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Spectroscopic Signatures of Uranium Speciation for Forensics

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SPECTROSCOPIC SIGNATURES OF URANIUM SPECIATION FOR FORENSICS

By

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Bachelors of Science – Chemistry
Bachelors of Science – Physics
Hope College
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A dissertation submitted in partial fulfillment of the requirements for the

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ABSTRACT

Spectroscopic Signatures of Uranium Speciation for Forensics

By

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Chemical speciation offers opportunities for development of signatures that arise from the production, conversion, and aging processes of nuclear materials. This information has been useful for environmental science and remediation and the ability to measure chemical signatures, from processed materials may be of great use to nuclear forensics. Many nuclear forensics analyses deal with radiochronometry and isotopic analysis, but because processing is chemical in nature, there are opportunities for chemical signatures from the bulk products, reagents, or reaction intermediates to be measured.

Many spectroscopic techniques can be utilized in a remote setting outside of the laboratory, with minimal or no sample preparation. Vibrational methods such as Raman and Infrared Spectroscopies can be useful for determining molecular structure and impurities. Photoluminescence spectroscopy can determine the chemical nature of samples. Laser Induced Breakdown Spectroscopy can be used to determine elemental impurities and has been shown to be useful for differentiating between samples of similar chemical nature.

A set of uranium compounds found throughout the life cycle of uranium, from mining to reprocessing, have been synthesized. These compounds range from tetravalent oxides and fluorides to hexavalent
uranyl compounds and uranium ore concentrates. Raman and FTIR spectroscopy are used to determine differences in the vibrational spectroscopy with changes in the uranium speciation. A multivariate principal component model has been built for both the Raman and the FTIR spectra to determine and observe trends within data. Photoluminescence spectroscopy can determine differences in the electronic structure and luminescence emission characteristics of the set of uranium compounds. Laser Induced Breakdown Spectroscopy has the ability to determine the elemental composition of the uranium compounds. Ratios between emission line intensities have been compared with mass ratios to determine the ability to differentiate between uranium compounds. A multivariate principal component model has been built for the LIBS data to determine the spectral trends.
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ABBREVIATIONS

UP = uranyl peroxide hydrate (UO₂O₂·2H₂O)
UN = uranyl nitrate hydrate (UO₂(NO₃)₂·6H₂O)
UA = uranyl acetate hydrate (UO₂(CH₃COO)₂·2H₂O)
US1 = uranyl sulfate hydrate (UO₂SO₄·2.5H₂O)
US2 = second sample of uranyl sulfate hydrate (UO₂SO₄·2.5H₂O)
UF = uranyl fluoride hydrate (a mixture of two hydrates: (UO₂)F₂(H₂O))(H₂O)₀.₅₇₁ and UO₂F₂·1.6H₂O)
ADU1 = ammonium diuranate ((NH₄)₂U₂O₇)
ADU2 = second sample of ammonium diuranate ((NH₄)₂U₂O₇)
ADU3 = third sample of ammonium diuranate ((NH₄)₂U₂O₇)
SDU = sodium diuranate (Na₂U₂O₇)
AUC = ammonium uranyl carbonate ((NH₄)₄UO₂(CO₃)₃)
AUS = ammonium uranyl sulfate ((NH₄)₄(UO₂)₄(SO₄)₂O₄)
USA = ammonium uranyl sulfate ((NH₄)₂(UO₂)₂(SO₄)₃)
UO₂ = uranium dioxide (UO₂)
U₃O₈ = triuranium octaoxide (U₃O₈)
UO3 = alpha – uranium trioxide ($\alpha$-UO₃)
UF₄ = uranium tetrafluoride (UF₄)
ADU170W = ammonium diuranate precipitated at 170 rpm, before drying
ADU170D = ammonium diuranate precipitated at 170 rpm, after drying
UO₂170 = uranium oxide fired from ammonium diuranate precipitated at 170 rpm
ADU280W = ammonium diuranate precipitated at 280 rpm, before drying
ADU280D = ammonium diuranate precipitated at 280 rpm, after drying
UO₂280 = uranium oxide fired from ammonium diuranate precipitated at 280 rpm
ADU400W = ammonium diuranate precipitated at 400 rpm, before drying
ADU400D = ammonium diuranate precipitated at 400 rpm, after drying
UO₂400F = uranium oxide fired from ammonium diuranate precipitated at 400 rpm, fired for full 16 hours
UO₂400H = uranium oxide fired from ammonium diuranate precipitated at 400 rpm, fired for only 8 hours
DI = deionized
p-XRD = Powder X-Ray Diffraction
FTIR = Fourier-Transform Infrared
IR = Infrared
LIBS = Laser Induced Breakdown Spectroscopy
HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital
PCA = Principal Component Analysis
PC = Principal Component
PRESS = Predictive Residual Error Sum of Squares
RMSECV = Root Mean Square Error of Cross Validation
HCA = Hierarchical Clustering Analysis
KBr = Potassium Bromide
DTGS = Deuterated Triglycerine Sulfate
PS = polystyrene
PDMS = poly(dimethyl) siloxane
U = uranium
N = nitrogen
O = oxygen
S = sulfur
F = fluorine
C = carbon
H = hydrogen
Chapter 1. Introduction

