LA-UR-93- 2935

Title: Uranium speciation in Fernald Soils. Progress Report: January 1, 1992 - May 31, 1992.

Author(s):
David E. Morris, INC-14
Steven D. Conradson, MEE-11
C. Drew Tait, INC-14
Catherine J. Shisholm - Brauise, INC-9
John M. Berg, NMT-6
John A. Musgrave, INC-9

Submitted to:

SEP 07 1993
OSTI

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Form No. 836 R5
ST 2629 10/91

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

URANIUM SPECIATION IN FERNALD SOILS

Progress Report:
January 1 - May 31, 1992

ISOTOPE AND NUCLEAR CHEMISTRY DIVISION
LOS ALAMOS NATIONAL LABORATORY

Principal Investigator: David E. Morris
Associate Investigators: Steven D. Conradson
C. Drew Tait
Catherine J. Chisholm-Brause
John Berg
John Musgrave

ABSTRACT

This report details progress made from January 1 to May 31, 1992 in this analytical support task to determine the speciation of uranium in contaminated soil samples from the Fernald Environmental Management Project site under the auspices of the Uranium in Soils Integrated Demonstration funded through the US DOE's Office of Technology Development. Our efforts have focused on characterization of soil samples collected by S.Y. Lee (Oak Ridge National Laboratory) from five locales at the Fernald site. These were chosen to sample a broad range of uranium source terms. On the basis of x-ray absorption spectroscopy data, we have determined that the majority of uranium (> 80-90 %) exists in the hexavalent oxidation state for all samples examined. This is a beneficial finding from the perspective of remediation, because U(VI) species are more soluble in general than uranium species in other oxidation states. Optical luminescence data from many of the samples show the characteristic structured yellow-green emission from the uranyl (UO_2^{2+}) moiety. The luminescence data also suggest that much of the uranium in these soils is present as well-crystallized UO_2^{2+} species. Some clear spectroscopic distinctions have been noted for several samples that illustrate significant differences in the speciation (1) from site to site, (2) within different horizons at the same site, and (3) within different size fractions of the soils in the same horizon at the same site. This marked heterogeneity in uranyl speciation suggests that several soil washing strategies may be necessary to reduce the total uranium concentrations within these soils to regulatory limits.

INTRODUCTION

A key factor in the successful and timely remediation of contaminated sites at US DOE facilities is the availability of speciation information on the contaminants. The actinides (uranium, neptunium, and plutonium) in particular can exist in a myriad of different chemical forms, and their response to remedial technologies, particularly those based on chemical intervention, will vary as the speciation varies. If there is an *a priori* characterization of the speciation (i.e., specification of the oxidation state, chemical form and structure, and physical state [surface precipitate, secondary mineral, or adsorbate]), several potential advantages accrue. The remediation technology can be devised with the specific form of the actinide in mind. This will lead to more efficient and less drastic remedial measures, and enhance the chance of leaving a viable soil substrate behind. In addition, a valid assessment can be made of the long-term stability of the actinide contamination in its present form. This information will be important to guide the remediation effort and to determine whether the contaminant site is stabilized with respect to transport and subsequent groundwater contamination.

We are presently involved in the characterization of uranium speciation in contaminated soils at the DOE's Fernald Environmental Management Project in southwest Ohio. This facility was formerly devoted to the processing of large quantities of uranium. Many different processes were employed at the site, and there are potentially many different source terms for uranium in the soils. While migration of uranium in general has not been extensive, the shallow subsurface requires significant remediation to bring the site into compliance with EPA standards. We have employed molecular-level probes including x-ray absorption spectroscopy and optical luminescence spectroscopy to characterize the uranium speciation in samples from several different sites at the facility. A summary of our findings to date and a brief discussion of their possible implications with respect to remediation are presented in this report.

EXPERIMENTAL

Samples

Most of the speciation characterization work that we have carried out to date has been on core samples that were provided to us by Dr. S. Y. Lee of Oak Ridge National Laboratory. A summary of these samples is provided in Table 1. Details concerning the sampling strategy, the collection process, and physical and chemical characterization can be found in the report "Characterization of Uranium Contaminated Soils from DOE Fernald Environmental Management Project Site: Results of Phase I Characterization" (S. Y. Lee and J. D. Marsh, Jr., ORNL/TM-11980). Dr. Lee provided us with portions of samples from five different sites. We have further focused our efforts on the samples from three of

Table 1. Summary of Fernald Soil Samples Obtained for Characterization Work from ORNL

Sample ID[a]	Site Descriptor
SP2-2-ABC[b]	Plant 2 / 3 Area
SP2-3-ABC[c]	Plant 2 / 3 Area
SP4-1A/2A	Plant 1 / Storage Pad Area
SP5-1AB	Decontamination Pad / Drum Bailing Area
SP8-1A/2A/3A	Plant 6 Area
SP9-1A/3A	Incinerator Area

[a] The sample identification scheme of Lee and Marsh (1992) has been preserved here.
[b] This sample was collected from the 10-20 in. horizon.
[c] This sample was collected from the 20-31 in. horizon.

these sites. Two of these sites, the Plant 1 / Storage Pad Area and the Incinerator Area, have been chosen as the locations for sample collection and homogenization for treatability studies. Therefore, we opted to look in detail at the samples collected by Lee at these sites to provide information to the Decontamination Task team to assist them in their efforts with the treatability samples. The third site on which we have focused is the Plant 2 / 3 site. The reason for focusing on samples from this site is that the site has a high level of uranium contamination, and the source term (the PUREX process) is fairly well understood. Thus, results can be interpreted with respect to the known surface discharge, etc. In general, based on information contained in the Remedial Investigation / Feasibility Study report for the main operable unit (OU-3) at Fernald, the uranium source term and therefore the contaminant speciation may be different for each of the sites at the plant.

The samples obtained from Lee contained a wide range of particle sizes from large sand and gravel chunks (~2-3 mm diameter) to fine clay-sized particles. The only sample preparation undertaken by us on these materials was homogenization by grinding portions of all samples for the initial x-ray absorption spectroscopy investigations. We also performed a crude size fractionation, based on gravimetry, for several luminescence spectroscopy investigations.

Very recently we have obtained a portion of the homogenized sample from the Incinerator Area that is being used as a benchmark sample for the treatability studies. Details of the sampling and homogenization procedures are not presently known to us, but are available from the ID Coordinator's office. It is our understanding that the soils were wetted to facilitate homogenization. (The sample was extremely wet when we received it.) Thus, both the concentration and the speciation of uranium in these samples may have been altered by the homogenization process. Portions of this sample were examined in the same form in which it was received. Some of the sample was also examined following air-drying.

Instrumentation

Uranium L_{III} x-ray absorption spectral data were obtained on powdered samples at both the National Synchrotron Light Source at Brookhaven National Laboratory and the Stanford Synchrotron Radiation Laboratory at Stanford University. All data were collected under ambient temperature and pressure. Absorption was detected in either transmission mode or fluorescence mode. Calibrations of the U L_{III} edge were obtained either simultaneously or between sample runs. Additional experimental and data reduction details will be presented in a forthcoming manuscript.

Luminescence data were collected using either continuous wave argon-ion laser excitation or monochromatized light from a xenon arc lamp. For the laser-excited experiments, data were collected on a SPEX Industries Model 1403 Double Monochromator. For the arc-lamp experiments, data were collected on a SPEX Industries Fluorolog system. In all cases the emitted light was detected using a photomultiplier tube. In the laser-excited experiments the near ultraviolet lasing lines at 336, 351, and 364 nm were used. The focus of the beam was varied from ~ 50 microns to ~ 2 millimeters to change the spatial resolution of the probe on the sample. The samples were contained in glass vials in their heterogeneous form and were manually rastered with respect to the excitation beam to probe different sites and features within the samples. In the arc-lamp experiments the exciting light was focused to illuminate large portions of the sample, and no spatial resolution was obtained. The excitation wavelength was chosen to optimize the emission intensity. In some cases, the arc-lamp experiments were conducted with the samples (in sealed capillary tubes) in a liquid helium cryostat (~ 10K) in an attempt to mitigate the quenching of the uranium luminescence and to sharpen the spectral features.

RESULTS AND DISCUSSION

X-ray Absorption Spectroscopic Data

X-ray absorption spectral data have been obtained for samples SP2-2, SP2-3, SP4-1, and SP9-1. (Note that sample IDs will henceforth be abbreviated as above.) Portions of all of these samples were ground to a homogeneous fine powder using an agate mortar and pestle for use in the x-ray absorption experiment. Several of the samples have been run at both NSLS and SSRL with excellent reproducibility of results in all cases. Figure 1 shows the x-ray absorption spectrum in the region of the U L_{III} edge for sample SP2-2, superimposed on the spectra for an aqueous UO_2^{2+} solution and solid UO_2. The position of the absorption edge (Section A in Fig. 1) is a very sensitive indicator of the oxidation state of the absorber (uranium) atom. Since the absorption edge energy increases with increasing charge on the uranium atom, it can be seen that the oxidation state of the Fernald sample is significantly higher than the one for UO_2 (i.e., a tetravalent uranium species), and the same as that for aqueous UO_2^{2+} (i.e., a hexavalent uranium species). The XANES (x-

ray absorption near edge structure) feature on the high energy side of the main absorption feature near 17192 eV (Section B in Fig. 1) is also diagnostic of UO_2^{2+}. Note that this feature is present in the Fernald sample and the aqueous solution of UO_2^{2+}, but is absent in the spectrum of UO_2. X-ray absorption spectroscopic signals are a population-weighted average of the spectra from all uranium species in the sample. Therefore, if the Fernald sample were a mixture of uranyl species and uranium species in other lower oxidation states (4^+ and/or 5^+), the absorption edge would have been shifted to lower energy, and the shoulder near 17192 eV would have been diminished. Consequently, we estimate that greater than 80-90% of the uranium in this sample exists as uranyl moieties.

