

# Spectroscopies for Environmental Studies of Actinide Species

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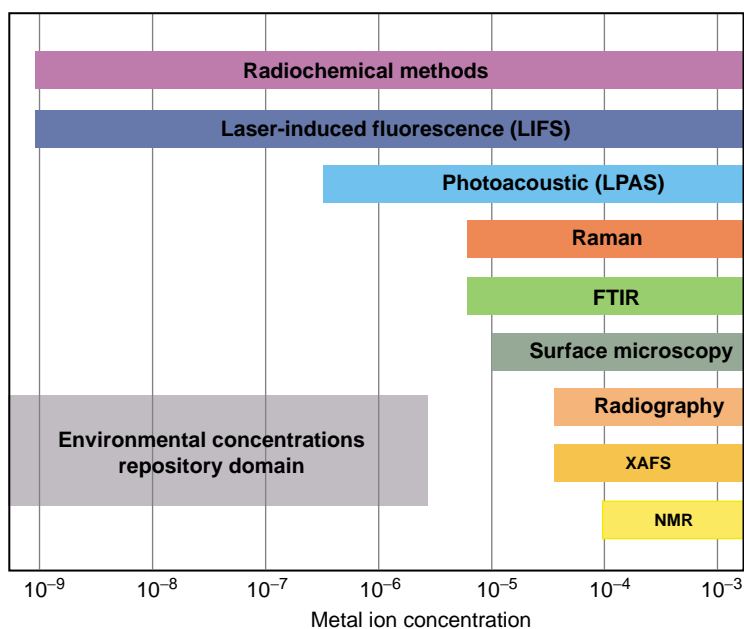


Figure 1. Spectroscopic Sensitivities

In order to understand the complex chemistry of actinides in the environment, we need to have detailed information about its chemical speciation in natural waters in association with natural mineral phases. Chemical speciation identifies not only the molecular formula, charge, and structure of an element's compounds, but also the isotopic composition of the molecule and the oxidation states of its constituents. This information is a prerequisite for making accurate assessments of the compound's thermodynamic and kinetic stability.

Unfortunately, actinide solubilities in natural waters are expected to be generally below micromolar ( $10^{-6}$ ) concentrations, and these low concentrations complicate a direct non-destructive investigation. A number of spectroscopic methods have been developed to optimize understanding and quantification of actinides' reactions on the molecular scale (see Figure 1). Because of differences in the physical properties among the actinides, no single spectroscopy can adequately probe all actinides. We have had to apply a range of spectroscopic techniques in order to gain maximum insight into the environmental chemistry of the actinides. Some examples of our multifaceted approach to studying solid-state and solution speciation are given below. Other examples are given in the main text.