Purpose

The goal of this dissertation is to determine whether uranium chemical speciation can be detected and differentiated, using optical spectroscopic techniques. The ability to determine chemical signatures, which arise from the chemical processes of materials, is of great use to nuclear forensics. The bulk of nuclear forensics work deals with radiochronometry and isotopic analysis. Many signatures that may be useful in the field are chemical in nature and may be detected using optical spectroscopic techniques. Raman spectroscopy, Fourier-Transform Infrared (FTIR) spectroscopy, Photoluminescence spectroscopy, and Laser Induced Breakdown Spectroscopy (LIBS) will be used to determine the feasibility of examining the chemical signatures for forensic sciences. These signatures will be used for comparison of anthropogenic uranium compounds, found in the mining, conversion, refining, processing, and reprocessing of uranium for nuclear fuel. Uranium containing compounds that are found throughout the cycle of uranium, from mining to reprocessing, will be synthesized and measured using a variety of optical spectroscopic techniques. The application of multivariate analytical methods to the spectroscopy of uranium compounds will be explored. Multivariate methods have been shown to be useful for discriminating uranium between uranium compounds using elemental concentrations, isotopics, anionic impurity concentrations, and vibrational structure. Advanced statistical methods may prove to be useful in quickly and easily analyzing the sometimes complex spectroscopy of uranium compounds.

Uranium

Uranium is one of two actinide elements that are present naturally on Earth in measurable quantities. Uranium is approximately as common as tin or zinc and ranges in concentration from 1.2 μg/g in sedimentary rocks to 120 μg/g in phosphate rocks. [1] In nature, uranium is found as $^{238}\text{U (99.27 \%)}$, $^{235}\text{U}$
(0.72 %), and $^{234}$U (0.005 %). The majority of contemporary uses of uranium stem from its unique nuclear properties, with $^{235}$U being the only naturally occurring fissile isotope; undergoing fission with thermal neutrons.

Uranium is found in four oxidation states U(III), U(IV), U(V), and U(VI) the most prevalent being U(IV) and U(VI). In near surface, low temperature environments, U(IV) is highly immobile, but is readily oxidized to uranyl U(VI) species that have an anomalously high solubility. [1] In oxidized sedimentary rocks, uranium levels are commonly less than 1 ppm. Uranium is readily precipitated in reducing environments. There are nearly 200 mineral species that contain uranium as a necessary structural constituent. The most abundant uranium phase is uraninite, $\text{UO}_2$.[1] Uraninite possesses the fluorite structure, in which the U$^{4+}$ cation is coordinated by eight O atoms in a cubic arrangement and each O atom bonds to four U$^{4+}$. Most minerals are placed in two categories: reduced species containing U$^{4+}$ and oxidized species containing U$^{6+}$. [1] There are many more U$^{6+}$ species than U$^{4+}$ species and the paragenesis and structures of U$^{6+}$ minerals are exceedingly complex. The U$^{6+}$ is invariably present as the $\text{UO}_2^{2+}$, uranyl ion. Depending on pH and solution composition a wide variety of uranyl complexes may form. Carbonate and organic complexes can be particularly important in determining uranium speciation and concentration in solution. The U-O bond lengths in the uranyl ion average 1.8 Å, suggesting very strong covalent bonds. [1] The uranyl ion occurs coordinated by four, five, or six ligands arranged at the equatorial corners of square bipyramids, pentagonal bipyramids, or hexagonal bipyramids, respectively. The O atoms of the uranyl ions are located at the apices of the bipyramids. [1] The U$^{6+}$ equatorial bonds are longer than the axial U - O bonds, and are substantially weaker. The axial U - O bonding mechanism is primarily through donation of electrons form the p orbitals of the O atoms into the empty d and f orbitals of the U$^{6+}$ cation. [1]
Uranium Fuel Cycle

Uranium goes through a series of differing stages during its use as a nuclear fuel. Uranium ore can be classified as high grade (1-4 % U), medium grade (0.1-0.5 % U), and low grade (<0.1 % U). [2] The first step is the mining of the uranium ore. After mining, the ore is concentrated in mills, where the uranium ore content is increased to 85 – 95 % U. Most concentration procedures involve chemical leaching from the ore. The normal choice for chemical leaching is acid leaching with sulfuric acid. For ores with high carbonate content, an alkaline leach with Na₂CO₃ is used. The first step in chemical leaching is the oxidation of any U(IV) to U(VI). The final product of acid leaching appears as UO₂^{2+}, [UO₂(SO₄)₂]^{2-}, and [UO₂(SO₄)₃]^{4-}, for the alkaline leach it is [UO₂(CO₃)₃]^{4-}. [2] After leaching, a purification to remove other materials leached from the ore is done by ion exchange or solvent extraction. Following the purification, uranium is precipitated from the solution to form the uranium ore concentrate, known as yellowcake.

