

Direct Speciation of Tin Compounds in Environmental Samples Using Sn K-edge XANES

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Tin K-edge XANES spectra show systematic broadening in the first peak upon increasing the number of organic ligands coordinated to the Sn atom, which can be used to determine Sn speciation in environmental samples. Although the method only provides the average number of organic ligands bound to Sn, a direct method like XANES for Sn speciation can be useful in view of the difficulties associated with chromatographic methods for Sn speciation.

Organotin compounds such as tributyltin (TBT) and triphenyltin (TPT) have been widely used as biocides in antifouling paints and fishing nets. However, it has been found that these compounds cause damage to marine organisms, such as imposex and deformity in mollusks.¹ Speciation of organotin compounds has been of great interest because of their species-dependent toxicity and their widespread application as biocides.² Generally, tri-substituted (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.^{3,4} In recent years, chromatographic techniques such as gas chromatography or liquid chromatography coupled with appropriate detectors have been widely used for the analysis of organotin compounds.⁵ These analytical methods essentially need many pretreatment procedures, such as decomposition, extraction, enrichment, and derivatization.⁵ In this study, we have tested the possibility of synchrotron-based X-ray absorption near-edge structure (XANES) as a nondestructive method for identifying organotin compounds in solid environmental samples such as marine sediments, biological samples, and antifouling paints. High-energy XANES for Sn K-edge (29.19 keV) was applied in this study to determine Sn speciation. It is better to employ the K-edge rather than the L-edge (3.9–4.5 keV) for Sn, as this enables us to measure XANES for environmental samples containing water, whereas the sensitivity would be lower using the L-edge, which is close to the soft X-ray region, as a result of X-ray scatterings. It was also expected that there would be no interference in the K-edge region from major elements such as Ca and K, which can interfere with L-edge XANES for Sn.

Tetrabutyltin (TeBT), dibutyltin chloride (DBTCl), and monobutyltin chloride (MBTCl) were purchased from Wako Pure Chemicals (Osaka, Japan). Tributyltin chloride (TBTCl) and $SnCl_4$ were obtained from Aldrich (Milwaukee, USA). These standard materials were diluted to 5 wt % with ethanol. A Sn metal foil was used for the energy calibration of all XANES spectra. All samples were sealed in a polyethylene bag for the XANES measurements. An antifouling paint sample was received from the National Maritime Research Institute (Tokyo, Japan). A sediment reference material (NIES CRM No. 12) was received from the National Institute of Environmental Studies (Tsukuba, Japan).

These environmental samples were stored at $-10^\circ C$ until used for XANES measurements. Tin K-edge XANES spectra were obtained at the beamline BL01B1 in SPRING-8 (Hyogo, Japan) with a Si (311) double-crystal monochromator with two mirrors.⁶ The measurements were carried out at room temperature under ambient air conditions. The energy calibration was conducted with Sn metal, where the maximum intensity of the first peak was fixed at 29.194 keV. In order to obtain the fluorescence XANES spectra, a 19-elements solid-state detector (SSD) was employed to collect fluorescence X-rays from Sn in the samples.

The background contribution was subtracted from the raw fluorescent XANES spectra by removal of a line extrapolated from the pre-edge region between 29.08 and 29.15 keV. Absorbance of the XANES spectra was normalized by defining the average absorption between 29.30 and 29.34 keV as unity. Figure 1 shows the normalized XANES spectra at the Sn K-edge for the standard samples (TeBT, TBTCl, DBTCl, MBTCl, and $SnCl_4$). It is obvious that the first peak exhibits systematic broadening upon increasing the number of butyl groups bound to Sn. Similar broadening has been reported for tetrabutyl tin as a result of hydrocarbon backscattering.⁷ We found a similar broadening for butyltin compounds with different counter anions (hydroxide, oxide, acetate, and hydride) and phenyltin and methyltin compounds, which confirms that the variation is due to the coordination of the organic ligand to Sn. These facts suggest that the broadening of the first peak can be employed for the speciation of Sn compounds in environmental samples. In order to achieve a quantitative analysis of the Sn species from the broadening, the XANES spectra were fitted by the combination of a Lorentzian function and an arctangent function, which is often used to simulate XANES spectra $\mu t(E)$ as follows:^{8,9}

$$\mu t(E) = a \arctan b(E - c) + df^2 / \{(E - g)^2 + f^2\} + h, \quad (1)$$

where a – h are fitting parameters and E (keV) is the incident X-ray energy. In order to reduce the number of fitting parameters, the position ($= c$ in Eq 1) and the slope ($= b$ in Eq 1) of the arctangent function were fixed at 29.198 keV and 300 for a nonlinear least-squares fitting using the Solver function in Microsoft Excel in the energy region from 29.172 to 29.214 keV. The results of the simulation are shown in Figure 1. In Figure 2, the FWHM (full-width at half maximum) of the Lorentzian function ($= f$ in Eq 1) is plotted against the number of butyl groups bound to Sn. It is clear that there is a linear correlation ($r = 0.972$) between the FWHM of the Lorentzian function and the number of butyl groups, as expected from the features observed in the first peak in the XANES spectra. In environmental samples, however, Sn species do not consist of one component but include various organic and inorganic species. Therefore, XANES spectra of mixtures of different Sn species (M1, M2, and M3) were also measured (Figure 1). The FWHM of the mixtures are plotted in

