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Speciation of heavy metals accumulated into land snails by XANES spectroscopy

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Introduction

We have reported in previous studies that the metals detected from the parts of land snail bodies reflect the amount of metals in their living environment, making land snails suitable for environmental monitoring [1]. In this study, mainly Cu and Zn, along with other heavy metals, of the shells and the body parts of *Bradybaena similaris*, land snail, were investigated using XANES technique. XANES spectroscopy, unlike biochemical analysis and serial chemical extraction, has an advantage as a chemical speciation technique, due to its nondestructiveness and admittance to a direct investigation. In addition, an attempt was made to quantify the chemical species of each heavy metal by applying partial least-squares (PLS) method, which can deconvolute overlapped XANES spectra of mixtures [2].

Materials and Methods

Cultivated snail samples, *Bradybaena similaris*, were dissected into four parts: shell, hepatopancreas, mantle, and the rest. Then, each sample was vacuum dried, powdered, and sealed into oxygen-impenetrable bags. To the samples prepared in such manner, Cu and Zn K-absorption spectra were measured in the fluorescence mode using a Si (111) two-crystal monochromator and a Lytle-type detector [3] at BL-9A of KEK Photon Factory, Japan.

The standard chemical reagents, whose ligands are S, N, and/or O were chosen to quantify the relative abundance of metals. As S-bound compounds, Cu diethyldithiocarbamate (Cu-S) and Zn diethyldithio-carbamate (Zn-S) were chosen. As organic O-ligand compounds, Cu acetate (Cu-Oo) and Zn acetate (Zn-Oo) were used. As N/O-bound compounds, Cu EDTA (Cu-NO) was used. Furthermore, Cu carbonate (Cu-Oi) and Zn carbonate (Zn-Oi) were chosen as inorganic O-bound compounds. These reagents were paired and powdered to make a series of standard pairs composed of different chemical composition percentage: Cu-S/NO (Cu-S and Cu-NO), Cu-SOo (Cu-S and Cu-Oo), Cu-SOi (Cu-S and Cu-Oi), Zn-SOo (Zn-S and Zn-Oo), and Zn-SOi (Zn-S and Zn-Oi). The standard reagents were diluted in BN powder and made into pellets, in a diameter of 10mm, sealed into oxygen-impenetrable bags, and were applied for PLS modelling.

Results and Discussion

By applying the PLS models obtained for the mixtures of standard compound series, the relative abundance of each compound was estimated. The curve-fitted spectra, resulting from PLS modelling were compared with that of hepatopancreas. In Table 1, the estimated content of S-bound and O-bound Cu species in each part of the snail bodies, along with the residual values are shown. The smaller the residual values created a better fit [4]. When negative values appear in O-bound result, it indicates that the actual spectra appear in the lower energy region than the pure S-bound reagent.

It shows the possibility that in the hepatopancreas, Cu is bound completely with S, or if not, in a more anoxic condition. However, since such conditions are not found in biological systems, it is necessary to choose other reagents for an S-bound Cu model reagent. The PLS result indicated that for Cu, S-bound compound was higher in the order of hepatopancreas > mantle > body >shell. From the agreement with the order of appearances of XANES spectra, hepatopancreas> mantle> body> shell from lower energy, it was concluded that XANES with modeling by PLS could open a pathway to a variety of environmental scientific studies.

Table1 Estimated content of S- and O-bound Cu species

		Cu		
		Cu-SOo	Cu-SOi	Cu-S/NO
hepatopancreas	S bound (%)	68	119	99
	O bound (%)	32	-19	1
	residue	0.0027	0.0032	0.037
body	S bound (%)	78	121	95
	O bound (%)	22	-21	5
	residue	0.040	0.040	0.040
mantle	S bound (%)	57	99	97
	O bound (%)	43	1	3
	residue	0.024	0.030	0.037
shell	S bound (%)	8	46	24
	O bound (%)	92	54	76
	residue	0.061	0.042	0.087

References

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