

## In-situ XANES measurement of change of oxidation states of Ce(III) to Ce(IV)

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### Introduction

Actinides migration are of great concern in the environment because of their radioactivity and long half-lives. Their migratory behavior depends on their oxidation states [1] that differ among the III, IV, V, and VI. For the present study, we developed a continuous flow system for in-situ XANES measurements of the oxidation state of Cerium (Ce). Ce was selected because it is an analogue of trivalent actinides. Further, the oxidation state of Ce(III) changes to Ce(IV) after exposure a desferrioximine B (DFO) solution [2].

### Experimental

#### In-situ flow system for XANES measurement

Figure 1 is a diagram of the continuous-flow system to measure the in-situ XANES spectra. The system is installed at beam line 27B in the Photon Factory of the High Energy Research Organization (Tsukuba, Japan). It employs two micro-tube pumps controlling flow rate of the contained solutions. Each solution pumped up from a polyethylene bottle is mixed at the system's mixing point. The hand-made mixer consisted of a silicon tube of 5 mm internal diameter. Through this tube, the mixed solution is introduced to the measurement cell made of a silicon plate with 5 x 5 mm trench. The reaction time,  $t$ , in seconds was determined by  $t=L \cdot A \cdot r^{-1}$ , where  $r$  is flow rate ( $\text{cm}^3/\text{s}$ ),  $L$  length between the mixing point and the measurement point (cm), and  $A$  is a cross section of the silicon tube ( $\text{cm}^2$ ). Note that the mixer is simply a tube, and nothing inside the tube to ensure that the two solutions were mixed.

#### Solution

Desferrioxamine B (DFO), purchased from Sigma Co. Ltd., was used as received. The chemicals employed were analytical grade. 1mM solutions of Ce(III)(NO<sub>3</sub>)<sub>3</sub> and DFO were prepared by dissolving them in deionized water. The pHs of the resulting solutions were adjusted to 7.0 by adding 1 M HCl and NaOH solution.

#### Measurement of XANES spectra

XANES spectra were measured in the fluorescence mode for the mixed solutions using a 7-element Ge array detector interfaced to single-channel analyzers. XANES spectra for the Ce  $L_{\text{III}}$  edge were obtained at the measurement point by changing the energy of the induced X-ray that was scanned at intervals of 0.2 eV. The fluorescent X-ray of the mixed solution was measured for 5 s at each energy interval of the induced X-ray.

XANES spectra were measured at different reaction times for the Ce  $L_{\text{III}}$  edge in the Ce(III) solution alone, and after the Ce solution was mixed with DFO solution. Cerium(III)(NO<sub>3</sub>)<sub>3</sub> and Ce(IV)O<sub>2</sub> were used as the standard materials for trivalent and tetravalent Ce, respectively. Energy calibration was performed based on the energy of the first peak of Ce(IV)O<sub>2</sub> at 5731 eV.

### Results

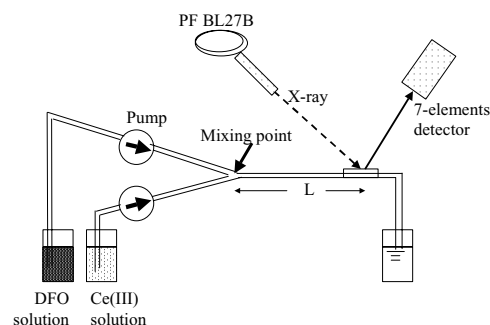


Fig. 1 Conceptual diagram of the mm-scale continuous flow system for measuring the oxidation states of elements by in-situ XANES analysis. PF BL27B means KEK, PF beam line, and  $L$  in cm. See the details of the system shown in Experimental.

#### XANES spectra measurements of Ce-DFO mixtures

The  $L_{\text{III}}$  edge Ce XANES spectra of a 1 mM Ce solution without DFO showed one strong peak at 5726 eV. The peak energy was the same as that in the spectrum of the Ce(III) standard, denoting that Ce was present as Ce(III) in the solution. For the mixture of Ce and DFO solutions, a peak at approximately 5738 eV was distinguishable in the spectrum. The energy of the first peak shifted to higher energy in the spectra. Yoshida et al. indicated that the energy of the first peak shifts with a change in the fraction of Ce(III) to Ce(IV) [2]. This finding showed that Ce(IV) oxidized by the reaction with DFO.

### References

- [1] R. J. Silva and H. Nitsche, *Radiochim. Acta* **70/71**, 377 (1995).
- [2] T. Yoshida, T. Ozaki, T. Ohnuki, and A. J. Francis, *Radiochimica Acta* **92**, 749 (2004)

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