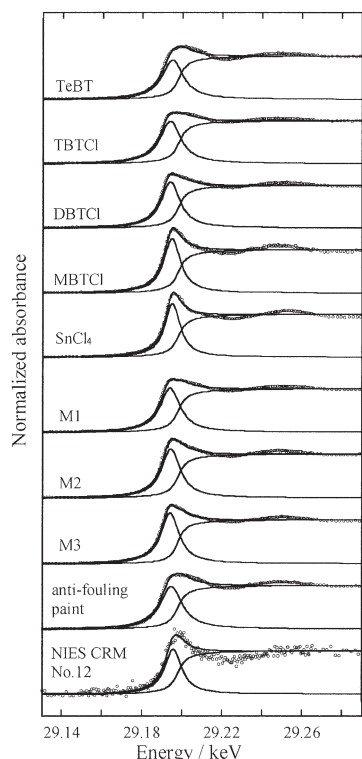


Figure 1. Tin K-edge XANES spectra of standard materials (TeBT, TBTCI, DBTCI, MBTCI, and SnCl_4), mixtures of standard materials (M1–M3), an antifouling paint, and NIES CRM No. 12 (sediment reference material) with the simulation results by arctangent and Lorentzian functions. M1 = 1:1 mixture of TBTCI and DBTCI by mole ratio; M2 = 1:1 mixture of TBTCI and MBTCI; M3 = 1:1 mixture of DBTCI and MBTCI.

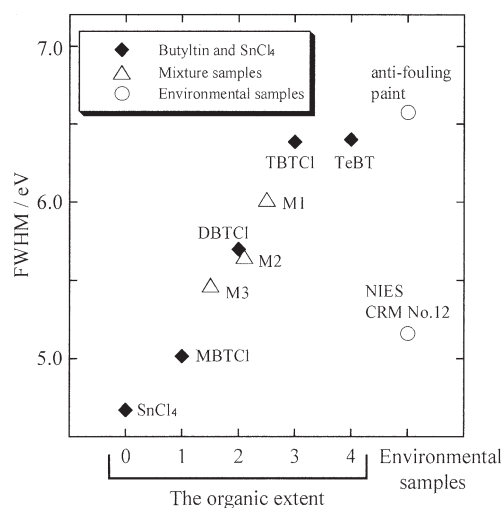


Figure 2. Relationship between the FWHM of the Lorentzian function in the simulation of Sn K-edge XANES spectra and the organic extent (= the average number of butyl groups bound to Sn). The results for the mixture samples (M1–M3) were also plotted. The FWHM of the antifouling paint and NIES CRM No. 12 are indicated in the right hand section.

Figure 2 against the average number of butyl groups bound to Sn in the mixtures, which we name “the organic extent” in this study. For example, the organic extent becomes 2.0 for the 1:1 mixture of TBTCI and MBTCI. The values of the three mixture samples are consistent with the calibration line (Figure 2), show-

ing that the FWHM of the Lorentzian function provides the organic extent for the Sn species in environmental samples.

Similar analyses were applied to environmental materials, the antifouling paint and NIES CRM No. 12. We could obtain XANES spectra for NIES CRM No. 12 containing only 10.7 ppm of Sn,¹⁰ suggesting that the detection limit of the fluorescent XANES can reach ppm level, which could be sensitive enough for Sn speciation in some sediments and biological samples. From the FWHM of the environmental samples, it was shown that tributyl or tetrabutyl compounds are the main Sn species in the antifouling paint, which is consistent with the fact that TBT is the main Sn species in the paint. The organic extent of Sn in NIES CRM No. 12 is about 1 from the calibration line (Figure 2), suggesting that inorganic species are the main Sn component in the sample. The organic extent for the NIES CRM No. 12 calculated by the reported data¹¹ including butyltin and phenyltin compounds is 0.20, which is fairly consistent with the present value estimated by XANES. The discrepancy may be caused by (1) the presence of other organotin compounds in the sample, such as methyltin compounds, (2) the quality of XANES spectra for the NIES CRM No. 12 not being sufficiently good for the fitting, and (3) the presence of Sn(II) species can cause a shift of the first peak to lower energy by overlapping the Sn(IV) species. The analyses of the environmental samples indicate that the present method can be used for Sn speciation in solid materials such as sediments, biocides, biological samples, etc.

Compared with chromatographic methods, it is difficult to obtain the precise concentration ratio of various butyl-, phenyl-, and methyl-substituted compounds by the present XANES method. However, it has often been noted that there are large discrepancies between different studies on the concentrations of organic and inorganic Sn species in environmental samples using chromatographic methods.⁵ It is suggested that the present method can be more reliable in terms of accuracy, since the method does not require any complicated pretreatment procedures that may induce various errors in conventional chromatographic analyses. Although the XANES method cannot give the precise concentration of each organotin compound, direct observation using XANES will be helpful for estimating roughly the ratio of organic and inorganic tin compounds in environmental samples.

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