The chemical nature of the uranium ore concentrate depends on the precipitant used. The most common uranium ore concentrate is ammonium diuranate (ADU), commonly given the formula (NH₄)₂U₂O₇, but is more accurately described by UO₃·xNH₄·yH₂O, with variable ratios of uranium, ammonium, and water. Ammonium diuranate is precipitated from uranium solutions using gaseous ammonia or ammonium hydroxide, although the precipitation conditions lead to differences in the precipitated product. [3, 4, 5, 6, 7] The use of sodium hydroxide as a precipitant leads to precipitation of sodium diuranates (SDU), Na₂U₂O₇, although also variable in composition based on precipitation conditions. [8, 9, 10] The uranyl peroxide complex, UO₂O₂·2H₂O, is formed when hydrogen peroxide is used to precipitate uranium. The uranyl peroxide tends to be devoid of other metal impurities, compared to uranium precipitates formed using hydroxide species. [11, 12, 13, 15, 16] Ammonium uranyl carbonate (AUC), (NH₄)₄UO₂(CO₃)₃, is precipitated using gaseous ammonia and carbon dioxide or a
solution of ammonium hydroxide and ammonium carbonate. The AUC precipitate is easily decomposed and reduced to UO₂ for fuel production. [17, 18, 19, 20, 21]

The yellowcake is shipped for refining and conversion. The yellowcake is purified by solvent extraction and then converted to UF₆ for enrichment. The solvent extraction begins with the dissolution of the yellowcake in nitric acid. [2] The uranyl nitrate is separated from metallic impurities by solvent extraction with tri-butyl phosphate (TBP). The purified uranyl nitrate is converted to UO₃ by a concentration by evaporation and a denitrification by heating. UO₃ is reduced to UO₂ using hydrogen. [2] UO₂ is hydrofluorinated with HF to produce UF₄, which is then burned in F₂ to yield UF₆. The UF₆ is then sent for enrichment of ²³⁵U, the fissile isotope. The UF₆ is enriched via gaseous diffusion, gas centrifugation, electromagnetic separation, or laser enrichment.

The enriched UF₆ is then converted to UO₂ for fuel fabrication. The UF₆ is reacted with water to produce uranyl fluoride, UO₂F₂. Ammonium hydroxide is added to the uranyl fluoride solution to precipitate ammonium diuranate. [2] The product is calcined in air to produce U₃O₈, and heated with hydrogen to make UO₂ powder. The powder is pressed into pellets, sintered, and loaded into zircalloy tubing filled with helium. The tubes are sealed and assembled into fuel bundles. [2]

After use in a reactor, the spent nuclear fuel contains about 3% fission products, 1% ²³⁵U, 95% ²³⁸U, and 1% higher actinides, by mass. Some countries reprocess this spent fuel to recover U or Pu from the spent fuel, to remove fission products from the actinides, and to convert the fuel to a safe form for storage. The main process used for almost all fuel reprocessing is the PUREX process. The irradiated UO₂ fuel is dissolved in nitric acid with the uranium being oxidized to UO₂(NO₃)₂ and the plutonium oxidized to Pu(NO₃)₄. [2] A solution of TBP in a high boiling hydrocarbon, such as n-dodecane, is used to
selectively extract the hexavalent $\text{UO}_2(\text{NO}_3)_2$ and the tetravalent $\text{Pu(NO}_3)_4$ from the other actinides and fission products in the aqueous phase. The TBP solution is then treated with a dilute nitric acid solution of a reducing agent, such as U(IV), to reduce the plutonium to a trivalent state, while leaving the uranium in the hexavalent state. [2] The plutonium is transferred to the aqueous phase, leaving the uranium in the organic phase. The only fission products that extract during the process are Zr, Ru, Nb, and Tc. Am and Cm are not extracted and Np is partially extracted, based on the prevalent oxidation state. [2]


Nuclear Forensics and Nonproliferation

Nuclear forensics is the technical means by which nuclear materials are characterized and interpreted. [22] Nuclear materials are described as fissile materials, their products, precursors, and associated materials. The scientific analysis aims to provide information on the intended use of the material and on its history. [23] Uranium and plutonium are the primary materials of concern to nuclear forensics investigations. Signatures provided for nuclear forensics analyses include the isotopic composition, the chemical impurities, the date of the last chemical purification, the morphology, and the isotopic signatures of trace elements. [23, 24] Signatures are material characteristics, not necessarily nuclear, that can be used to distinguish materials from one another, identify the process history of the material, or link the material to people, places, or processes. Signatures tend to fall into two categories, comparative and predictive. Comparative signatures compare properties of an unknown sample to properties of known, or reference, samples. Predictive signatures tend to be derived from some underlying scientific principles and are used to calculate material characteristics based on an understanding of the underlying scientific principle. [25]

