

Improvement of speciation of chromium by X-ray absorption fine structure and estimation of the reduction of hexavalent chromium in soil

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1 Introduction

The determination of the ratio of Cr(III)/Cr(VI) in soil samples was investigated by X-ray absorption fine structure (XAFS). In the previous methods [1], the normalization energy of the Cr K-edge in X-ray absorption near-edge structure (XANES) spectra was not clearly defined. So, it was difficult to determine Cr(VI) contents in soil or sediment samples with sufficient accuracy. Therefore, we investigated to find the best normalization energy in the XANES spectra for the improvement in determination of Cr(VI) in soil.

2 Experiment

The XANES spectra of standard reference samples prepared by mixing various ratio of Cr₂O₃ (Cr(III)) and CrO₃ (Cr(VI)) particle reagents. Two different types of soil were prepared; Andosol (0-25 cm), Brown forest soil (0-20 cm). Soil samples were packed into the column, respectively. And the Cr(VI) 1000 μg L⁻¹ solution flow into a column. After the spiking, the soil samples were pressed out column and separated into each 1 cm. All layers were measured by XANES just after spiking and after 24 hours. The ratio of Cr(III)/Cr(VI) in the soil samples were calculated based on the area of pre-edge peak in the Cr K-edge XANES spectra of standard reference samples. Cr K-edge XANES spectra were measured in the fluorescence mode using a Lytle type detector at the BL-12C equipped with a double crystal monochromator of Si(111). The spectra were treated by the REX2000.

3 Results and Discussion

It was considered that the peak in the spectrum of the standard reference was due to transition of Cr (III). The peak observed near 6010 eV in K-edge is peculiar to Cr(III), ascribing to the transition of 1s (a_{1g})→3d ($t_{2g}^2e_g$) (Fig. 1) [2]. By normalization at this position, we were able to obtain the better calibration curve ($R^2=1.000$) (Fig. 2).

In order to estimate the behavior of Cr(VI) in soil, we observed the valence of Cr in soil after spiking Cr(VI) solution. After 24 hours, the reduction of Cr(VI) was observed in all samples of the two different types of soil. The reduction to Cr(III) starts just after Cr(VI) adsorbed to soil, the 20% of the total Cr(VI) was reduced to Cr(III) in the 24 hours.

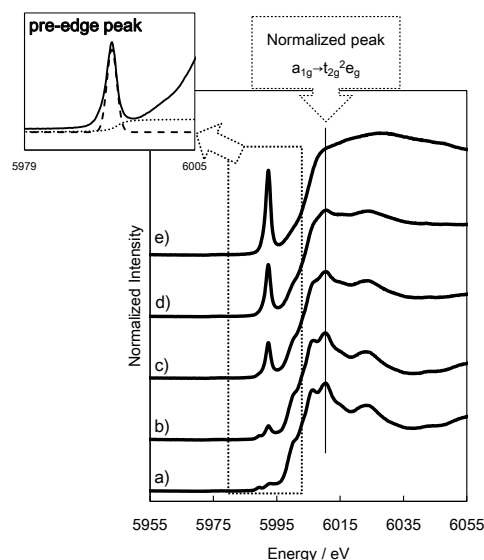


Fig. 1: XANES spectra of mixtures of Cr₂O₃ and CrO₃, Cr(III)/Cr(VI) ratio a) 100/0, b) 75/25, c) 50/50, d) 25/75, e) 0/100, respectively. Pre-edge peak at 5990 eV was due to transition from 1s to 3d orbitals peculiar to Cr(VI). Pre-edge peak is approximated by linear combination of two function, that is Gaussian (dashed) and Arctangent (dotted). Peak area was determined by the area of Gaussian from 5979 eV to 5995 eV.

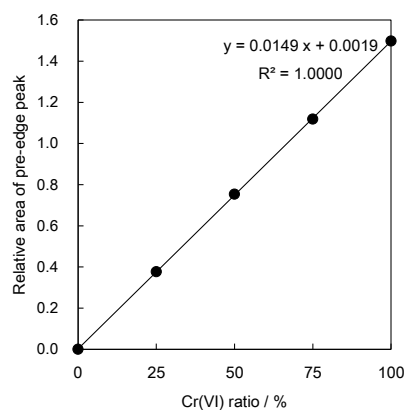


Fig. 2: Calibration curve of the area of pre-edge peaks shown in Fig. 1.

References

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