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Uranium Associated with Organic Ligands and Anaerobic Bacteria Using Synchrotron FTIR Microspectroscopy

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Introduction: We used synchrotron IR microspectroscopy to characterize the nature of the association of Uranium with organic ligands and bacteria.

Methods and Materials: Equimolar amounts of the organic ligands (catechol, salicylic acid, malic acid or fulvic acid) and uranyl nitrate solutions were combined and pH was adjusted to 3.5. Protocol of uranium reduction by *Clostridium sp.* was designed by Francis et al¹. The samples were freeze-dried were mounted on Cu tape and analyzed using synchrotron FTIR microspectroscopy at the NSLS. Automatic baseline and automatic smoothing were applied to each spectrum.

Results: Detailed information about the associations between the uranium, organic ligands and bacteria in samples was obtained using the bright intensity infrared light emitted from the synchrotron, which generated good quality infrared (IR) spectra. No mixing of the samples with KBr powder was done, since it may affect the bonding between uranium and functional groups of the organic ligands. IR studies (Figure 1) of the aromatic compounds showed that the ring stays intact after complexation. In general, the uranium usually binds to the hydroxyl or carboxylate groups found organic ligands. The uranium was found to be associated with both phenol groups in the catecholate complex, with a uranyl (UO_2^{2+}) vibration at $\sim 890\text{ cm}^{-1}$, which was obscured by C-H deformations. Two types of carboxylate coordination can be characterized using FTIR: unidentate or bidentate/bridging. The difference in the wavenumbers of the asymmetric ($\sim 1550\text{-}1650\text{ cm}^{-1}$) and symmetric stretching ($1340\text{-}1440\text{ cm}^{-1}$) of unidentate carboxylate bonding is greater than the bidentate/bridging bonding. IR shows that both the carboxylate (1599 and 1412 cm^{-1}) and phenol group participate in the uranium-salicylate complex, which had a U-O vibration at $\sim 910\text{ cm}^{-1}$. Bidentate (1562 and 1420 cm^{-1}) and unidentate (shoulders: 1614 and 1341 cm^{-1}) coordination between the uranium and carboxylate groups were found in the uranium-malate complex, which also had a U-O vibration at $\sim 910\text{ cm}^{-1}$. Uranium-fulvate samples were then compared to these analogs and it was found that the uranium complexes to the fulvic ligand via the carboxylate group in a unidentate fashion (1644 cm^{-1}) with some uncoordinated carboxyl groups (1770 cm^{-1}). The U-O stretching frequency was found to be at $\sim 920\text{ cm}^{-1}$, which was higher than the other u-organic analogs.

Preliminary IR analysis (Figure 2) of *Clostridium sp.* cells exposed to uranyl nitrate under anaerobic conditions show a very intense and broad $\nu(\text{OH})$ (not shown) indicating the increase in hydration of cells compared to bacteria that was not exposed to uranium. In the $1600\text{-}1700\text{ cm}^{-1}$ range, there is a doublet (1653 and 1639 cm^{-1}) for the unexposed bacteria sample, which is mostly due to peptidic $\nu(\text{C}=\text{O})$ vibrations of cellular proteins. The bacterial samples that were exposed to uranium show a strong peak at $\sim 1660\text{ cm}^{-1}$ with a very slight shoulder at $\sim 1640\text{ cm}^{-1}$. A possible explanation for this result is that structural changes in the cellular proteins are occurring when the bacteria is exposed to uranium. The increase and broadening of the peaks found in the $1150\text{-}1000\text{ cm}^{-1}$ range indicate increase in C-O-C, C-C-O vibrations and CN stretching, suggesting buildup of biopolymers, a result of the bacteria's response to the stress caused by the uranium in the environment. No uranyl ion peak was found in samples exposed to bacteria, indicate that the uranium present is in tetravalent state or below detection limits despite the strong synchrotron IR source. However, after exposure to ambient air and light, IR spectra (not shown) indicated small peaks at $\sim 900\text{ cm}^{-1}$, suggesting uranyl U-O stretching or degradation of organics on the surface.

Conclusions: The use of synchrotron IR microspectroscopy has its advantages in that no mixing with KBr of the sample is needed and that more accurate bonding information of the uranium to the organic ligands is readily obtained.

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Reference: Francis, A.J., C.J. Dodge, F. Lu, G.P. Halada, and C.R. Clayton, "XPS and XANES Studies of Uranium Reduction by *Clostridium sp.*" *Environ. Sci. and Technol.*, 28(4), 636-639.