The same analytical and interpretative techniques used in nuclear forensic applications can be used to investigate suspected proliferation at undeclared sites or verify declared sites. [25] The ability to identify the intended use and history of material is needed for both nuclear forensics evaluations of illegally trafficked material and nonproliferation verification in either declared or undeclared sites. Nonproliferation and treaty verification is a key element in stopping the spread of nuclear weapons to states that do not already have them. The more states that have nuclear weapons, the higher the likelihood of non-state entities, i.e. terrorist organizations, acquiring nuclear weapons or the nuclear material and technical ability to construct a nuclear weapon of their own.
Chronometric analysis of materials can concurrently provide insight into the time elapsed since last purification, the actinide concentrations, and relevant isotopic ratios. [24] This analysis depends on the predictable laws of in growth and the Bateman equations that nuclides linked through radioactive decay processes follow. [26] This predictability allows for the concentrations of linked species to be calculated at any time following the last material purification. [26] Age dating depends on a few critical assumptions. The first assumption is that the initial purification is complete and that there is no daughter nuclide present at \( t_0 \). The second major assumption is that it is a closed system, and that all progeny is retained in the system and no outside nuclides are introduced. If these assumptions are not held then the calculated age of the material will not represent the true age of the material, or there will be a larger error in the measurement.

The development of new signatures is always a need in forensics investigations. The ability to decrease the time needed for forensics analysis and to increase the fidelity of interpretation could both be aided by the development of new signatures. Much has been published regarding isotopic signatures and age dating for nuclear forensics. There has also been work performed on elemental concentrations and morphology on nuclear materials for forensics. Many signatures arising from the production, conversion, and aging processes are chemical in nature. There is potential to detect persistent molecular signatures characteristic of material origin, age, or process history. These chemical or molecular signatures can play an important role in the continuing evolution of nuclear forensics.

Background

**Vibrational Structure and Spectroscopy**

Molecular vibrations are modeled by an inharmonic quantum oscillator. The inharmonic quantum oscillator builds on the harmonic quantum oscillator, but includes the anharmonic effects of true
interatomic potentials. Solving of Schrödinger’s equation leads to energy levels built on the vibrational quantum number and empirically determined anharmonicity constants. Due to the anharmonic effects, the spacing between vibrational levels decreases with increasing energy and the equilibrium bond length increases for high vibrational levels, and the expansion of material upon heating is due to anharmonic effects.

In vibrational spectroscopy, light is used to examine the vibrational nature of the sample and can interact with the vibrations in different ways. The frequency of molecular vibrations matches the frequency of light in the infrared portion of the electromagnetic spectrum. In FTIR spectroscopy, infrared light is absorbed by the compound to be analyzed. In order for infrared light to be absorbed, the oscillating electric field of the photon resonates with the changing electric dipole caused by the vibration. [27, 28] This occurs when the energy of the vibration matches the energy of the photon. For the vibration to be considered IR active it must result in the change of dipole moment. The dipole moment is due to a difference in electron density across the vibration, i.e. one atom has a net negative charge. Molecules that do not have a dipole moment, such as homonuclear diatomic molecules, tend to have a weak infrared absorption, if any. Polyatomic molecules have infrared absorption proportional in intensity to the magnitude of the change in dipole moment. Polyatomic molecules with no net dipole moment, have infrared absorptions in the vibration causes a change in the dipole moment. Vibrations that have transitions with a change of vibration quantum number greater than one are allowed, but have much weaker intensities. [27]

In Raman spectroscopy, the incident photons are scattered in every direction. When the light is scattered, it can interact elastically or inelastically. If the scattering is elastic, it is known as Rayleigh scattering and the photon does not change energy. In general 1/1,000 photons elastically scatter. [27] If the scattering is inelastic, the photon can gain energy, known as an anti-Stokes’ shift, or the photon can lose energy, known as a Stokes’ shift. The inelastic scattering is known as the Raman effect. In general
1/1,000,000 photons inelastically scatter. [27] The energy difference of both the anti-Stokes’ and the Stokes’ shift matches the energies associated with vibrational transitions of the molecule. The incident light, typically much higher in energy than the vibration, deforms the electron distribution around the molecule during the scattering process, causing the nuclei to move and follow the electron distribution and inducing the vibration. For a vibration to be Raman active the molecule must be polarizable. As in IR spectroscopy, transitions with a change of vibration quantum number greater than one are allowed, but have much weaker intensities. [28]