In Figure 2 the x-ray absorption spectrum of all four samples in the region of the U L_{III} edge are compared. Note that these spectra are all very similar from the position of the edge feature into the first extended x-ray absorption fine-structure (EXAFS) feature (~17220 eV). Thus, the majority of the uranium in the soil samples from these three different sites must be present as hexavalent uranium species. Close inspection reveals that Sample SP4-1 has slight differences in both the XANES feature and the first EXAFS feature. This is manifested as a shift in the peak position to lower energy and a change in intensity. These differences are borne out in the EXAFS analysis (*vide infra*).

Additional information concerning the structure and the speciation of these hexavalent uranium species can be obtained from analysis of the EXAFS region of the spectra. To facilitate the following discussion, a cartoon representation of the basic structural motif for the UO_2^{2+} moiety is presented in Fig. 3. This moiety is characterized by two axial or "yl" oxygen atoms typically at distances varying from 1.7 to 1.9 Å. This structural feature is essentially invariant and is the defining feature in terms of both spectroscopy and chemistry of the uranyl moiety. In contrast, the number and types of atoms constituting the "equatorial" shell can vary substantially from one uranyl species to another. These atoms introduce perturbations to both the chemistry and the spectroscopy of the uranyl species, and are primarily responsible for the changes seen in the spectroscopic data. For this reason, spectroscopic techniques serve as useful probes for uranyl speciation.

Analysis of the EXAFS portion of the x-ray absorption spectrum in general provides direct information concerning the bond distances, the numbers of bound atoms, and the identities of the bound atoms about the sorber (i.e., uranium). Because the "yl" oxygen atoms remain essentially invariant, their contribution can be filtered from the EXAFS spectrum to focus on the contributions from the more speciation-sensitive equatorial atoms. A comparison of these filtered EXAFS spectra for samples SP2-2, SP4-1, and SP9-1 is shown in Fig. 4. The large amplitude feature at a distance of ~ 2 Å (uncorrected for phase shift) is due to the equatorial atoms. The position of this band is about the same for all three samples indicating that the average bond distance between uranium and the equatorial atoms is approximately the same for the uranyl species in all these samples. Furthermore, because the amplitude is approximately the same in this feature for Samples SP2-2 and SP9-1, the

number of equatorial atoms is about the same. However, the amplitude for Sample SP4-1 is significantly reduced relative to the others. This suggests that the number of equatorially coordinated oxygens is lower for the uranyl species in this sample and/or the disorder (for example, from having several different uranium-oxygen bond distances) is greater. In either case, these results show that, while the average uranyl speciation is comparable for Samples SP2-2 and SP9-1, it is different in Sample SP4-1. Interestingly, Sample SP4-1 is also the only sample in the suite SP2-2, SP2-3, SP4-1, and SP9-1 for which no structured optical luminescence is observed (vide infra). A summary of the structural parameters that have been extracted from the EXAFS analysis for these samples is provided in Table 2.

Table 2. Structural Parameters for Average Uranyl Species in Fernald Soil Samples

Sample	Axial Oxygens		Equatorial Oxygens	
	Bond Distance (Å)	No. of Atoms	Bond Distance (Å)	Amplitude Relative to SP2-2[a]
SP2-2	1.81	1.9	2.34	1.00
SP2-3	1.82	2.2	2.34	0.97
SP2-3[b]	1.81	2.0	2.35	1.07
SP4-1	1.81	2.1	2.39	0.68
SP9-1	1.81	1.8	2.35	0.96

[a] The absolute number of coordinated atoms cannot be determined from the existing data. However, relative amplitudes demonstrate the near invariance for these samples with the exception of the SP4-1 Sample.
[b] This was a replicate determination at NSLS to the one preceding it in the table (from SSRL) to demonstrate the excellent reproducibility obtained in these studies.

Another important observation from the EXAFS analysis can be seen in the comparison of the spectra of Samples SP2-2 and SP2-3 (Fig. 5). For Sample SP2-3, several additional features (indicated by the arrows) are seen at longer distances (~ 4 and ~ 7 Å) than the uranium-equatorial oxygen feature. These new features are most probably due to scattering off atoms at farther distances than the equatorial oxygens. Their obvious presence in this spectrum suggests that the uranyl species in this sample has longer-range order than those in the other samples. A possible origin for the higher order would be a more crystalline environment for the uranyl species. In fact, as discussed below, the optical luminescence for Sample SP2-3 also suggests that the uranyl species are in a more highly crystalline environment.

Luminescence Spectroscopy Data

Optical luminescence spectroscopy data have been obtained for all samples listed in Table 1 and for the treatability sample from the Incinerator Area. Typical uncorrected spectra are shown in Figure 6 for Samples SP2-3

and SP4-1. All samples show the broad, unstructured emission band with a maximum at ~ 22,500 cm^{-1}. While we do not know the specific source of this emission, it is probable that it derives either from natural organic materials or natural iron-bearing minerals in the soils. The portions of Samples SP5-1 and SP8-1 that have been examined thus far show only this broad-band emission. However, these two samples have not yet been examined under xenon arc-lamp excitation conditions at either room or low temperatures. Furthermore, the absence of a characteristic emission from a uranium-bearing sample is not positive evidence for the absence of uranyl moieties, as many naturally-occurring agents (organics and heavy metals) are capable of quenching the uranyl emission effectively. Sample SP4-1 is unique in that it shows an additional broad, unstructured emission centered at ~ 18,000 cm^{-1} (Fig. 6). Samples SP2-2, SP2-3, and SP9-1 all contain one or more regions within the samples that show the characteristic structured yellow-green emission spectra typical of uranyl species (Fig. 6, top).

This highly structured emission spectrum, even at room temperature, is one of the unique aspects of the spectroscopic behavior of the uranyl moiety. This structure provides a wealth of information that can be used to help deduce speciation and, in many cases, serves as a fingerprint for the uranyl species. The speciation diagnostics that can be extracted from these structured emission spectra are illustrated in the idealized spectrum shown in Figure 7. Note that four distinct, independent parameters can be readily extracted from these spectra, and each will be influenced to some degree by the speciation and changes therein of the uranyl moiety. (See, for example, Figs. 12 and 13.)

Structured uranyl emission spectra have been obtained from many seemingly different domains within the bulk portions of the two samples from the Plant 2 / 3 Area (SP2-2 and SP2-3). For example, most emission appears to come from particulates or from microcrystals coating the edges of the larger sand particles, but some emission also appears to originate from a more dispersed source. However, the spectra from these domains seem to be the same within either bulk sample. In contrast to this similarity within bulk samples, there is a marked difference in the spectra for the samples from the two different horizons at the Plant 2 /3 Area as shown in Figure 8. Note that the spectrum for the SP2-3 sample has much more well-resolved vibronic bands than that of SP2-2, and the positions of these bands are different in the two spectra. An increase in the resolution of vibronic bands may be attributable to an increase in the degree of crystallinity of the sample. This interpretation is consistent with the appearance of the more distant EXAFS features in the x-ray absorption spectrum of this sample (vide supra). In fact, we have found such highly resolved uranyl emission spectra only for well-crystallized uranyl minerals and salts, some of which are illustrated below.

Another pronounced difference in the structured spectra occurs on going from the uranyl associated with the sand / gravel fraction to that associated with the clay / silt fraction. (These size fraction distinctions are only qualitative, as no rigorous effort to fractionate the soils was made. Furthermore, the sand / gravel fraction may include aggregates containing clay-sized particles.) This is true for

both the SP2-3 sample (Figure 9) and the SP9-1 sample (Figure 10), although the nature of the difference is not the same for both samples. For example, in SP2-3 the spectrum from the clay / silt fraction appears to have broader vibronic bands than that from the sand / gravel fraction and is possibly composed of two different spectra from distinct uranyl species. For SP9-1 the spectrum from the clay / silt fraction has narrower vibronic bands than that from the sand / gravel fraction and appears to be composed of only a single spectrum. Other samples have not been investigated for this effect yet.

The emission data that have been obtained from the Incinerator Area Treatability Sample are shown in Figure 11. For comparison, the spectrum obtained from the sand / gravel fraction of SP9-1 (i.e., from the same site) is included in Fig. 11. Note that there is a significant diminution in the intensity of the structured emission on going from the (as received) wet sample to an air-dried sample. In addition, there seems to be a shift in the band positions in these two spectra that would suggest a change in speciation associated with drying, rather than a simple loss of intensity. The nature of the apparent change in speciation for the Treatability Sample on drying is unknown. It is unlikely that the change is associated with a redox transformation for uranium, because aerobic conditions were maintained in the drying process. It is also possible that the drying process *per se* is not responsible for the observed differences. Overall, the spectrum of the wet sample looks quite similar to that obtained from the SP9-1 fraction, but with a greater component of broadband background emission. X-ray absorption spectral data will be collected for this and other Treatability Samples during the scheduled July synchrotron beam time.

Fingerprinting of the Uranyl Luminescence Spectra

Because the uranyl emission spectra in many cases are quite distinct, it should be possible to use these data as fingerprints for the uranyl species in the soil samples. This will be particularly true if some information concerning the contaminant source term, the groundwater composition, and the soil mineralogy is available, because deductions concerning possible species can be made while other species can be eliminated from consideration. An example of the procedure is presented in Figures 12 and 13 for the highly structured spectrum obtained from the sand / gravel fraction of Sample SP2-3. In Fig. 12 (top) the spectrum of the uranyl hydroxide mineral schoepite is shown. It might be expected that any time an aqueous uranyl solution encounters a basic soil (such as exists in the vicinity of the Plant 2 / 3 area) the uranyl will promptly hydrolyze to insoluble hydroxide precipitates. However, schoepite and all other uranyl hydroxide precipitates that we have examined show a weak, broad, and essentially structureless emission comparable to that of schoepite. Thus, the species giving rise to the SP2-3 spectrum cannot be a simple uranyl hydroxide. Note, however, that the additional emission feature observed from SP4-1 (Fig. 6, bottom) does have this broad, structureless appearance common to uranyl hydroxides.

