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

Speciation, identification of the chemical states of elements in the environment, is indispensable in determining the environmental behavior, bioavailability, and the influence of elements on the quality of the environment. For speciation, X-ray absorption fine structure (XAFS) is a powerful tool, because it is a direct method by which we can avoid the change of the chemical state of target elements in environmental samples. XAFS is reasonably sensitive especially when conducted in the fluorescence mode using sensitive detection techniques such as the use of a multi-element semiconductor detector. The water solubility, bioavailability, and toxicity of an element depend on the oxidation state and the ligand coordinated to the element. We have studied the environmental behavior of arsenic, lead, iodine, and other elements [1-3] in terms of the redox reaction and the determination of tin species particularly organotin species [4,5].

Organotin compounds such as tributyltin (TBT) and triphenyltin (TPT) have been widely used as biocides in anti-fouling paints and fishing nets. However, it has been found that these compounds cause damage to marine organisms, such as imposex and deformity in mollusks. The speciation of organotin compounds has been of great interest due to the species-dependent toxicity and the widespread application of organotin compounds as biocides. 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. These analytical methods essentially require many pretreatment procedures, such as decomposition, extraction, enrichment, and derivatization. In this study, we have tested the possibility of using an X-ray absorption near-edge structure (XANES) as a nondestructive method for identifying inorganic and organic tin species in solid environmental samples. A high-energy XANES for the Sn *K*-edge (29.19 keV) was applied in this study to determine Sn speciation [4]. 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 the 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 is 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 the *L*-edge XANES for Sn.

Tin *K*-edge XANES spectra of all reference materials of inorganic and organic tin compounds, an anti-fouling paint sample, and a sediment reference material (NIES CRM No. 12) were obtained at beamline **BL01B1**. In order to obtain the fluorescence XANES spectra, a 19-element solid-state detector (SSD) was employed to collect fluorescence X-rays from Sn in the samples.

Figure 1 shows normalized XANES spectra at the Sn *K*-edge for the standard samples such as tetrabutyltin (TeBT), tributyltin chloride (TBTCl), dibutyltin chloride (DBTCl), monobutyltin chloride (MBTCl), and $SnCl_4$. It is obvious that the first peak
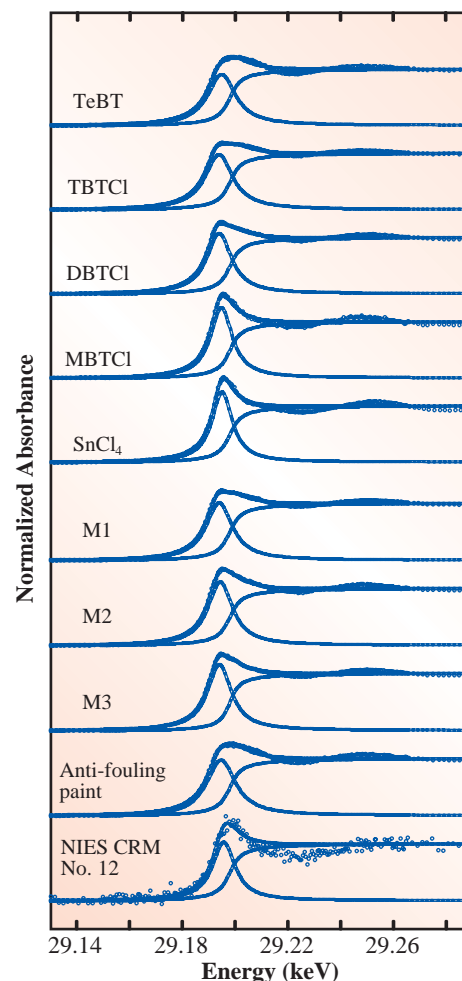

Fig. 1. Tin *K*-edge XANES spectra of standard materials (TeBT, TBTCl, DBTCl, MBTCl, and $SnCl_4$), mixtures of the standard materials (M1, M2, and M3), an anti-fouling paint sample and NIES CRM No. 12 (reference sediment sample) with simulation results by arctangent and Lorentzian functions. M1 = 1:1 mixture of TBTCl and DBTCl by mole ratio; M2 = 1:1 mixture of TBTCl and MBTCl; M3 = 1:1 mixture of DBTCl and MBTCl.

exhibits systematic broadening upon increasing the number of butyl groups bound to Sn, which is presumably due to multiple scatterings by the butyl groups bound to Sn. 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 ligands to Sn. These findings suggest that the broadening of the first peak can be employed for the speciation of Sn compounds in environmental samples. To quantitatively analyze the Sn species from the broadening, the XANES spectra were fitted by a combination of a Lorentzian function and an arctangent function (Fig. 1). There is a linear correlation between full width at half maximum (FWHM) of the Lorentzian function and the number of butyl groups (Fig. 2). In environmental samples, 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 (Fig. 1). The FWHM values of the mixtures are plotted in Fig. 2 against the average number of butyl groups bound to Sn in the mixtures, which we name "the organic extent." For example, the organic extent becomes 2.0 for the 1:1 mixture of TBTCl and MBTCl. The values of the three mixture samples are consistent with the calibration line (Fig. 2), showing 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 anti-fouling paint, and NIES CRM No. 12. We could obtain XANES spectra for NIES CRM No. 12 containing only 10.7 ppm of Sn, suggesting that the detection limit of the fluorescent XANES can reach the ppm level, which could be sufficiently sensitive 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 anti-fouling 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, suggesting that inorganic species are the main Sn component in the sample. The analyses of the environmental samples indicate that the present method can be used for Sn speciation in solid materials such as sediments, biocides, and biological samples.

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 conventional chromatographic methods. It is considered that the present method can be more reliable in terms of accuracy, since the method does not require any complex pretreatment procedures that may induce various errors in 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.
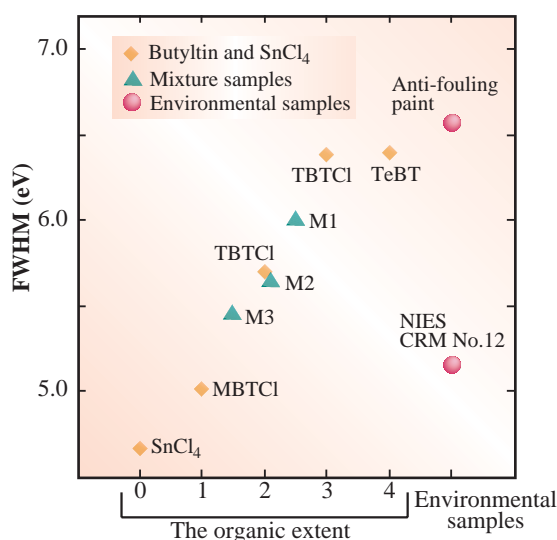

Fig. 2. Relationship between the FWHM of the Lorentzian function in the simulation of Sn K-edge XANES spectra and the organic extent (= the average number of butyl groups bound to Sn). The results for the mixture samples (M1, M2, and M3) are also plotted. The FWHM values of the anti-fouling paint and NIES CRM No. 12 are indicated at the right-hand section.

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