The first step in vibrational analysis is the calculation of the number of normal modes. For polynuclear molecules containing \( N \) atoms, there are \( 3N - 6 \) vibrational normal modes. Each normal mode has a characteristic frequency associated with it. Overtones, where the change of vibration quantum number greater than one, and combination, where more than one vibration is excited, are allowed in both IR and Raman spectroscopies. Predicting whether a vibration is IR or Raman active is accomplished using symmetry and point group theory. Point group theory describes the symmetry of a molecular by combining symmetry operations of a molecule into point groups. Character tables are used to summarize symmetry operations and irreducible representation for each point group. [28] The table consists of characters that denote how an irreducible representation transmutes when a symmetry operation is applied. As discussed above, infrared photons are absorbed with a change in dipole moment during vibration. Thus, any vibrational mode that corresponds to translations will be IR active. Modes are Raman active when they are related to non-zero components of the polarizability tensor for the molecule, and share symmetry with one or more components of the tensor. It is typical for one or more vibrational modes to be inactive. In character tables, the mode \( A \) corresponds to a single symmetrical rotation around the principal axis, the mode \( B \) corresponds to a single asymmetrical rotation around the principal axis, modes \( E \) and \( T \) are doubly and triply degenerate representation, respectively, and subscripts \( g(gerade) \) and \( u(ungereade) \) correspond to modes with symmetric and
asymmetric modes of inversion, respectively. [28] For point groups with an inversion center IR active modes are never Raman active and Raman active modes are never IR active. The diagonal elements of the polarizability tensor are always Raman active modes of highest symmetry and tend to be the strongest Raman bands. In general, the more symmetric a vibration, the more intense it is in Raman and the weaker in IR, while IR modes are generally associated with asymmetric modes. The lowering of overall symmetry of the molecule can lead to modes that are normally either only IR or Raman active to become active in both IR and Raman. [27]

Photoluminescence Spectroscopy

Photoluminescence spectroscopy deals with measuring the light that is emitted from a sample that is in an electronically excited state. Once a molecule absorbs electromagnetic radiation and transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), vide infra, it exists in an electronically excited state. [29] The molecule will not remain in an excited state indefinitely and invariably will relax back to its electronic ground state. The molecule can do this through a radiative decay process, in which the energy is discarded as a photon, or through a nonradiative decay process, in which the energy is transferred into the vibration, rotation, and translation of the surrounding molecules and is dissipated as heat. The two radiative decay processes are fluorescence and phosphorescence, and will be discussed further. [30] Photoluminescence spectroscopy includes excitation and emission spectroscopy. Excitation spectroscopy gives similar results as absorbance spectroscopy, but allows for the elimination of impurity effects, by specifically targeting the analyte, and gives more precision. Photoluminescence spectroscopy measures the light emitted or absorbed during electronic transitions, which correspond to the energy differences between electronic levels, and thus, gives information regarding the electronic structure of the sample. [30]

The absorption of a photon promotes an electron from the HOMO to the LUMO, when the photon has an energy equal to the difference between the two electronic levels. Molecular orbitals are linear
combinations of the atomic orbitals of the constituent atoms. Atomic orbitals are mathematical functions that describe the wave-like behavior of electrons. The wave-function of the electrons can be used to calculate the probability of finding the electron in a given region, and thus the can be visualized as three dimensional shapes. Each atomic orbital has its own unique set of quantum numbers, and each electron has its own unique set of quantum numbers. The quantum number \( n \) gives the energy of the electron, the quantum numbers \( l \) and \( m \) specify the angular momentum of the electron, and the quantum number \( m_s \) specifies the spin of the electron. [29] What shell of the atom the orbitals form is given by the principal quantum number. The subshell is formed by orbitals of the same \( n \) but different values of \( l \). The names \( s \) orbital, \( p \) orbital, \( d \) orbital, and \( f \) orbital correspond to orbitals with angular quantum number \( l = 0, 1, 2, 3 \), respectively. The quantum number \( m_l \) denotes orbitals in which the electrons have different angular momentum, but the same magnitude of momentum. The \( s \) orbitals are shaped like spheres. There are three \( p \) orbitals, each shaped like a dumbbell, oriented at right angles with lobes pointing along each primary axis. There are five \( d \) orbitals, four shaped similarly, each with four pear shaped lobes three on the \( xy, xz, \) and \( yz \) planes, and the fourth centered on the \( x \) and \( y \) axes. The fifth \( d \) orbital has two pear shaped lobes symmetrically on the \( z \) axis with a torus around the middle. There are seven \( f \) orbitals, four having six lobes pointing to the corners of a regular hexagon in the \( xy, yz, xz \), and \( xy \) planes. Two orbitals have eight lobes pointing to the corners of a cube with four lobes above and four lobes below the \( xy \) plane. The final \( f \) orbital has two lobes pointing along the \( z \) axis with two bowl shaped rings above and below the \( xy \) plane. [30, 31] The placement of electrons within the atomic orbitals follows the Pauli Exclusion Principle, stating no more than two electrons may occupy an orbital unless their spins are paired, and the Aufbau principle, stating the order in which orbitals must be filled, approximately the order of energies of individual orbitals. [29] Molecular orbitals can be: bonding, which arise from constructive interactions of atomic orbitals and are lower in energy than the interacting atomic orbitals; antibonding, which arise from destructive interactions of atomic orbitals and are high in
energy than the interacting atomic orbitals; or non-bonding, which do not arise from any atomic orbital interactions due to lack of symmetry. If there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, then the sample will be transparent to that radiation. The elevation of electrons to higher energy levels is the primary mechanism for the absorption of visible light photons. Due to the number of available states, visible light is absorbed strongly. The energy of the photon in visible light is not high enough to cause ionization of the molecule, although the absorption can cause heating of the sample. The near ultraviolet region is also absorbed by many molecules, but increasing of the energy of the photon leads to ionization of the molecule.

