

# Uranium (VI) Complexation Studied by Time-Resolved Laser-Induced Fluorescence Spectroscopy

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The speciation of uranium directly affects its transport rate in the environment. There is great interest in the development of models which reliably predict uranium speciation. These models require a thermodynamic database of thermodynamic complex stability constants for possible uranium species.<sup>1</sup> Except under reducing conditions, uranium is present as the U(VI) dioxo-cation  $\text{UO}_2^{2+}$ . The  $\text{UO}_2^{2+}$  ion may complex with organic and inorganic ligands as well as soil bacteria and mineral surfaces. In environmental systems, the ligands may include carboxylic acid groups of humic and fulvic acids.

Time resolved laser induced fluorescence spectroscopy (TRLFS) is used to study U(VI) systems to determine the stability constants with a variety of ligands. TRLFS gives direct species-specific information on the lifetime and intensity of a fluorescing species. Under certain conditions this information can be used to calculate the concentration. We are studying simple model compounds containing carboxylic acids. Currently we are continuing our systematic study of the effect of carbon chain length of carboxylic acids on the complex stability constants.

TRLFS measurements using a pulsed Nd-YAG MOPO laser system were made on the  $\text{UO}_2^{2+}$  ion and the first hydrolysis species  $\text{UO}_2\text{OH}^+$  between pH 1 and 5 and characterized for the fluorescent signal of interest. It can be seen that at pH 1.43 through pH 3.14 the peak positions are relatively constant and are those of the free uranyl (i.e. main peaks at 489nm, 510nm, and 533nm) this is shown in figure 1. At pH 4.10 a shift in peak position indicates a second species as shown in figure 1. Time resolved measurements indicate a single fluorescent species in solution until pH 3.8. The single species below pH 3.8 is that of the free uranyl ion whose measured lifetime is  $1.8 \pm 0.3 \mu\text{s}$ . This compares to the literature value of  $2 \pm 0.1 \mu\text{s}$ .<sup>2,3</sup> The first hydrolysis product which appears around pH 3.8 and continues to increase in concentration has a lifetime of  $80 \pm 20 \mu\text{s}$ . This value for the hydrolysis compares well with the literature value of  $80 \mu\text{s}$ .<sup>3</sup> This consistency between our data and literature indicates our technique is reliable.

Uranium acetate complexation between pH 1 and 5 was examined as well. Figure 2 shows at pH 2 and 3 the main species present is that of free uranyl and at pH 4 and 5 a second species, that of uranyl triacetate is present. A speciation diagram was predicted using MINEQL and showed free uranyl to dominate until pH 3, where the first uranyl acetate complex reaches a maximum of about 50% of the concentration. Uranyl monoacetate studies were carried out at pH 3. TRLFS studies indicate only one fluorescent species in solution at pH 3, although the speciation diagram indicated two

should be present. The peak positions as those of the free uranyl however, the lifetime is much shorter  $0.7 \pm 0.2 \mu\text{s}$ . It has been determined that the acetate ion is causing quenching of the fluorescence intensity and lifetime. Using mass balance equations and the equilibrium between uranyl and acetate, the stability constant was determined to be  $3.24 \pm 0.02$ . These results are preliminary and are currently being confirmed.

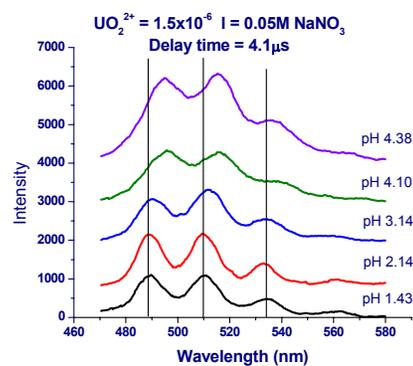


FIG. 1: Spectrum showing peak position and relative intensity vs. pH for U(VI) in 0.05M  $\text{NaNO}_3$ .

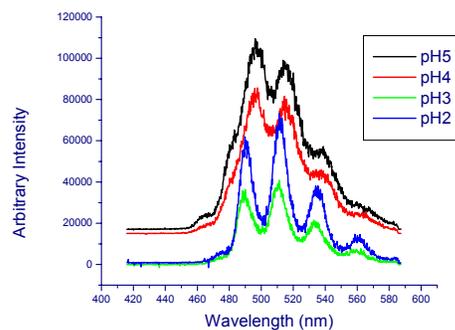


FIG. 2: Spectrum showing peak position and relative intensity vs. pH for U(VI) in 0.05M  $\text{NaNO}_3$  and 0.05M acetate.

## REFERENCES

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