

# Spectroscopic Characterization of Aqueous Am(III) Species

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## 1. Introduction

Minor trans-uranic (TRU) radionuclides including Am in spent nuclear fuels are the major concerned long-lived radionuclides in the high-level radioactive waste managements. Understanding their physicochemical interactions in groundwater systems is essential for the safety assessments of the high-level radioactive waste managements. Due to relatively weak luminescent properties (luminescence half-life: ~23 ns) [1] and high specific radioactivity (radioactivity half-life  $^{241}\text{Am}$ : 432 yr), there are limited number of spectroscopic studies on aqueous Am(III) species [2-4]. Upon complex formation with hydroxyl group [2] or organic ligands [3,4], Am(III) absorption peak shifts towards longer wavelength [2,3], while luminescence intensity and lifetimes increase [4]. However, many of the thermodynamic properties of Am(III) species are still adapted from the results of Cm(III) and Eu(III) studies [5]. In this study, we directly characterized the spectroscopic properties  $\text{Am}^{3+}$  and its hydrolysis products progressively formed upon increase in the pH conditions. Temperature-dependent changes of the spectroscopic properties will be also discussed in relation to the species distribution.

## 2. Experimental

### 2.1 Am(III) sample preparation

$^{241}\text{Am}$  was used as a Am(III) source. Am(III) samples were prepared in the concentration of 2-6  $\mu\text{M}$  in 0.1 M  $\text{NaClO}_4$  under the Ar condition to prevent dissolution of  $\text{CO}_2$ . Pre-estimated amount of diluted NaOH was added to adjust the pH. Precipitation was separated from supernatant by centrifugation at 18000 rpm for 1 hour. Concentration of Am(III) in the supernatant was measured by Liquid Scintillation Counting (TriCarb, PerkinElmer). Presence of colloidal particles in the supernatant was determined by Laser Induced Breakdown Detection (LIBD) method. pH of each

sample was measured by combined glass electrode (Orion) at the last step of the experiments.

### 2.2 Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)

Nd:YAG pumped OPO laser (Vibrant, Opotek Inc.) was used as an excitation source of 503 nm. Emission per wavelength was collected by a spectrometer (Semrock) connected to an ICCD (Andor Tech.). A delay generator triggered by the laser flashlamp was set to control the timing of the Q-switch of the OPO laser and the ICCD gating times. Series of luminescence measurements were carried out as increasing the ICCD gating delay time in stepwise to measure luminescence decay curves. Luminescence half-lives were calculated from linear regression of the luminescence intensity decays in natural log unit as a function of gate delay time.

## 3. Results and Discussion

### 3.1 pH-dependent Luminescence Spectra

Luminescence spectra of Am(III) solutions under different pH conditions were obtained for the  $^5\text{D}_1 \rightarrow ^7\text{F}_1$  transition as shown in Fig. 1. The center of the peak is 689 nm with FWHM of 15 nm at pH 2. As increasing the pH of the solutions, the concentrations of the supernatants decreased as measured by LSC, indicating formation of  $\text{Am}(\text{OH})_3(\text{s})$  precipitations. Luminescence intensity of Am(III) in the supernatants decreased accordingly. While the peak positions of the supernatants do not change, peak widths become slightly broadened towards longer wavelength region. These observations indicate formation of  $\text{Am}(\text{OH})_n(\text{aq})$  upon increase of the available hydroxyl groups at high pHs. Our results support a previous report by showing red-shifted absorption as hydrolysis reaction progresses [2]. Currently, we are working on measurements of luminescence spectra at different temperatures in attempt to increase the signal to noise

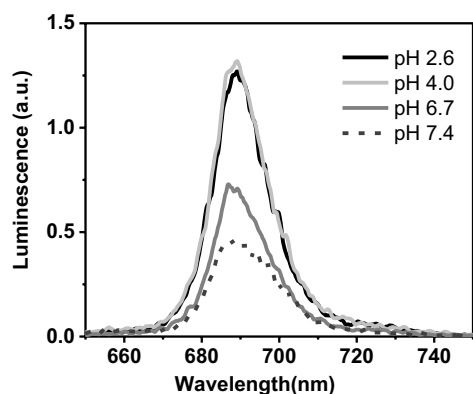


Fig. 1. Luminescence spectra of Am(III) at different pHs in 0.1 M NaClO<sub>4</sub>. Concentrations of the Am(III) in the supernatants decreased from 5.8 μM to 1.1 μM as Am(OH)<sub>3</sub> precipitated upon increasing the pH of the solutions from pH 2.6 to pH 7.4. Spectra were averaged over 2000 shots at a 30 ns delay from the excitation at 503 nm (3.5 mJ) with a gate width of 150 ns (pH 2.5).

ratio, which can enable luminescence measurements of higher pH conditions with lower Am(III) concentrations. Spectral deconvolution results will be also discussed.

### 3.2 pH-dependent Luminescence Lifetimes

Lifetimes of the Am(III) luminescence were measured from linear regression of the luminescence decays in the natural log scale as a function of ICCD gate delay time. Under the acidic conditions (pH 1-2.6), where all the Am(III) present as Am<sup>3+</sup>, the lifetime was measured to be 23.4 ± 0.4 ns, as previously reported [1]. As increasing the pH, lifetimes also gradually increased as shown in the Fig. 2. These results suggest that displacing water molecules by hydroxyl group also results in the increased luminescence lifetimes as other organic ligands [4]. Based on the results from spectral deconvolutions, speciation and their distributions will be presented.

## 4. Conclusions

We demonstrate here that luminescence of Am(III) can be useful in the study of Am speciation. pH-dependent luminescence spectral changes were observed along with increased lifetimes. Our results suggest that hydrolyzed Am(III) species have distinguished luminescence properties and can be resolved from the TRLFS studies. Luminescence measurements at different temperatures will be discussed in attempt to probe higher pH conditions,

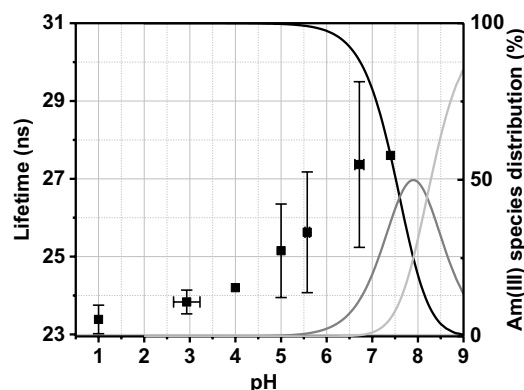


Fig. 2. Luminescence lifetimes (square) of Am(III) under the different pH conditions. Lifetimes were obtained from linear fitting of luminescence decays in the natural log scale as a function of gate delay time. Gradual increase in the lifetimes are displayed along with distribution changes of Am<sup>3+</sup> (black line), Am(OH)<sup>2+</sup> (gray line), and Am(OH)<sub>2</sub><sup>+</sup> (light gray line), calculated from formation constants of log<sup>\*</sup>β<sub>1,1</sub> = -7.6, log<sup>\*</sup>β<sub>1,2</sub> = -15.8, log<sup>\*</sup>β<sub>1,3</sub> = -26.9 at I = 0.1 M NaClO<sub>4</sub> [5].

where more hydrolyzed Am(III) species are present. Temperature-dependent speciation distribution changes will be discussed in relation to the thermodynamic properties of the hydrolysis of Am(III).

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