As stated above, radiative decay processes are either fluorescence or phosphorescence. In fluorescence, spontaneous emission of radiation occurs on the order of a few nanoseconds after the exciting radiation is complete. The absorption promotes the molecule to an electronically excited state, which can then lose energy via collisions and vibrations, and decays to the lowest vibrational level of the electronically excited state. The molecule then emits the remaining excess energy as radiation with energy equal to the energy difference between the electronic states. Because the excited molecule loses energy in nonradiative processes, the emitted radiation has a lower frequency, longer wavelength, than the absorbed radiation. [29, 30] The first steps of phosphorescence occur the same way as fluorescence. Phosphorescence happens on slower time scales, due to a “forbidden” transition occurring between a singlet and triplet state. A singlet state is one in which all electron spins are paired. A triplet state is one in which the total spin is nonzero due to parallel spins of electrons. During phosphorescence an excited electron in a singlet state undergoes intersystem crossing during relaxation to a triplet state, via spin-orbit coupling. Spin-orbit coupling occurs when the vibrational levels of the two excited states overlap and the coupling is large when a heavy atom is present in the molecule. The electron, now in a triplet state, continues to move down vibrational levels, before emitting. The
absorption of the photon takes about $10^{-14}$ to $10^{-15}$ seconds, fluorescent emission has lifetimes ranging from about $10^{-10}$ to $10^{-8}$ seconds, and phosphorescent emission has lifetimes ranging from $10^{-6}$ to 10 seconds. [30]

Laser Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS) utilizes a focused laser to ablate, vaporize, and excite a sample. The ensuing plasma emits light, which can be spectroscopically resolved to determine the atomic composition of the plasma, using characteristic atomic emission lines. Laser Induced Breakdown Spectroscopy can be used to determine elemental composition of a variety of samples in solid, liquid, or gas phase. It can be used for in situ analysis or remotely, with no need for sample preparation, and has the ability to measure multiple elements simultaneously. [32] The plasma, and thus analysis, is greatly affected by the experimental setup, including laser parameters, the environment, and the sample itself.

The LIBS plasma begins with the irradiation of the sample with a focused laser. When absorbed laser irradiances are above the optical threshold of the sample, typically $10^6 – 10^7 \text{ W/cm}^2$, a plasma can be formed. [33] High laser irradiances are achieved through the combination of short pulses (typically ns or shorter), focused beam spots (hundreds of microns), and energies ranging from 1 to 1,000 mJ. The plasma formation begins with the ablation of material from the surface of the sample. The sample material is heated locally by absorption of the incident laser radiation to the boiling temperature and evaporates. In the high temperature environment of the resulting plasma there exists some free electrons, present from the photoionization of the sample material following multiple photon absorption, which can gain energy from the radiation field and transfer the energy to atoms in the vapor via collisions. [33] The electrons can continue to gain energy from the oscillating electric field of the
laser beam. In a short amount of time, \( \approx 10^{-12} \) seconds, the electrons have gained enough energy to ionize atoms of the vapor and a plasma is induced.

The plasma can be described in three zones: plasma front, shock front, and absorption front. [34] At the lowest laser intensities the shock front precedes the absorption and plasma front, which are coupled. The energy from the shock front, deposited in the atmosphere behind it, and the radiation from the plasma are both required to move the absorption front towards the laser beam. This is known as a laser-supported combustion wave. At higher laser intensities the shock front is strong enough to heat the gas leading to absorption of the laser. This brings the absorption front just behind the shock front, but ahead of the plasma front. This is known as a laser-supported detonation wave. At the highest laser intensities, radiation from the plasma itself heats in the atmosphere in front of it to the point at which it becomes absorbing. The absorption front and the plasma front are coupled. This is known as a laser-supported radiation wave. When the laser irradiance is not much larger than the breakdown threshold, the plasma is typically in the laser-supported detonation mode. At higher irradiances LIBS plasmas can be described by a laser-supported radiation wave, where all three zones have essentially merged. After the laser pulse has ended, the plasma loses energy and decays leading to recombination, radiation being emitted, and conduction. [34]