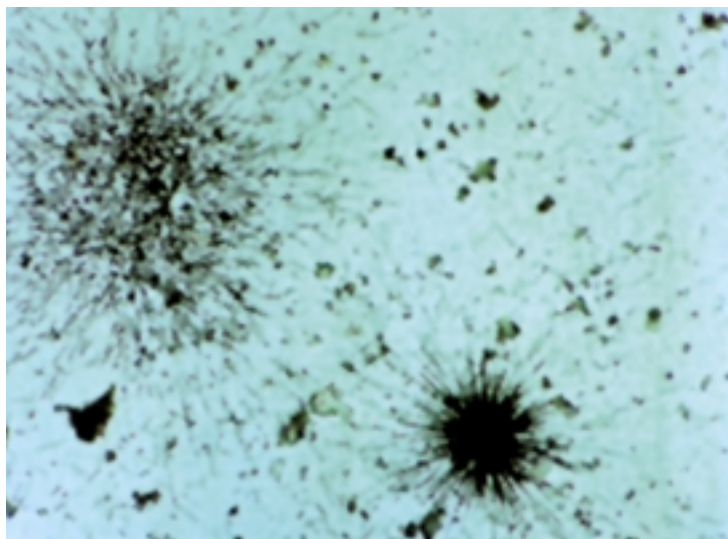


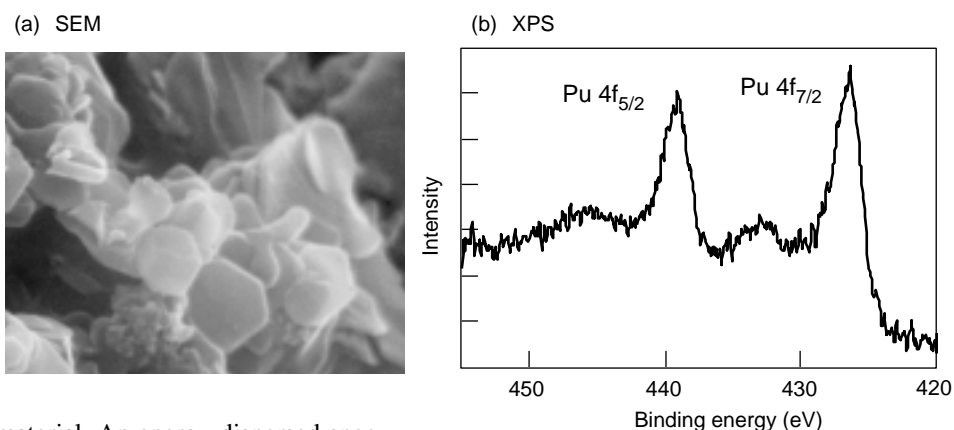
Figure 2. Autoradiograph of Plutonium in Rocky Flats Soil

**Autoradiography.** Autoradiography is one of the oldest techniques in radiochemistry, having been pioneered by Becquerel in 1896. It uses photographic emulsions to detect and determine the distribution of radioactive material in media and on surfaces. While used extensively for medical and biological research, the technique can also provide qualitative visual information on the distribution and density of radioactive material in soil. The photo seen in Figure 2 is a microautoradiograph of a  $3.5 \text{ mm} \times 4.5 \text{ mm}$  soil sample from the Rocky Flats Environmental Technology Site. The sample is contaminated with plutonium and americium, and alpha particles emitted by either of those radioactive elements leave omni-directional tracks in the emulsion. We used this visualization technique to separate and concentrate 'hot' soil particles for further spectroscopic analysis. XAFS spectroscopy and SEM/EDS (see below) identified plutonium as the major contaminant in the soil, which contained only minor amounts of americium.

### Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS)

The interaction of actinides with mineral surfaces have been studied by radiochemical techniques (isotherm tracer experiments) or spectroscopic techniques. SEM and XPS are two surface analysis techniques that are widely used to investigate speciation at a solid-liquid interface. We use SEM to examine the crystallinity of micron-scale actinide and lanthanide solid phases.

As an example, the SEM picture seen in Figure 3(a) shows particles of  $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$  that precipitated from a Np(V) solution oversaturated with carbonate. The image clearly shows the crystalline nature of the solid and the lack of amorphous material. An energy-dispersed spectrometer was used to evaluate the chemical composition of those solids, which showed that only sodium, neptunium, and carbon are present in the solid. XPS is sensitive to an element's electronic state and can be used to examine the oxidation state of a metal ion. The oxidation state is revealed by a shift in the binding energy in the XPS photoemission spectra. Figure 3(b) shows that when Pu(IV) compounds sorb onto  $\text{SiO}_2$  (one of the simplest metal oxide surfaces), the characteristic  $4f_{7/2}$  photoemission peak shifts by several electron volts away from the peak position of metallic plutonium.