It might also be expected that the soils in the vicinity of Plant 2 / 3 would have elevated levels of phosphates (PO_4^{3-}) as a result of hydrolysis of tributylphosphate from the PUREX process. Many stable uranyl phosphate minerals exist, but they all seem to have the same emission spectral signature as that shown in Fig. 12 for meta-autunite [$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$]. (This is not surprising, since they are all isostructural.) Note that, compared to the spectrum of Sample SP2-3, the spectrum for the phosphate mineral has all peaks shifted in energy, and the relative intensity pattern is different. Thus, it appears that the species giving rise to the SP2-3 spectrum is not a uranyl phosphate solid.

The soils in and around the Fernald site are known to contain appreciable quantities of 1:1 and 2:1 clay minerals. Clay minerals have a good affinity for uranyl species, and they have been shown to take up uranyl into surface and interlayer sites by several different mechanisms. However, our previous work with uranyl / clay systems suggests that the emission spectra are usually only poorly resolved as shown in Fig. 13 (top) for a calcium montmorillonite laden with uranyl species from an acidic, aqueous solution. The high degree of resolution seen in the spectrum of the SP2-3 sample is, therefore, inconsistent with this uranyl species being associated directly with a clay. Note however that we cannot rule out the possibility of surface precipitation of uranyl on clay particles, because our uranyl / clay work has never probed conditions under which surface precipitation is expected.

A reasonable match to the SP2-3 spectrum is provided by the uranyl silicate mineral sklodowskite [$Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$] shown in Fig. 13 (bottom). This sklodowskite sample is impure and contains additional uranyl species that are responsible for the shoulders filling in the intensity between each prominent vibronic band. If one considers only these prominent vibronic bands due to sklodowskite, then the match with the SP2-3 spectrum is good with respect to the position of the bands and the degree of vibronic resolution. The relative intensity pattern appears to differ from that of the SP2-3 species, but this may be skewed as a result of the spectrum from the emissive uranyl impurity. The presence of a uranyl silicate mineral in the Plant 2 / 3 soils is reasonable because the waste stream was highly acidic, and silicates in the soil (e.g., from the clays) can dissolve readily in aqueous acidic solutions.

At this time we do not have sufficient evidence to suggest definitively that the species responsible for the emission spectrum in SP2-3 is a uranyl silicate mineral. However, we do feel confident based on the high degree of vibronic resolution that it is some uranyl mineral or salt other than a hydroxide. We can also rule out a number of uranyl minerals containing heavy metals (e.g., beta-uranophane, kasolite, and cuprosklodowskite), because we have shown that the luminescence is strongly quenched for these materials. We are now in the process of obtaining library spectra for other candidate minerals for fingerprinting purposes. Uranyl carbonates (e.g., rutherfordine) in particular are candidate species given the overburden of limestone gravel used throughout the Fernald site.

Preliminary Investigations of Treated Samples

We have also undertaken some simple leaching experiments to determine our capabilities to track uranium speciation in the soil samples following the types of leach treatments that will be carried out by the Decontamination Task Team. In our experiments, two samples (SP2-2 and SP9-1) were washed with dilute nitric acid solution. The washing began with 0.01 M acid and proceeded to 0.1 M acid solution. The final equilibrium pH values attained were 2.8 for SP2-2 and 3.8 for SP9-1. Copious quantities of acid were consumed to reach these pH values suggesting that the soil samples contain large quantities of calcite or other acid-consuming minerals. No quantitative mass balance of uranium was attempted. However, assay of the resulting leachate solutions did indicate that this procedure removed significant quantities of uranium in the case of SP2-2 (~25% based on an assumed 5000 ppm concentration in the untreated soil sample), and relatively little in the SP9-1 sample. The treated SP2-2 sample was examined by x-ray absorption spectroscopy. Reasonable signal-to-noise was achieved in the spectrum, indicating that the treated soil still contained significant amounts of uranium. More notable was the fact that the spectrum still had all the characteristics of those seen for uranyl species. Unfortunately, the data quality was insufficient to draw specific conclusion regarding changes in the equatorial coordination sphere. However, the implication is that acid washing may selectively remove some, but not all, uranyl species.

Implications with Respect to Remediation

The single most significant finding from our speciation characterization work thus far is the prevalence of the hexavalent oxidation state in the uranium species. This is a beneficial result from the standpoint of remediation, because U(VI) species are more soluble in general than uranium species in the tetravalent oxidation state. Thus, powerful oxidizing / complexing agents and their commonly disadvantageous secondary waste streams should not be required. Instead, remediation strategies that employ relatively simple aqueous complexants should enjoy some high level of success. However, there is a possible drawback to the dominance of hexavalent uranium; namely, the existing contamination is more mobile in the soils, and the extent of contaminant migration and the timeliness with which it is remediated become important issues.

Our results also demonstrate that, even within the relatively small subset of contaminated soils we have sampled, the uranium speciation varies substantially. This is true from site to site (e.g., SP9-1 vs SP4-1), within horizons at the same site (e.g., SP2-2 vs SP2-3), and within size fractions in the same horizon at the same site (e.g., SP9-1 coarse vs fine fractions). It is reasonable to expect some variability in the solubility of these many different uranyl species, so it is prudent at this time to continue to develop and investigate several potentially useful soil washing chemistries. Further

speciation investigations of the "treated" soil samples will then enable us to identify any intransigent forms of uranium, and propose alternate / additional remediation strategies.

Several specific results merit further comment here. The first concerns the speciation changes observed with depth for the Plant 2 / 3 Area samples. The simplest interpretation of the observed behavior is that the uranyl species is weathering as episodic influx of rain transports the uranium down into the soil. This would make sense in terms of the proposed increase in the degree of crystallinity of the uranyl species, because continual dissolution and reprecipitation can frequently have this effect. However, we cannot rule out the possibility that these two spectra (Fig. 8) derive from two entirely different uranyl species. This latter possibility would imply that the soil chemistry itself is changing in the horizons. In this case, it might be necessary to devise different remediation strategies for each horizon. The possible influence of changes in soil chemistry in the different horizons on uranium speciation should be a target for investigation in the Conceptual Model task of the Characterization Task Team. Finally, there is some evidence based on vibronic linewidths, particularly for portions of Samples SP9-1 and SP2-3, that the uranyl contamination is intimately (chemically) associated with the substrate, rather than present as particulates and/or surface precipitates. If this is true, this material may require more rigorous conditions for remediation, because the sorptive interactions with the metal oxides and clay minerals in these soils can be quite strong.

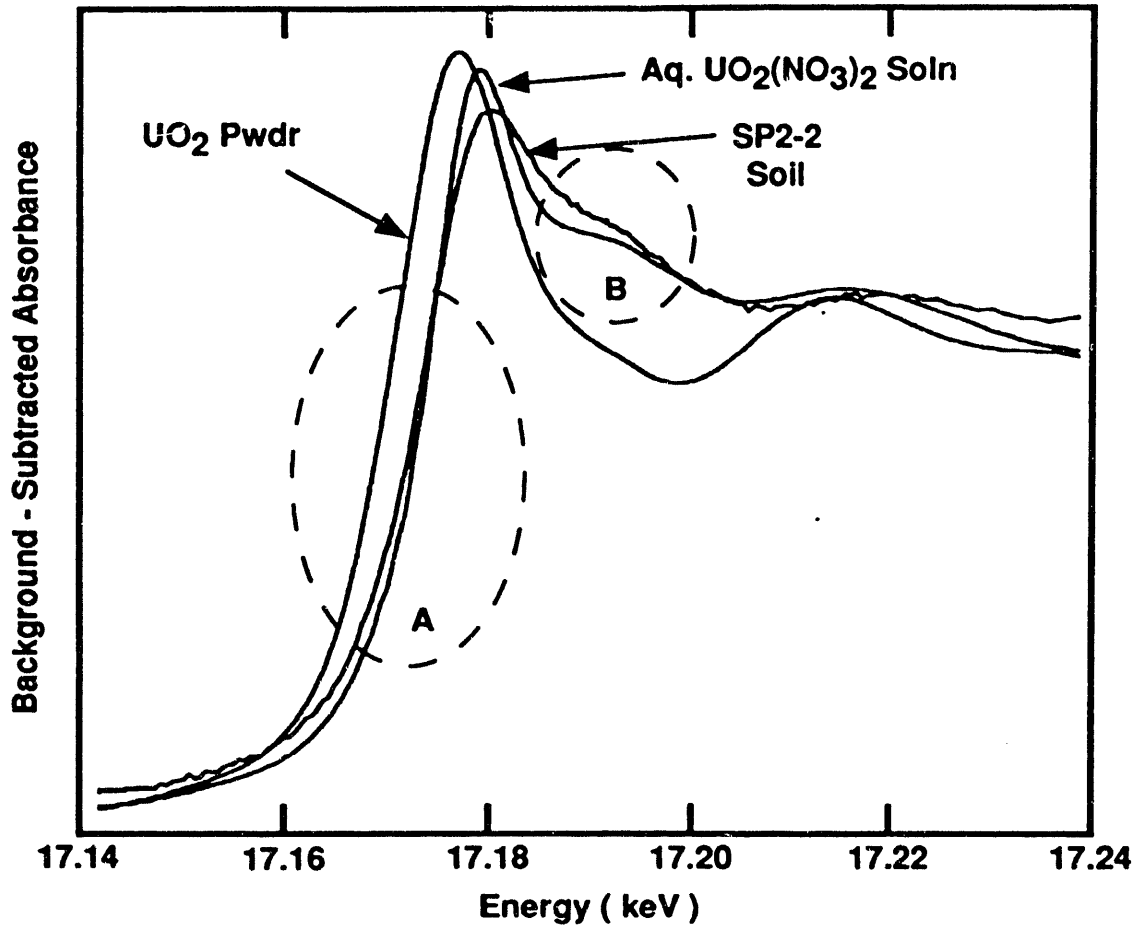

Figure 1. Background-corrected x-ray absorption spectra for Fernald Sample SP2-3 compared to a tetravalent uranium species (UO_2 powder) and a hexavalent uranyl species (50 mM $UO_2(NO_3)_2$ in H_2O). The edge position (Region A) and the XANES feature (Region B) are characteristic of speciation and demonstrate that the Fernald sample consists predominantly UO_2^{2+} species.