The surrounding atmosphere, whether it be air at atmospheric pressure, CO\(_2\) at low pressure like Mars, or Ar at high pressures, has an effect on the plasma formation and the radiation emitted. At pressures less than 1 atm (760 torr), LIBS spectra tend to have a higher signal-to-noise ratio, an increase in spectral intensities, an increase in ablation, and an improved spectral resolution. [35] The improved spectral resolution is likely explained by a decrease in electron density of the plasma. The increased spectral intensities is likely due to the increased lifetime of the LIBS plasma, leading to stronger emission for a
longer period of time. At reduced pressures, the shock wave produced by the plasma is less dense, leading to reduced plasma shielding and thus more laser photons reaching the sample. [35] The increase in ablation also leads to an increase in spectral intensity. At pressures greater than 1 atm (760 torr), LIBS spectra tend to show a decrease in intensity and signal-to-noise ratio. Significant peak broadening and self-absorption can occur. The composition of the surrounding atmosphere has effects on the LIBS plasma. An Ar atmosphere, at 760 torr, leads to higher plasma temperatures and electron density than either He or air, while He has the lowest temperature and electron density. The increase in electron density for Ar compared to He is due to Ar having a lower ionization potential. The increase in electron density leads to an increase in line broadening. Ablation is less under Ar compared to He or air, due to an increase in plasma shielding. [34]

The spectral emission from a LIBS plasma is due to 3 main sources: Bremsstrahlung emission, recombination events, and line emission. Both Bremsstrahlung and recombination events contribute to a continuum in the LIBS spectrum. Bremsstrahlung radiation arises from transitions between free states of electrons, moving in Coulomb fields generated by electrons. These electrons are accelerated or decelerated during collision and emitted photons. Recombination radiation arises from transitions between free electrons and bound electrons. This occurs when a free electron is captured by an ion and gives up its remaining kinetic energy. [34] The ability to time-gate during the collection of a LIBS plasma allows for removal of some of the continuum, as these emissions decay more quickly with time than line emission. The spectral profile of the emission lines is determined by the dominant broadening mechanism. The two main broadening mechanisms are Doppler broadening and Stark broadening. Doppler broadening is due to the vibration of the emitting species and depends on the temperature and atomic weight of the species, and results in a Gaussian line profile. Stark broadening is a collisional broadening mechanism, caused by collisions with ions and electrons in an electric field. An electric field
splits energy levels into sublevels asymmetrically about the unperturbed energy level. [34] This electric field, in LIBS plasmas, is primarily due to collisions with electrons. Stark broadening results in a Lorentzian line profile. Thus, the resulting profile of the spectral line tends to be a convolution of the two, known as a Voight line profile. The Doppler width can be used to determine plasma temperature and the Stark width can be used to determine electron density in the plasma. A very small amount of line broadening is due to natural line broadening, dictated by the Heisenberg Uncertainty principle, and tends to be unobservable at most spectral resolutions. [34]

**Multivariate Analysis and Principal Component Analysis**

Multivariate analysis refers to a set of statistical techniques used when multiple measurements are made on a sample or set of samples. [36] The most widely used technique is Principal Component Analysis (PCA). Principal Component Analysis transforms a dataset, composed of samples and variables, into orthogonal components that maximize variance, finding a combination of factors that describe the major trends in the data. The factors are a set of scores and loadings, with the scores describing how samples relate to each other and the loadings describing how the variables relate to each other. The scores and loadings are paired together, with the original data being equal to the sum of the products of the respective score and loading. The scores and loadings are determined mathematically based on an eigenvector decomposition of the correlation matrix of the variables. The scores and loadings arranged in descending order by the amount of variance described by each pair. The data is usually described in much fewer factors than the original number of variables. [37]

The input for model building is an \( M \times N \) matrix, where \( M \) rows correspond to each sample and \( N \) columns correspond to the variables, in this case the spectral wavenumber or wavelength. Building models starts with preprocessing the data, such that important assumptions are fulfilled. Mean
centering and autoscaling are two typical preprocessing techniques. In a mean centering technique, the mean of every column is calculated and subtracted from the column, changing the data so that the difference from the average is shown for each sample. [37] Mean centering is not applicable here, as forcing the PCA model to include zero is more relevant from a physical aspect of a sample not having an IR absorbance at a certain wavenumber. Autoscaling mean centers the data and then divides each column by the standard deviation of the column. This method can be useful in PCA if variables have different units and scales, but it does not make sense here as each spectrum has the same units and scales. [37] As discussed below, the preprocessing techniques chosen here are a Whittaker smoothing function, an asymmetric least squares baseline subtraction, and normalizing the most intense peak to one.

