9A/2002G244

Direct determination of the organic extent of tin species in environmental samples by X-ray absorption near-edge structure (XANES)

Naoki SAKAKIBARA and Yoshio TAKAHASHI
Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

Introduction

Organotin compounds have been used since the 1960s as an effective antifouling agent in paints applied to ships and aquaculture nets in the marine environment. However, organotin compounds cause damage to non-target marine organisms by leaching from the coating applied to boat hulls into the marine environment. For Sn analyses, speciation of the organotin compounds has been of great interest due to their species-dependent toxicity. Generally, trisubstituted (R_3SnX) organotins (R = butyl or phenyl) are more toxic than di- and mono-substituted organotin compounds, and the anion (X) has little influence on the toxicity. In recent years, chromatographic techniques such as gas chromatography (GC) or liquid chromatography (LC), coupled with appropriate detectors such as FPD (flame photometric detector), MS (mass spectrometer), and ICP-MS (inductively coupled plasma mass spectrometer) have been widely used for the analysis of organotin compounds. These analytical methods need many complicated pretreatment procedures, such as extraction, enrichment, and derivatization, which may cause some errors due to alteration of Sn species and poor recovery in the analyses. In this study, we have established a method for determining Sn speciation using synchrotron-based X-ray absorption fine structure (XAFS) as a non-destructive method to identify organotin compounds in solid environmental samples such as marine sediments, biological samples, and antifouling paints.

Experimental

Tin L_I- and L_{III}-edge XANES (energy region: 3.9–4.5 keV) were measured at beamline BL-9A using bending magnet at the Photon Factory, KEK. An Si(111) monochromator was used and the beam was focused by a pair of bent conical mirrors coated with Rh. The beam size used in this study was smaller than 1 mm x 0.5 mm at the sample position. All spectra were recorded at room temperature in a fluorescence mode using a Lytle detector. To suppress the absorption of X-rays by air, all the paths, including an I_0 ion chamber and a sample cell, were purged with He. The influence of self-absorption was examined by using reference samples containing Sn at various concentrations. It was found that the effect of self-absorption was not observed when the Sn concentration was below 5 wt.%.

Results and Discussion

XANES spectra for butyl-, phenyl-, and methyltin compounds exhibit two major peaks between 3.930 and 3.937 keV. In each system, systematic variations were found in the XANES spectra, such as (1) the energy gap between the two peaks (ΔE) decreases and (2) the relative peak intensity of the first peak relative to the second peak ($R_{1/2}$) increases, as the organic extent increases. The variation can be ascribed to the effect of the hydrocarbons coordinated to Sn, such as the multiple scattering by the ligands. The variation of the XANES spectra, including other characteristics, allows us to identify the Sn species in the antifouling paint simply by comparing the spectra. The XANES of the antifouling paint is quite similar to that of TBT, showing that this compound is the main Sn species in the paint. This is consistent with the fact that TBT is the main component of the antifouling paint, which was confirmed by GC-MS analysis of the sample.

Based on the systematic variation, a more quantitative analysis of the spectra can be conducted. To extract parameters representing the shape of the XANES, the spectrum between 3.910 and 3.942 keV was fitted by two pairs of Lorentzian (= L(E); E: energy (keV)) and arctangent (= A(E)) functions using non-linear least-squares analyses:

$$L(E) = a\,b^2 / \{(E - c)^2 + b^2\} \quad (1)$$

$$A(E) = d \arctan\{e\,(E - f)\} + g \quad (2)$$

Initially, the fitting was conducted for DBT, which shows that the simulation using two Lorentzian and two arctangent functions can fit the data. The two arctangent functions for other compounds were fixed to be identical to those used for the simulation of DBT to reduce the number of parameters. The fitting was successfully conducted for other Sn species. The value of ΔE, defined as the difference in the values of c for the two Lorentzian functions, varies depending on the organic extent (= average number of organic ligand bound to Sn), showing that the speciation of Sn compounds is possible by this approach. Based on this plot, the organic extent of the antifouling paint is estimated to be around 3, identical to the result by GC-MS analyses.

The present results have shown that the Sn L_{III}-edge XANES can be used for Sn speciation. Similar information can be extracted by Sn L_I-edge XANES. The organic extent that can be determined by the present method does not give the detailed content of each Sn species. However, it is an advantage that we can conduct the Sn speciation without any pretreatment of the samples using the X-ray beam, which should be useful for the screening of environmental samples to estimate the ratio of organotin compounds against inorganic Sn.

References

[1] N. Sakakibara, et al., Physica Scripta, in press.
[2] Y. Takahashi et al., Anal. Chem., in press.

* takahasi@geol.sci.hiroshima-u.ac.jp