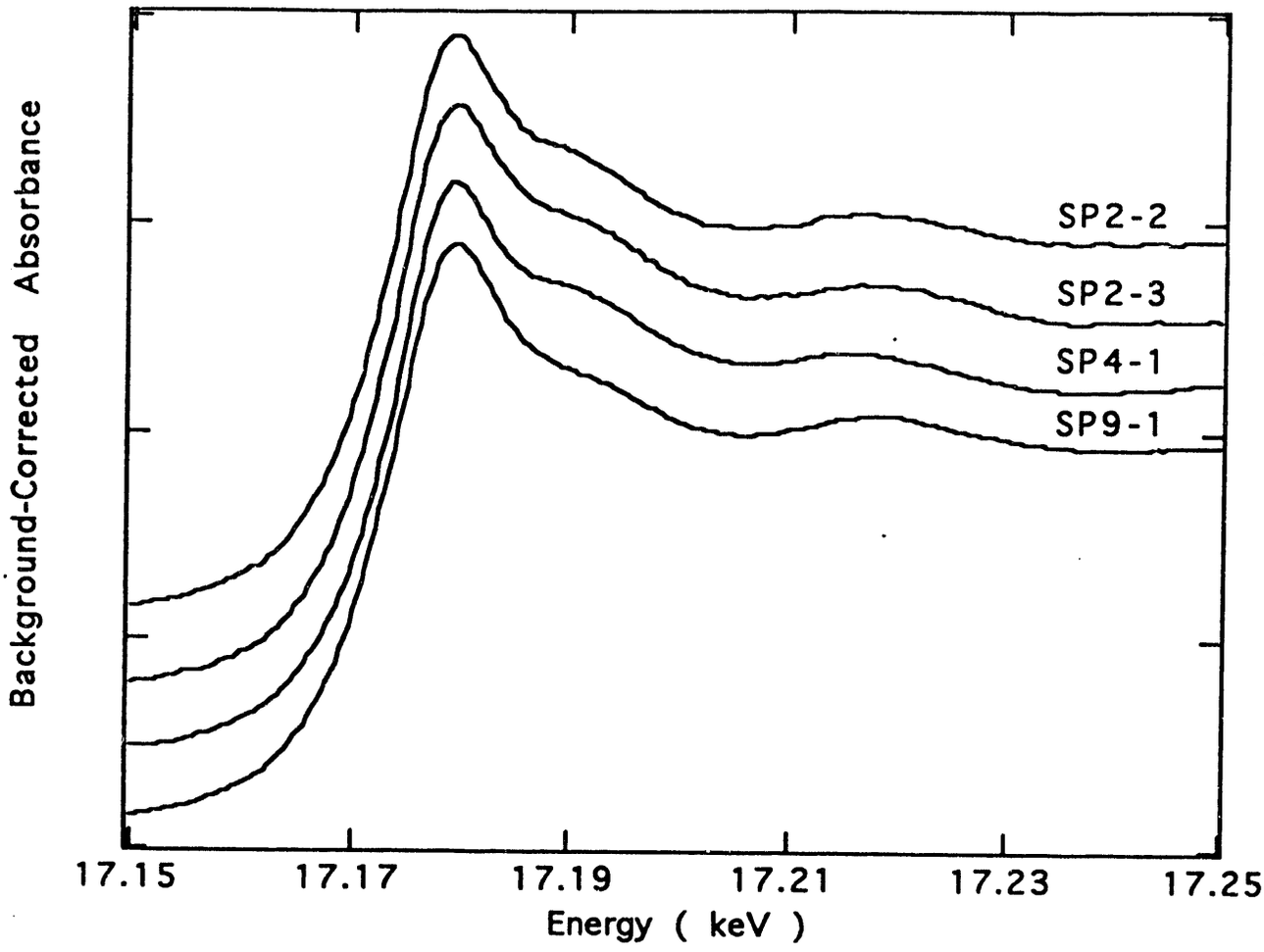

Figure 2. Background-corrected x-ray absorption spectra for Fernald soil samples from two horizons within the Plant 2 / 3 Area; 10 - 20 inches (SP2-2), and 20 - 31 inches (SP2-3), and from the Plant 1 / Storage Pad Area (SP4), and the Incinerator Area (SP9).

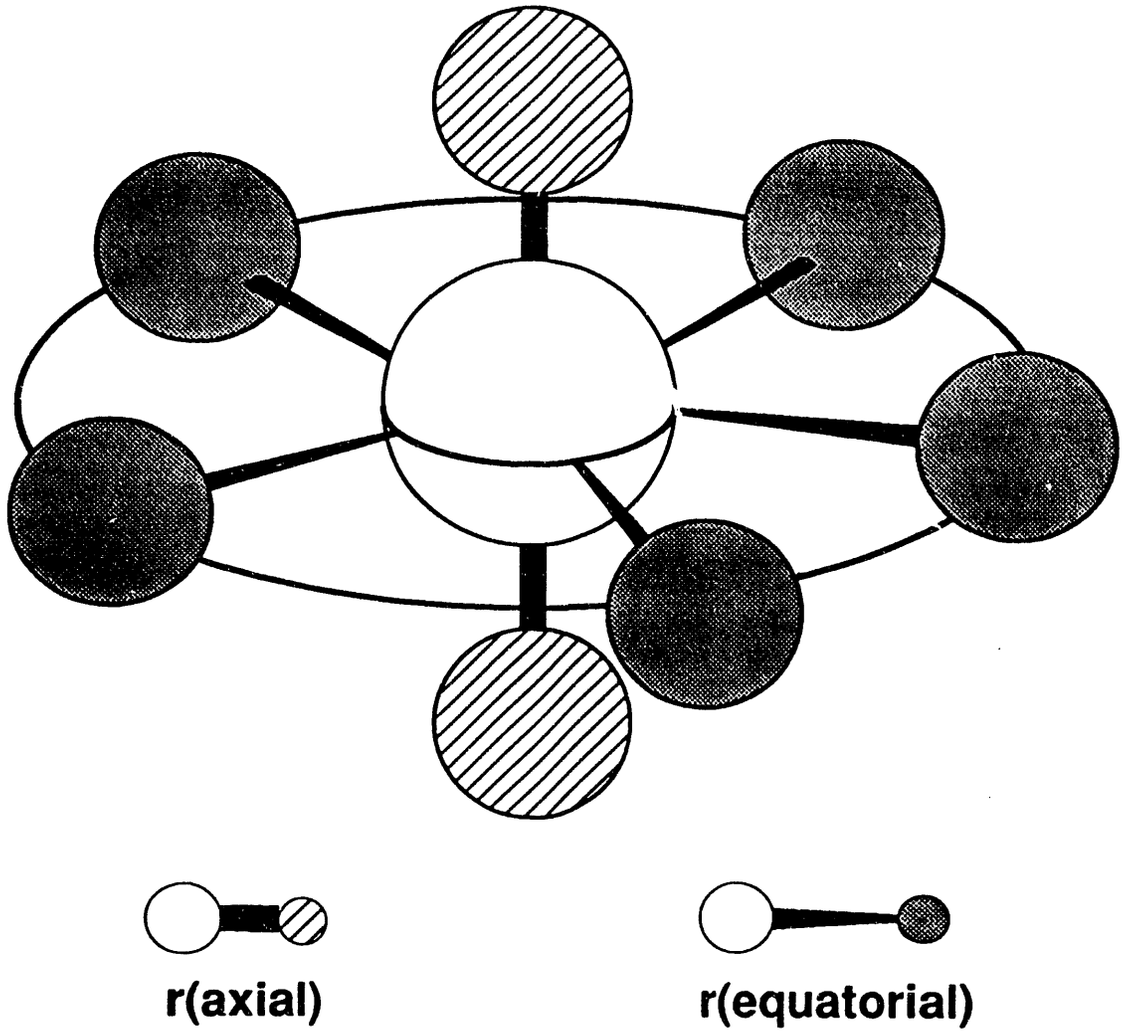

Figure 3. Cartoon representation of the structural motif of UO_2^{2+} species. The typical axial U-O bond length is 1.7 to 1.9 Å. The equatorial bond lengths can vary from ~2.2 to 2.5 Å and the number of coordinating atoms can vary from ~4 to 6.