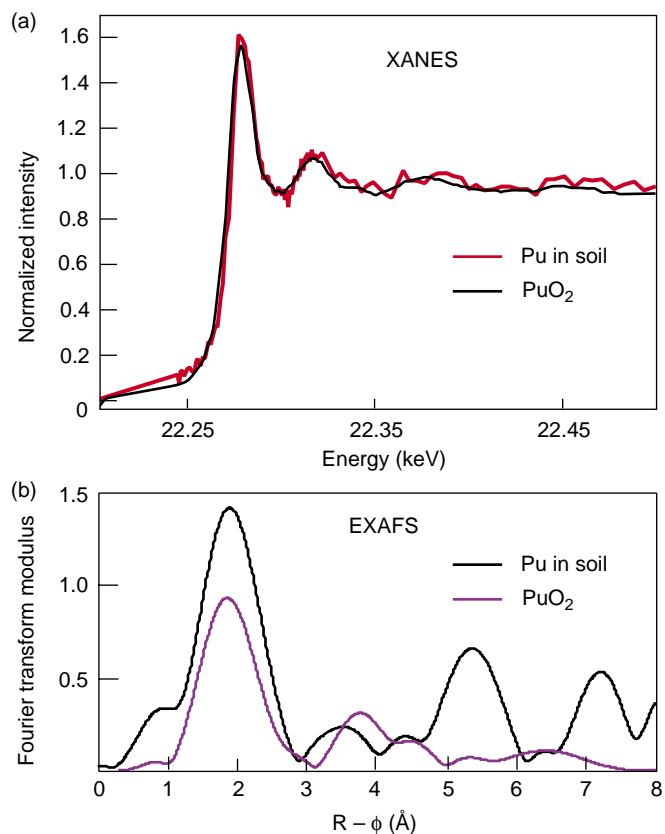
**Figure 3. Surface Analysis of Np and Pu Compounds**

Figure 3(b) is courtesy of R. Schulze and M. Neu.

### X-Ray Absorption Fine Structure (XAFS) Spectroscopy.

The use of XAFS to gather information about the actinides has increased dramatically in the last five years. XAFS is element specific and allows us to deduce speciation without perturbing the sample's original distribution. The spectroscopy can yield information on the actinide's oxidation state, coordination number, bond length, and nearest-neighbor atoms. We have used XAFS to determine those features for solid (amorphous and crystalline) and solvated actinide compounds. Samples typically must have actinide concentrations in the lower millimolar range. More information about XAFS spectroscopy is found in the Conradson's article on page 422.

As discussed above, we used XAFS to identify the predominant plutonium species in contaminated soil at Rocky Flats. This was the first definitive spectroscopic data on plutonium in an environmental sample. The x-ray absorption near-edge structure data (XANES) of the  $L_2$  absorption edge, seen in the graph in Figure 4(a), indicate that the plutonium in the most concentrated samples is in the highly stable and immobile form of plutonium dioxide,  $\text{PuO}_2$ . The extended x-ray absorption fine structure (EXAFS)—Figure 4(b)—shows eight oxygen neighbors at a Pu–O distance of 2.33 Å, consistent with the fluorite structure  $\text{PuO}_2$ . The data also show that plutonium is most concentrated in soil layers that are about 0.25–0.5 millimeters below the surface, is dispersed on both macro- and microscopic scales, and is not highly associated with any other particular element. These results help Rocky Flats personnel who must address potential plutonium migration paths from the site and remediate the area.



**Figure 4. XAFS of Plutonium-Contaminated Soil Sample**

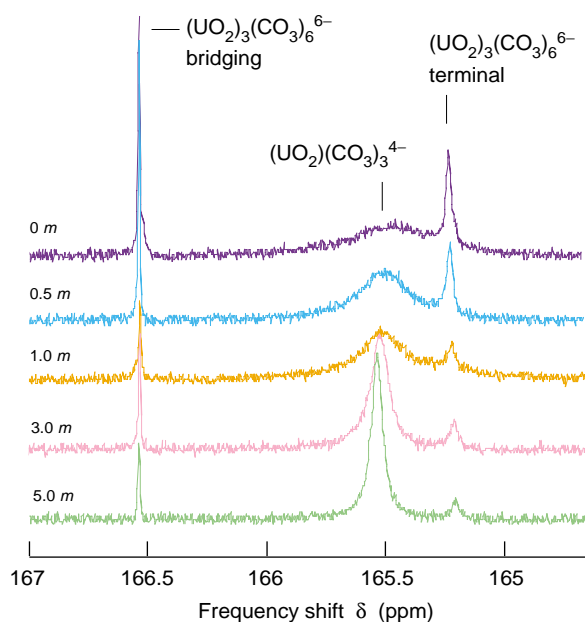
**Nuclear Magnetic Resonance (NMR) Spectroscopy.** NMR is a standard analytical method in organic and inorganic chemistry. It is used for probing the electric quadrupole moments or magnetic dipole of some elements, which provides information about the structure and conformation of chemical species. Modern

