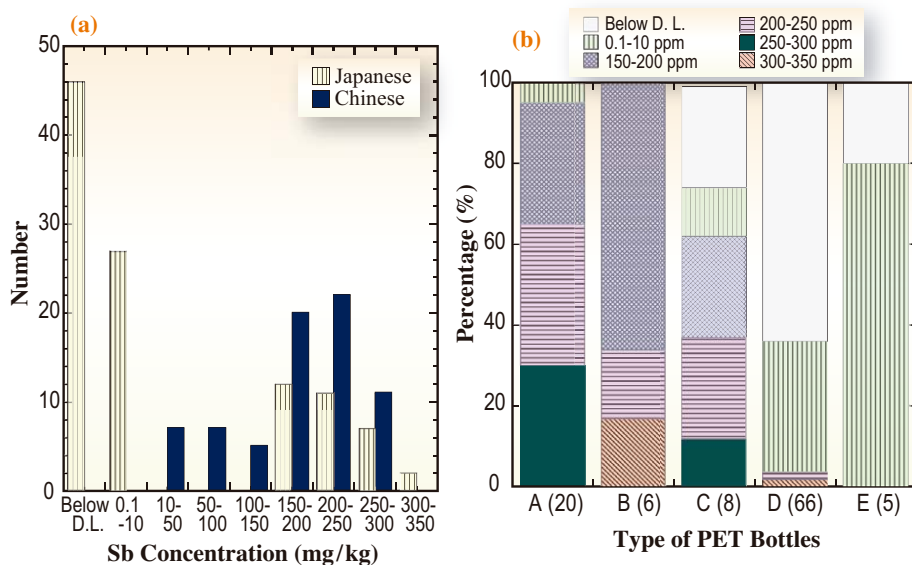


Fig. 1. (a) Concentrations of Sb in PET bottles sold in Japan and China. (b) Concentrations of Sb in PET bottles in Japan for various uses. (A) bottles for aseptic cold filling normally used for noncarbonated cold drinks; (B) pressure-tight bottles for carbonated drinks; (C) heat resistant and pressure tight bottles for semi-sparkling drinks; (D) heat resistant bottles for hot filling such as those for hot tea; and (E) bottles for freezer. Numbers in parentheses indicate the number of samples for each type. D.L. means detection limit.

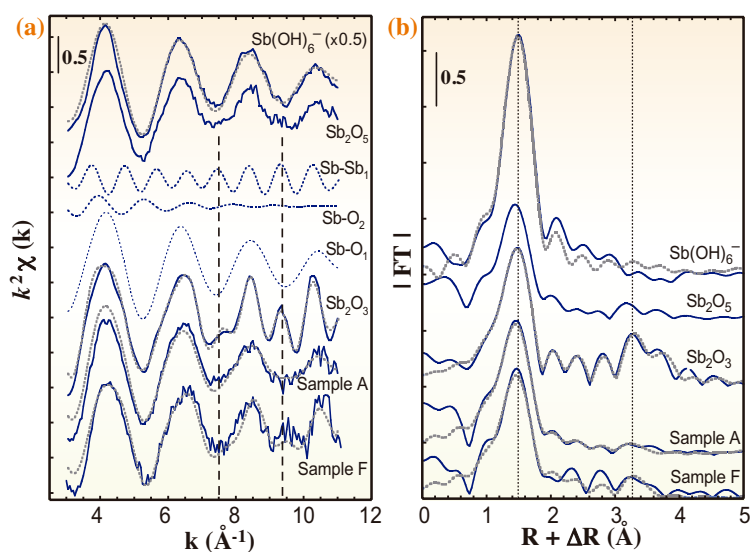


Fig. 2. EXAFS spectra at Sb K-edge for Sb in PET samples (A and F) in k space (a) and R space (b). Gray curves indicate the simulation results. Contributions of Sb-O<sub>1</sub>, Sb-O<sub>2</sub>, and Sb-Sb<sub>1</sub> in the spectrum of Sb<sub>2</sub>O<sub>3</sub> in k space were also indicated.

The oxidation state and coordination environment of Sb incorporated into the PET bottles were estimated by XAFS at the Sb K-edge at beamlines **BL01B1** and **BL37XU**. Results of the EXAFS of Sb in PET bottles were interpreted by assuming that the nearest-neighbor atom of Sb is either carbon or oxygen (Fig. 2). On the basis of the possible bond lengths of Sb-O and Sb-C, it was shown that the first neighboring atom of Sb in PET was estimated to be oxygen with a coordination number of about three. In addition, the contribution of Sb to Sb shells was discounted in the EXAFS, showing that Sb was not present as Sb<sub>2</sub>O<sub>3</sub> in PET, although Sb was initially added as Sb<sub>2</sub>O<sub>3</sub> in PET production. This information is consistent with the coordination environment estimated from the polycondensation reaction catalyzed by Sb, where Sb can be present as either Sb glycolate or Sb glycolate binding to the end group of the PET polymer.

Antimony K-edge XANES showed that the Sb(III) initially added as Sb<sub>2</sub>O<sub>3</sub> into PET was partially oxidized, and, that the Sb(V) fractions reached approximately 50% in some samples (Fig. 3). However, the oxidation state and coordination environment of Sb in PET had no relationship with the concentration of Sb that leached into water from PET. This conclusion is supported by Westerhoff *et al.* [2] who showed the effects of pH, temperature, and sunlight on Sb leaching. First, the acidification did not increase the Sb concentration in their study. If the Sb release is a function of inorganic Sb(III) fraction that has lower solubility at higher pH, then Sb leaching can be a function of pH, which is not the case for Sb leaching in PET [2]. On the other hand, higher temperature and sunlight enhanced the release of Sb. It is most likely that temperature and sunlight can facilitate the degradation of PET itself. Based on this information coupled with the speciation of Sb in PET observed in this study [4], the degradation of PET itself is more important for Sb leaching rather than Sb speciation in PET bottles.

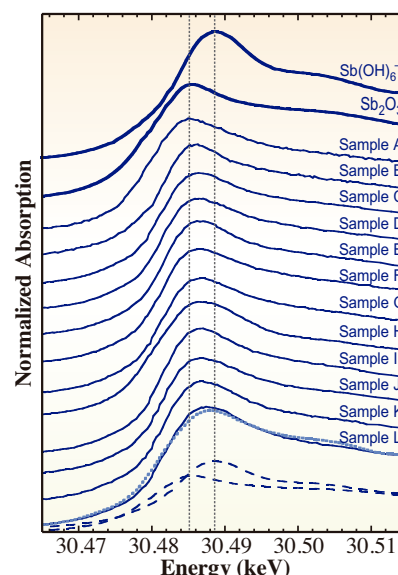


Fig. 3. XANES spectra at Sb K-edge for Sb in various PET samples (A – L) with those for Sb<sub>2</sub>O<sub>3</sub> and Sb(OH)<sub>6</sub><sup>-</sup>. The presence of both Sb(III) and Sb(V) at various Sb(III)/Sb(V) ratios is suggested. The simulation result is shown for Sample L with the contributions of Sb(III) and Sb(V) indicated by the broken curves.

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