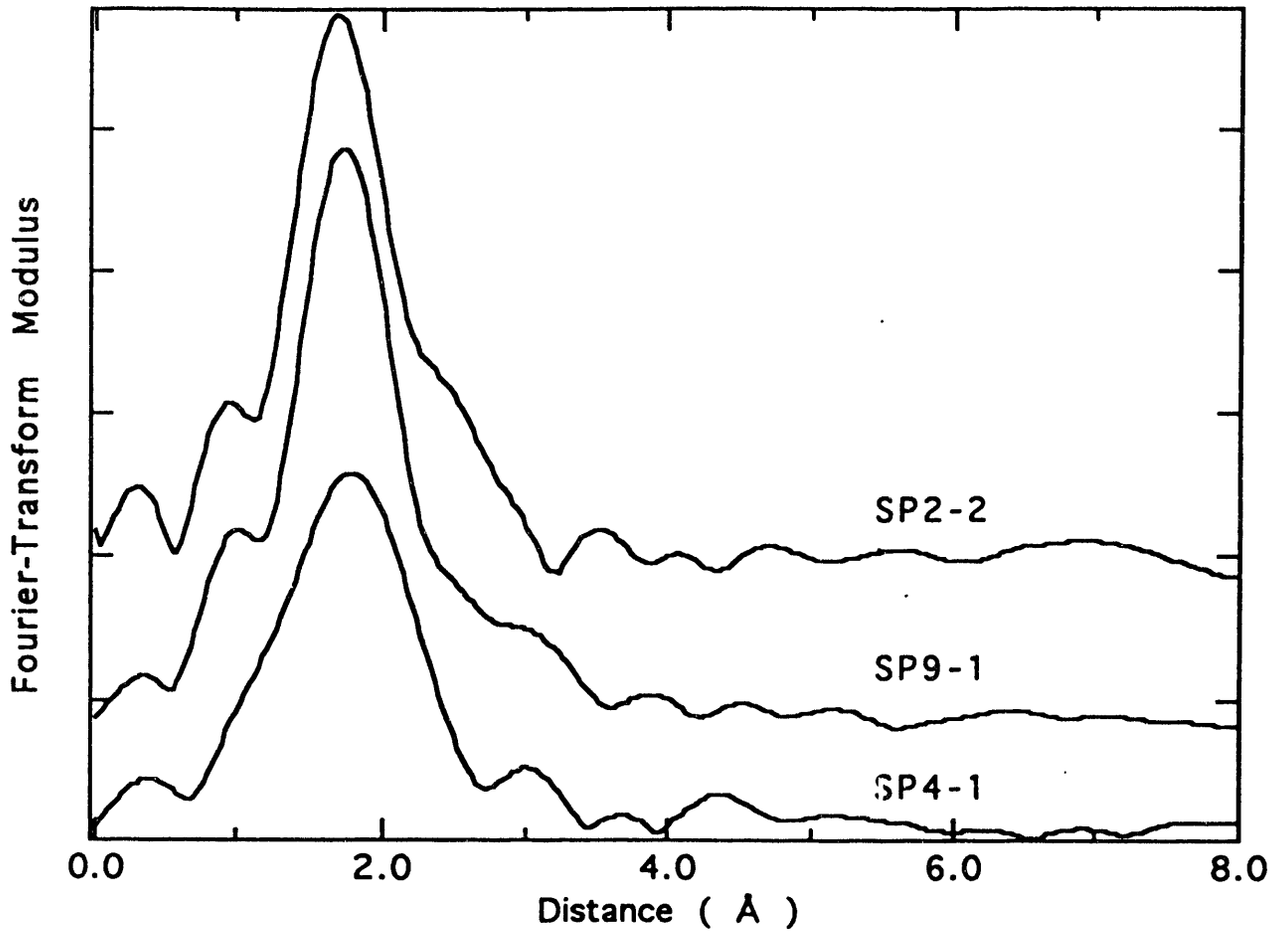

Figure 4. Fourier-Transform representations of the extended x-ray absorption fine structure spectra of uranyl contaminated Fernald soils from three different sites. Plant 2 / 3 Area (SP2-3). Incinerator Plant Area (SP9-1). Plant 1 / Storage Pad Area (SP4-1). The contribution from the axial oxygen atoms has been filtered out of these spectra to facilitate comparison of the equatorial features.

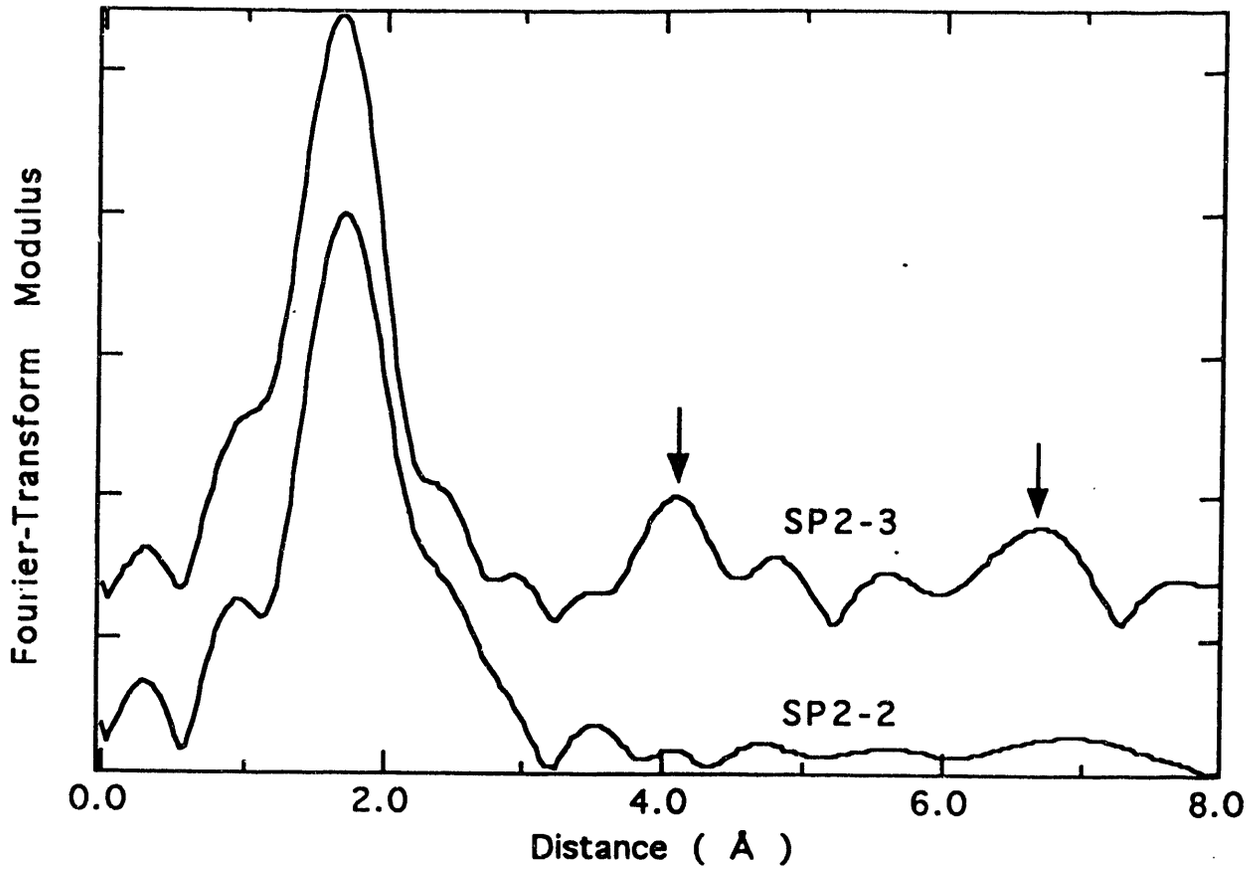

Figure 5. Fourier-Transform representations of the extended x-ray absorption fine structure spectra of uranyl contaminated Fernald soils from two different horizons within the Plant 2 / 3 Area. SP2-2 is the 10 - 20 inch horizon. SP2-3 is the 20 - 31 inch horizon. The contribution from the axial oxygen atoms has been filtered out of these spectra to facilitate comparison of the equatorial features. The new features (marked by arrows) in the spectrum of SP2-3 arise from scattering off atoms more distant than the equatorial coordination shell.

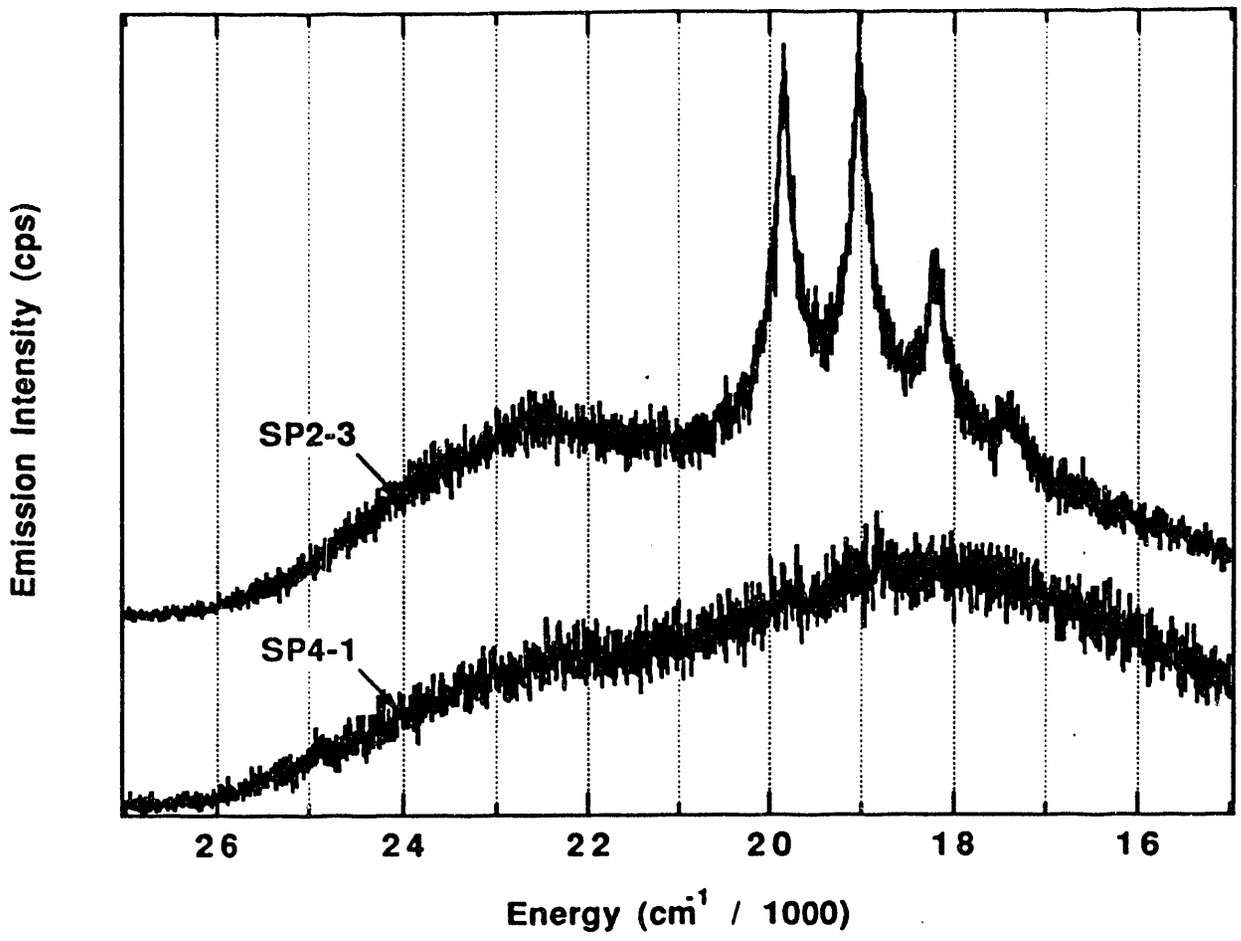

Figure 6. Emission spectra obtained from bulk samples of Fernald soils obtained from the Plant 2 / 3 Area (SP2-3) and the Plant 1 / Storage Pad Area (SP4-1). Spectra were obtained at ambient temperature using defocused (~ 2 mm beam waist) 364 nm excitation from a continuous-wave Ar^+ laser. The structured emission centered about 19,000 cm^{-1} in SP2-3 is characteristic of uranyl luminescence. The broad, unstructured band centered about 22,500 cm^{-1} is intrinsic to the Fernald soils.