high-field superconducting magnets allow us to investigate the speciation down to millimolar concentrations.

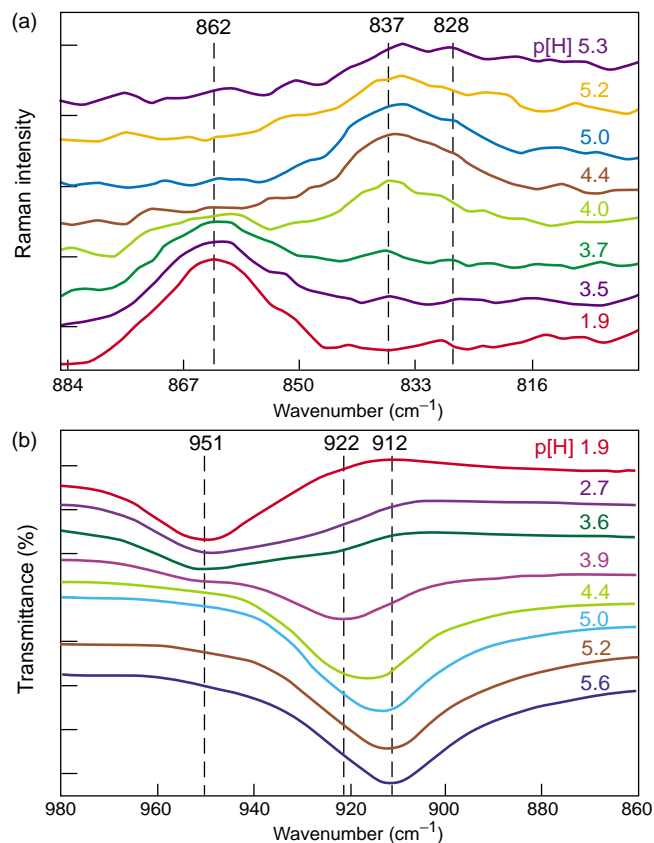
At Los Alamos, we have used  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR to study the stability of the highly soluble triscarbonato complex,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , in NaCl solutions. This U(VI) anion is stable at relatively high carbonate concentrations, but with decreasing pH, the complex protonates and forms the trimer,  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ .

The trimer's structure was determined previously by single-crystal x-ray diffraction and by XAFS spectroscopy. As illustrated in Figure 5, we have used the chemical shifts to characterize and quantify the U(VI) species involved in the chemical equilibrium. The  $\text{UO}_2(\text{CO}_3)_3^{4-}$  complex has three equivalent terminal carbonate ligands (see Figure 4(c) in the main text) and thus it produces a single  $^{13}\text{C}$  NMR frequency shift at  $\delta = 165.6$  parts per million (ppm). The trimer has two different carbonate ligand environments—the outside of the complex (terminal) and between the uranyl ions (bridging)—that give rise to two signals:

$\delta = 165.2$  ppm for the three terminal ligands and at  $\delta = 166.5$  ppm for the three bridging ligands. By integrating the signal, we obtain the stability constants. These indicate that increasing the ionic strength favors and stabilizes the more soluble triscarbonato complex. Our studies are relevant for the transport behavior of An(VI) in geologic salt formations, such as those at the WIPP site.