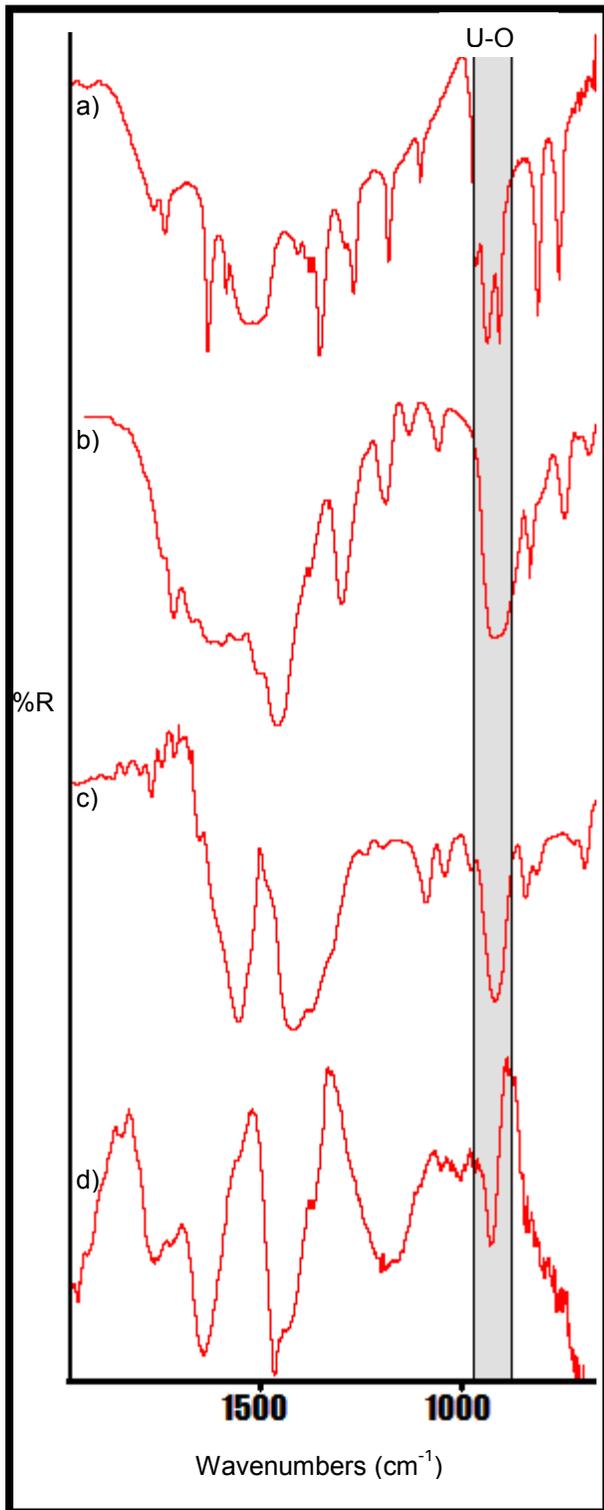


Figure 1: IR Spectra of a) U-catecholates b) U-salicylates c) U-malates and d) U-fulvates

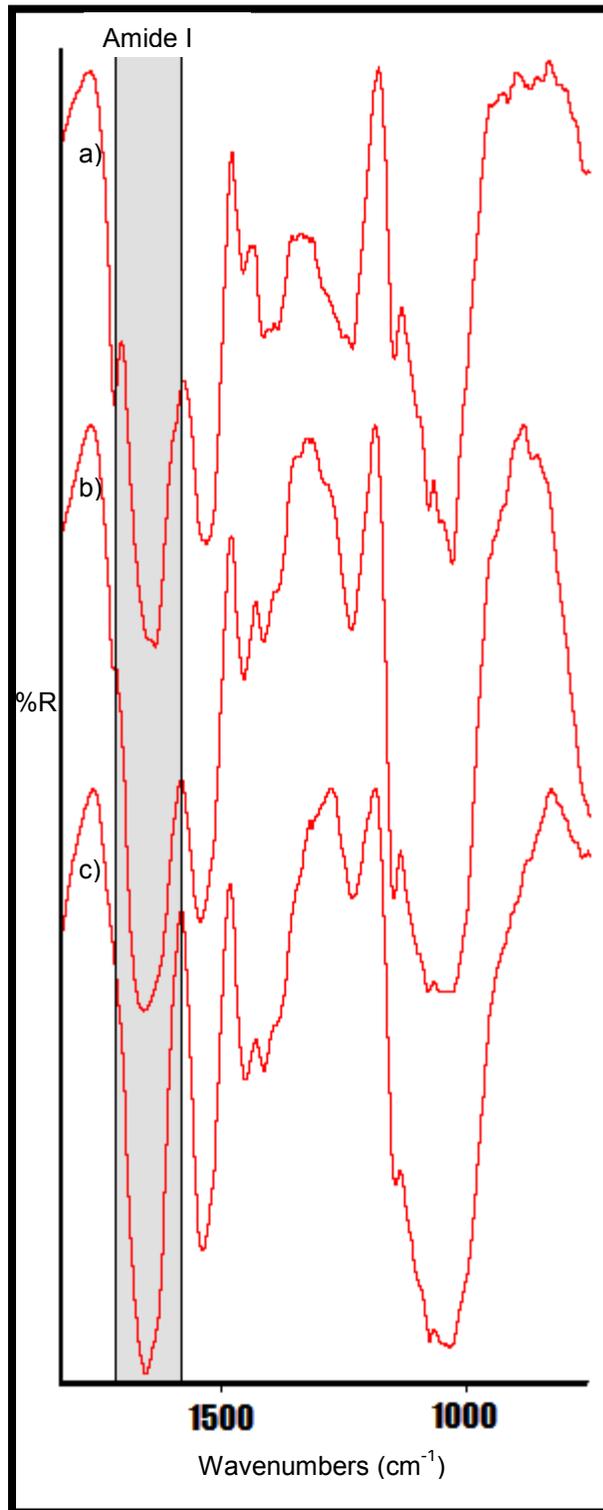


Figure 2: IR Spectra of a) Clostridium sp. b) Clostridium sp. exposed to 0.5 mM uranyl nitrate solution and c) Clostridium sp. exposed to 0.5 mM uranyl-citrate solution