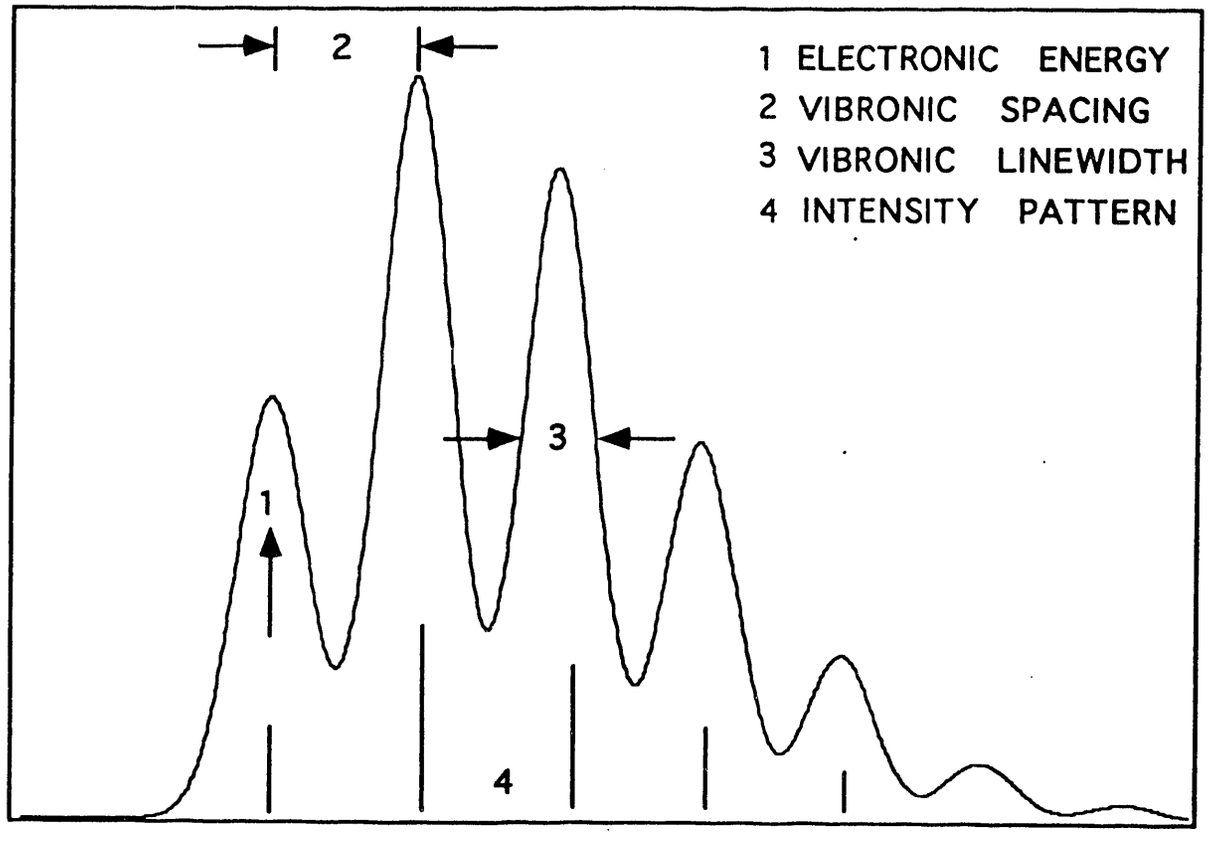

Figure 7. Model of a vibronically structured emission spectrum illustrating the four main features that can be used as diagnostics in characterizing uranyl speciation.

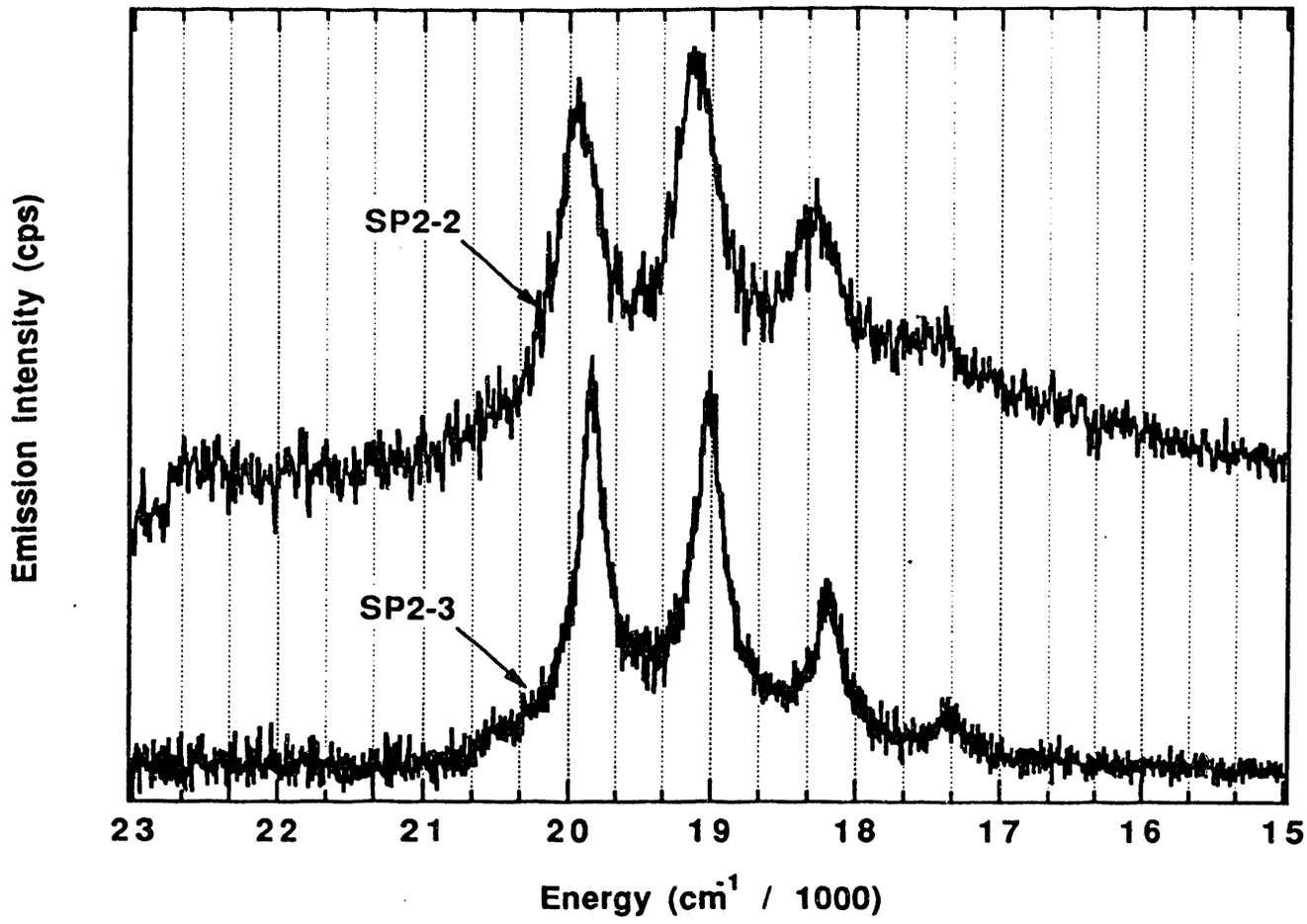

Figure 8. Background-corrected emission spectra of uranyl contaminated Fernald soils from two different horizons within the Plant 2 / 3 Area. SP2-2 is the 10 - 20 inch horizon. SP2-3 is the 20 - 31 inch horizon. Spectra were obtained at ambient temperature using defocused (~ 2 mm beam waist) 364 nm excitation from a continuous-wave Ar^+ laser. In both cases the emission was clearly emanating from a particulate source in the sample.