**Figure 5. NMR Spectra of U(VI) Complexes**



**Figure 6. NMR Spectra of U(VI) Complexes**

**Fourier Transform Infrared (FTIR) and Raman Spectroscopies.** These two techniques measure the vibrational spectrum of molecules and provide information on the molecular structure and the characterization of functional groups. We have used them to study the relationship between bond strength and length in An(V,VI) compounds, including U(VI) complexes with hydroxide, chloride, phosphate, or chloride ligands.

As seen in Figure 6(a), the Raman-active symmetric ( $\nu_1$ ) stretch of the  $\text{UO}_2^{2+}$  ion in solution, normally at  $873\text{ cm}^{-1}$ , is shifted to  $862\text{ cm}^{-1}$  as coordinated water molecules are replaced with chloride ions in 5-M NaCl. With increasing pH, hydrolysis species can be observed at different frequencies. Interestingly, solution speciation in chloride brines depart significantly from predictions based on previous investigations of U(VI) in non-complexing sodium perchlorate ( $\text{NaClO}_4$ ) solutions. For example, the vibrational frequency of the first polynuclear hydrolysis product  $(\text{UO}_2)_2(\text{OH})_2^+$ , normally seen at  $852\text{ cm}^{-1}$  in  $\text{NaClO}_4$ , is not observed in chloride brines because of its lower stability. Instead, the signal for  $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$  is observed at  $837\text{ cm}^{-1}$  while the tetramer  $(\text{UO}_2)_4(\text{OH})_7^+$  appears at  $828\text{ cm}^{-1}$ . Analogous shifts of the vibrational frequencies for the  $(\text{UO}_2)_2(\text{OH})_2^+$  can be observed in the corresponding FTIR spectra seen in Figure 6(b). The IR frequency of the ion in 5-M NaCl shifts in  $\text{NaClO}_4$  solution from  $951\text{ cm}^{-1}$  to  $961\text{ cm}^{-1}$ , the trimer shifts from  $922\text{ cm}^{-1}$  to  $924\text{ cm}^{-1}$  and the tetramer shifts to  $912\text{ cm}^{-1}$ .

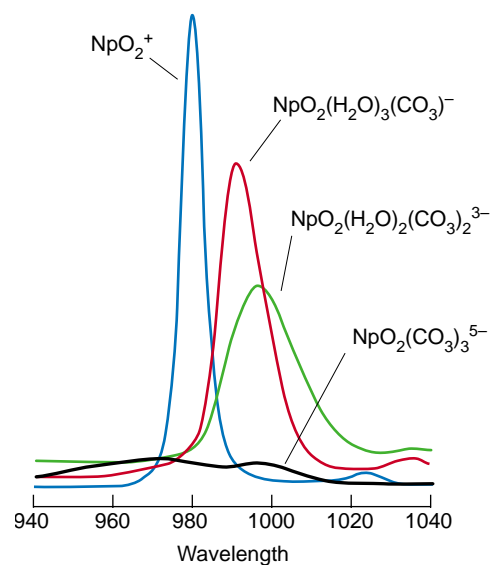
### Ultraviolet, Visible, and Near-Infrared (UV-vis-NIR) Spectroscopy.

Absorption studies employing UV-vis-NIR spectroscopy have been widely used to study the complexation reactions of actinides in solution. The technique has a sensitivity down to micromolar concentrations, and actinide species in all oxidation states can be characterized because the actinides exhibit characteristic Laporte forbidden f-f transitions. (See Table I.) Complexation reactions of the non-complexed ion can be tracked because the absorption band is shifted significantly with the addition of ligands. For example, the non-complexed Np(V) aquo ion,  $\text{NpO}_2(\text{H}_2\text{O})_5^+$ , exhibits a strong absorbance at 980 nm.

As seen in Figure 7, the monocarbonato species  $\text{NpO}_2(\text{H}_2\text{O})_3(\text{CO}_3)^-$  absorbs at 991 nm, the bicarbonato complex absorbs at 997 nm, and the tricarbonato complex absorbs at 974 nm. Combining these spectroscopic results with those from XAFS experiments has given us insight into the molecular structures of environmentally relevant Np(V) complexes.