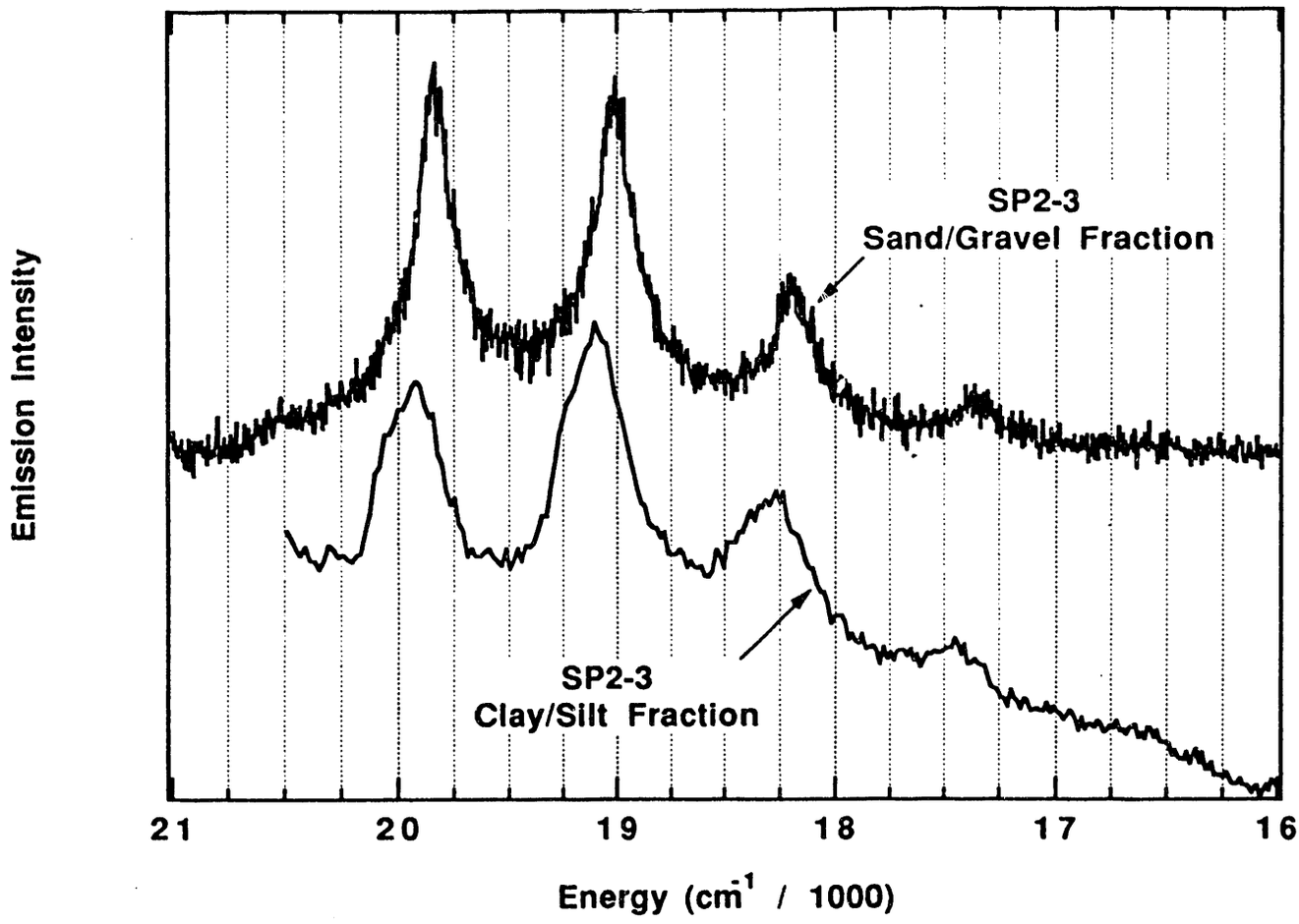

Figure 9. Comparison of the uranyl luminescence spectra versus size fraction for Fernald sample SP2-3 (Plant 2 / 3 Area, 20 - 31 inch horizon). The upper spectrum was obtained at ambient temperature using defocused (~ 2 mm beam waist) 364 nm excitation from a continuous-wave Ar^+ laser. The lower spectrum was obtained using 425 nm excitation from a xenon arc lamp with the sample cooled to ~ 10 K.

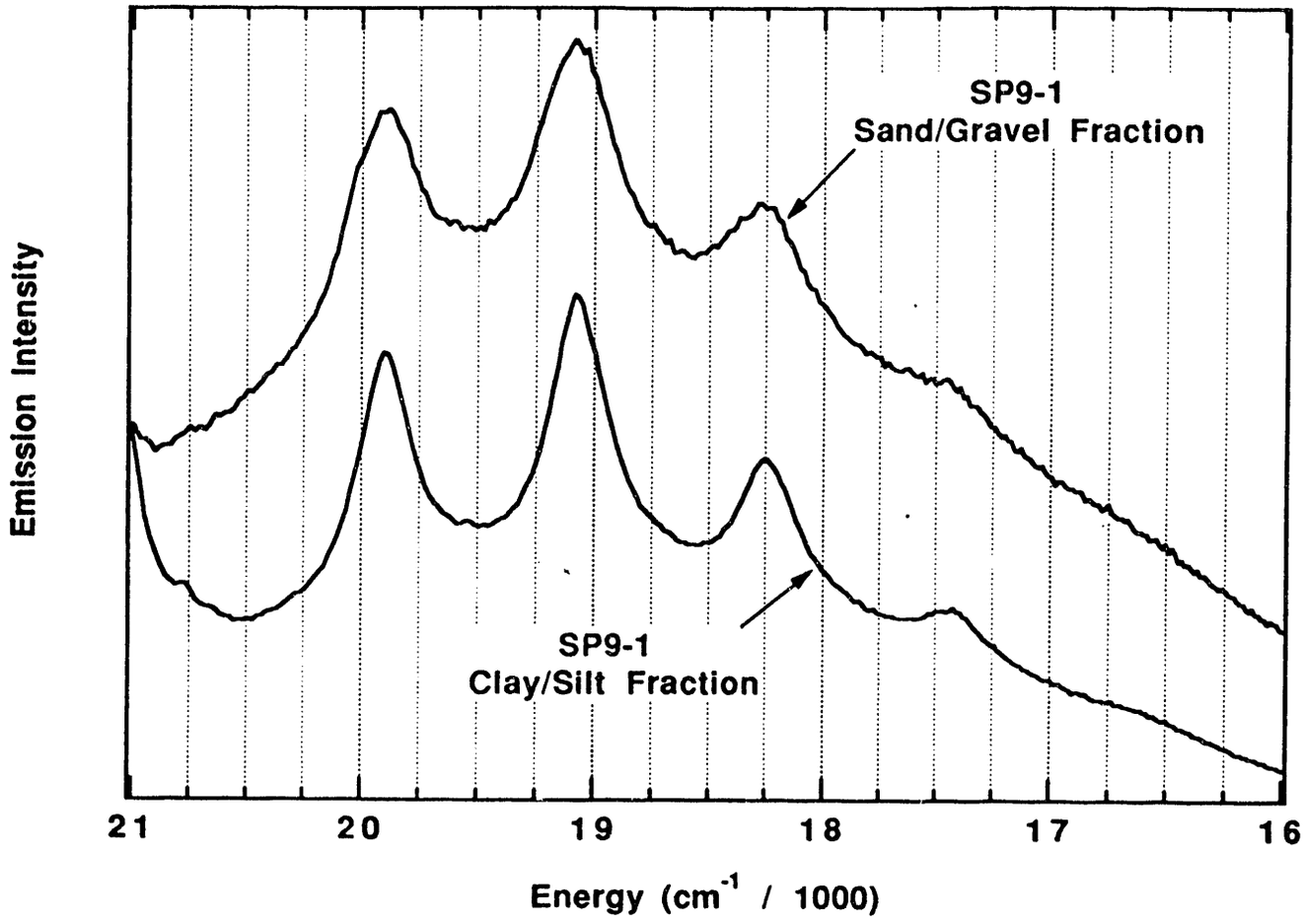

Figure 10. Comparison of the uranyl luminescence spectra versus size fraction for Fernald sample SP9-1 (Incinerator Area). Both spectra were obtained at ambient temperature using 422 nm excitation from a xenon arc lamp.

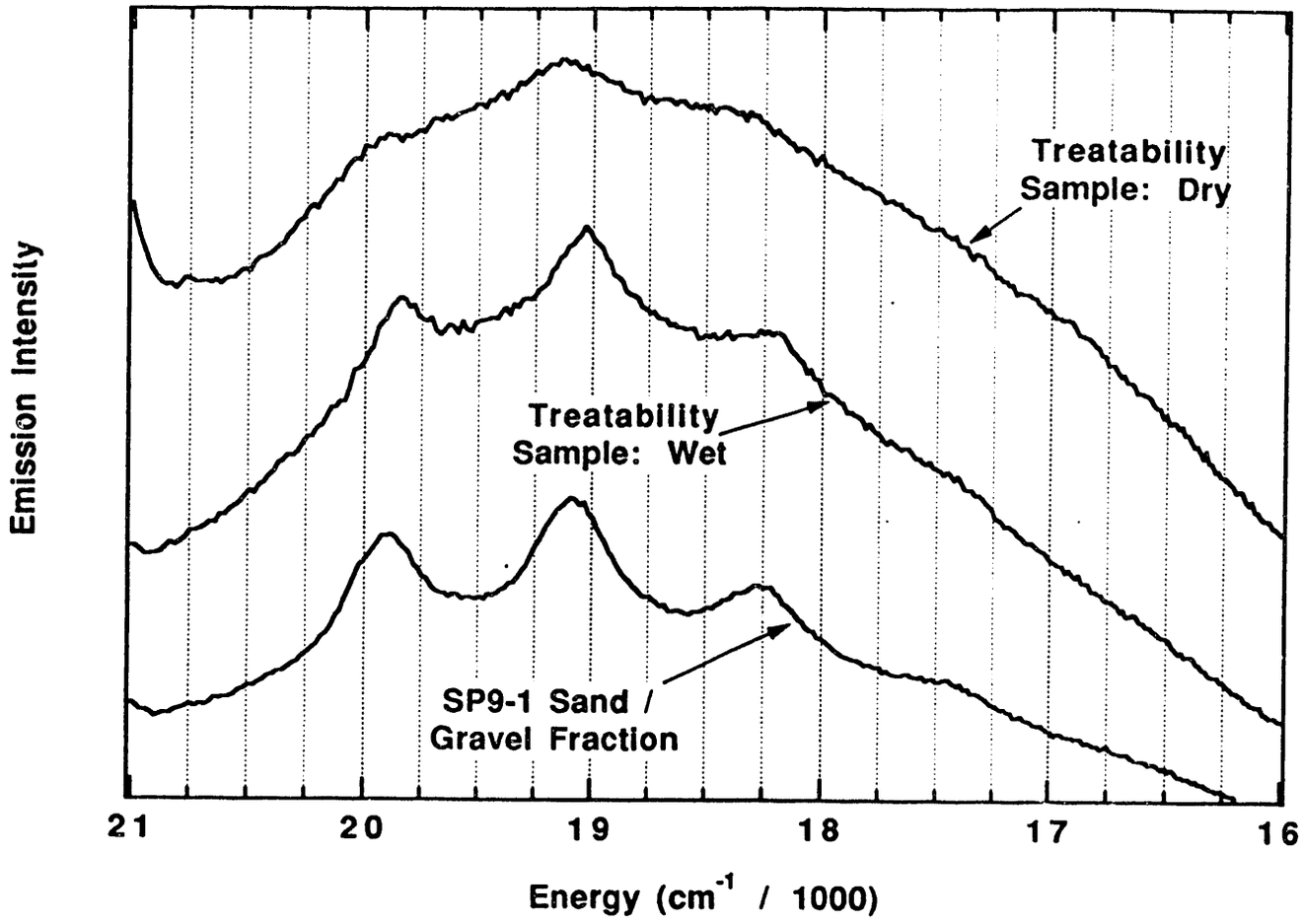

Figure 11. Comparison of the uranyl luminescence spectra obtained for the Treatability Samples from the Incinerator Area (wet as received and following air drying) with the spectrum of Incinerator Area core sample SP9-1. All spectra were obtained at ambient temperature using 422 nm excitation from a xenon arc lamp.

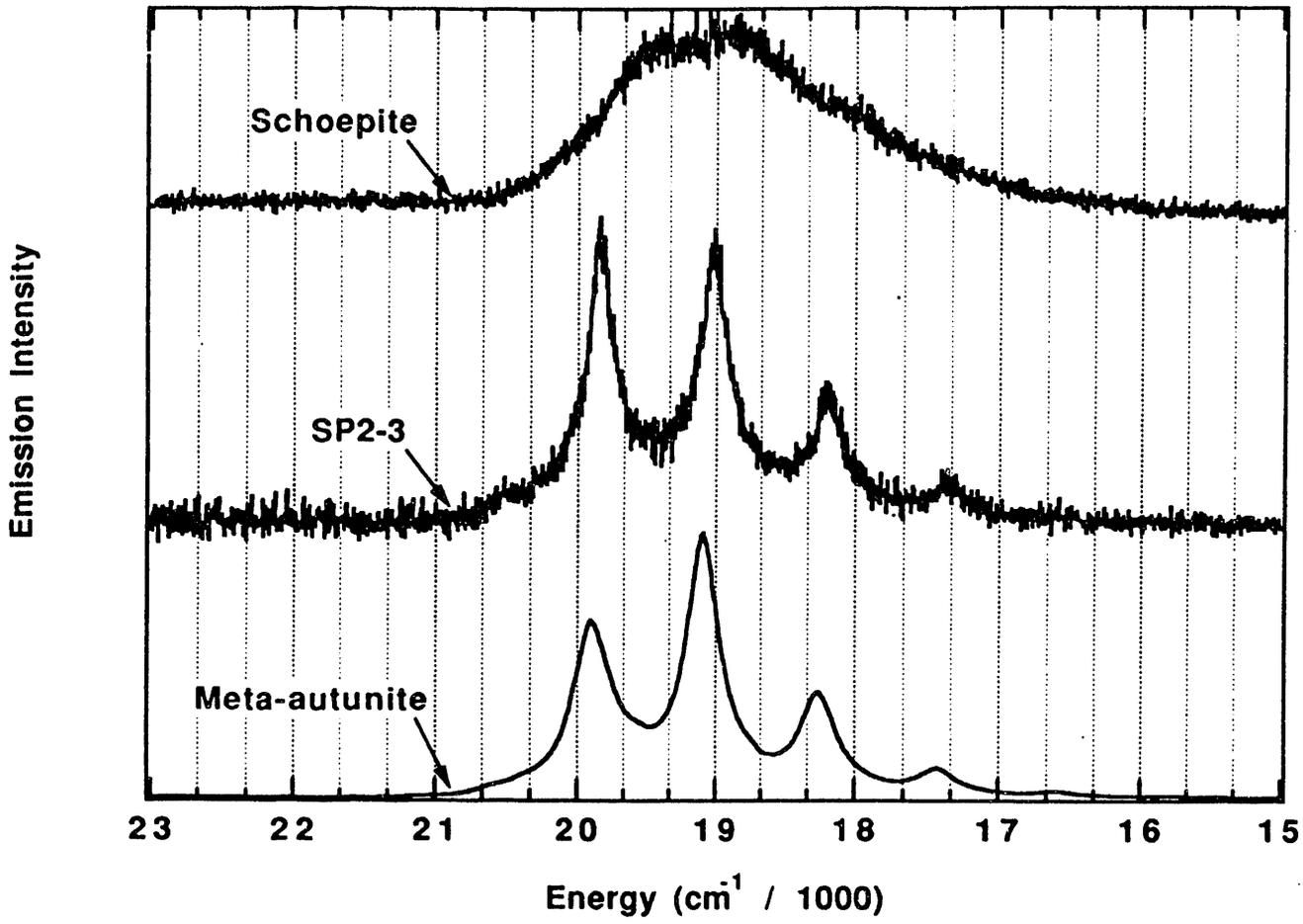

Figure 12. Fingerprinting comparison of the luminescence spectra of Schoepite (a uranyl hydroxide mineral) and Meta-autunite (a uranyl phosphate mineral) with the spectrum of Fernald Plant 2 / 3 Area Sample SP2-3. All spectra were obtained at ambient temperature with 364 nm excitation from a continuous-wave Ar^+ laser.

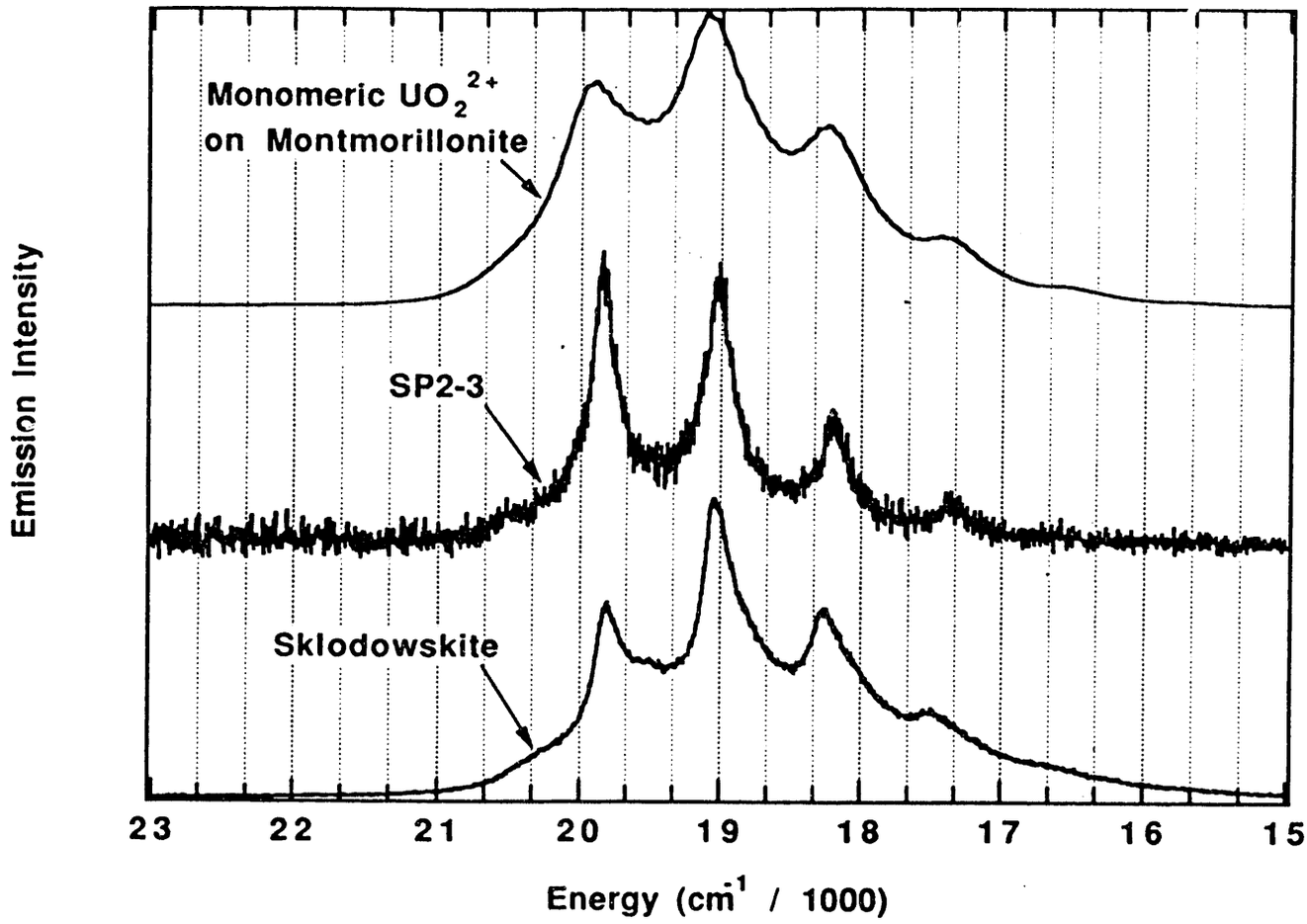

Figure 13. Fingerprinting comparison of the luminescence spectra of uranyl-laden Montmorillonite (a 2:1 layered silicate clay mineral) and Sklodowskite (a uranyl silicate mineral containing a uranyl impurity) with the spectrum of Fernald Plant 2 / 3 Area Sample SP2-3. All spectra were obtained at ambient temperature with 364 nm excitation from a continuous-wave Ar^+ laser.

END

DATE FILMED

10 / 18 / 93