**Table I. Characteristic Absorption Wavelengths**

| Species | Wavelength (nm) |
|---------|-----------------|
| U(IV)   | 650             |
| U(VI)   | 414             |
| Np(IV)  | 960             |
| Np(V)   | 980             |
| Pu(IV)  | 470             |
| Pu(V)   | 569             |
| Pu(VI)  | 830             |
| Am(III) | 503             |
| Cm(III) | 400             |

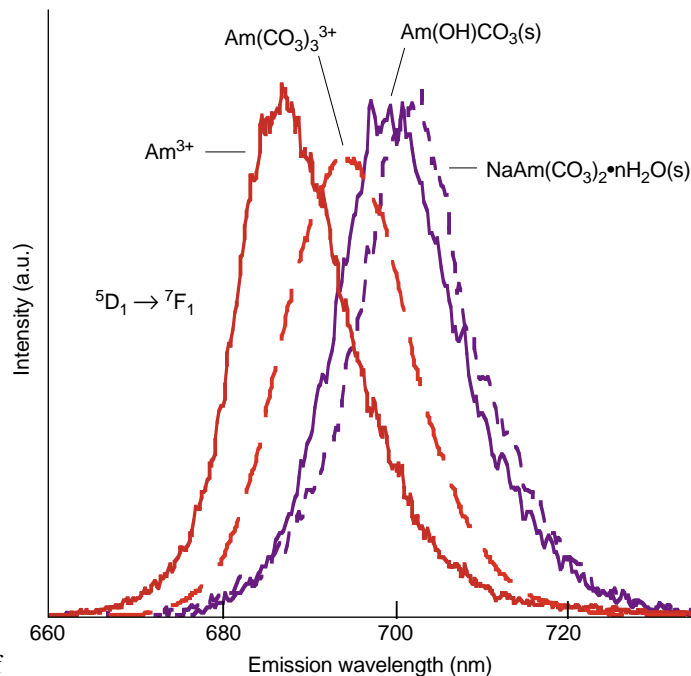


**Figure 7. UV-vis-NIR Spectra**

### Laser-Induced Fluorescence (LIF) Spectroscopy (LIF).

Fluorescence spectroscopy can be used to probe the excited and ground states of only a few actinides species—for example U(VI), Am(III), and Cm(III). The fluorescence decay rate of the emission spectra depends on the nature of ligands that are present in an actinide's inner coordination sphere. When combined with information about the lifetime of non-radiative relaxation processes, LIFS is sufficiently sensitive to probe chemical speciation at nanomolar concentrations.

We have used this method to characterize the environmentally relevant solid and solution compounds of U(VI) and Am(III). As inner-sphere water molecules are replaced with carbonate ligands, the emission wavelength changes. One of the strongest absorption transitions for Am(III) compounds is the  $^5\text{D}_1 \rightarrow ^7\text{F}_1$  band at 685 nm, and as seen in Figure 8, the peak emission for  $\text{Am}^{3+}(\text{aq})$  (at 685 nm) shifts towards higher wavelengths with carbonate complexation. The fluorescent lifetime of the ion's excited state also increases, for example, from 20.4 nanoseconds for  $\text{Am}^{3+}(\text{aq})$  to 34.5 nanoseconds for  $\text{Am}(\text{CO}_3)_3^{3-}$ . The increase follows the known trend for Eu(III) and Cm(III) complexes. From the measured lifetime of the excited state we determine that there are  $11.1 \pm 0.5$  water molecules around the  $\text{Am}^{3+}$  ion and  $6.0 \pm 0.5$  water molecules for  $\text{Am}(\text{CO}_3)_3^{3-}$ . Since the three carbonate ligands bond in a bidentate fashion, our results agree with a coordination number of 12 for the latter complex. Thus far, we have been unable to obtain fluorescence data on the mono- and bicarbonato complex due to the low solubility of Am(III) at lower carbonate concentration.



**Figure 8. LIF Spectra**