When building a PCA model, cross-validation is essential. Cross-validation provides a valuation for the complexity of the model, i.e. the number of principal components. It also allows for estimation of the performance of the model on unknown data. [37] Cross-validation involves removing a subset of data from the dataset, building the PCA model, and applying the model to the subset not used to build the model. The results of a cross-validation process are the Root Mean Square Error of Cross-Validation (RMSECV), determined from the cross validation process, and the Root Mean Square Error of Calibration (RMSEC), determined from the full model, and always decreases with the addition of more principal component. [37] A Leave-One-Out method was used here, where one sample at a time was systematically left out of the model building, and then fit with the subsequent model.
Chapter 2. Materials and Instrumentation

Materials

An aqueous solution of uranyl chloride was taken from LANL stock. The enrichment of the uranium was determined by Thermal Ionization Mass Spectrometry (TIMS) to be 99.47 % $^{238}\text{U}$. The concentration of the uranium solution was approximately 0.1 g/mL uranium. The concentrated nitric acid (HNO$_3$) (Trace Metal Grade), concentrated hydrochloric acid (HCl) (Trace Metal Grade), concentrated acetic acid (CH$_3$COOH) (Trace Metal Grade), concentrated sulfuric acid (H$_2$SO$_4$) (Trace Metal Grade), ammonium hydroxide (NH$_4$OH) (Trace Metal Grade), hydrogen peroxide (H$_2$O$_2$) (A.C.S. certified, 30 %), and platinum foil (Pt) (Alpha Aesar 00261) were purchased from Fisher Scientific and used as received. The ammonium carbonate ((NH$_4$)$_2$CO$_3$) (Trace Metal Grade) and potassium bromide (KBr) (FTIR grade, Trace Metal Grade) were purchased from Sigma Aldrich and used as received. The sodium hydroxide (NaOH) (Reagent Grade) was purchased from GFS chemicals and used as received. The Reillex-100 HPQ resin is a crosslinked poly-4-vinylpyridine macroporous polymer and was taken from LANL stock.

Sample preparation

UO$_2$O$_2$·2H$_2$O (UP) Uranyl peroxide hydrate (UO$_2$O$_2$·2H$_2$O) was synthesized as follows, a concentrated HCl solution containing ~0.1 g/mL uranium (99.47 % $^{238}\text{U}$), in the form of UO$_2^{2+}$, was purified by ion exchange, using Reillex-100 HPQ resin. The ion exchange resin was packed into a glass column, rinsed with H$_2$O, and then rinsed with approximately 30 mL of concentrated HCl. Approximately 20 mL of the uranium stock solution is loaded onto the column, before rinsing again with ~30 mL of concentrated HCl. The purified UO$_2^{2+}$ was eluted from the column in 0.01 M HCl. From this solution, the uranium was precipitated as uranyl peroxide hydrate by adjusting the pH to 3 using NH$_4$OH and adding H$_2$O$_2$ dropwise causing the solid to precipitate and the pH to drop to about 1. More NH$_4$OH is added to bring the pH...
back to 3, before adding H₂O₂ again to precipitate. This step is repeated until addition of H₂O₂ does not cause a drop in pH. The solid UO₂O₂·2H₂O precipitated was filtered from the solution and washed with water. The washed precipitate was then ground with a mortar and pestle and dried in a heating block at 70 °C to remove any residual water. The structure and degree of hydration was confirmed using powder X-Ray Diffraction (p-XRD) analysis (Figure 2-1).

![Figure 2-1. Powder X-Ray Diffraction pattern of uranyl peroxide hydrate (UP), with matching pattern from PDF database.](image)
UO₂(NO₃)₂·6H₂O (UN) The uranyl nitrate hydrate (UO₂(NO₃)₂·6H₂O) was synthesized from the UO₂O₂·2H₂O. The UO₂(NO₃)₂·6H₂O was synthesized by stirring and heating UO₂O₂·2H₂O in concentrated nitric acid (70 % HNO₃) and de-ionized(DI) water to dissolve the solid. The solution was heated to dryness resulting in a yellow-green solid. The solid was ground using a mortar and pestle and the structure and degree of hydration was confirmed using p-XRD analysis (Figure 2-2).

Figure 2-2. Powder X-Ray Diffraction pattern of uranyl nitrate hydrate (UN), with matching pattern from PDF database.
The uranyl acetate hydrate \((\text{UO}_2\text{(CH}_3\text{COO})_2\cdot2\text{H}_2\text{O})\) was synthesized by dissolving \(\text{UO}_2\text{O}_2\cdot2\text{H}_2\text{O}\) in 99.5 % acetic acid \((\text{CH}_3\text{COOH})\) and DI water. The solution was heated to dryness resulting in a yellow solid. The solid was ground using a mortar and pestle and the structure and degree of hydration was confirmed using p-XRD analysis (Figure 2-3). The resulting p-XRD pattern’s best match is to metastudtite, the mineral name for uranyl peroxide hydrate. This indicates that the crystalline phase of the material is probably the starting material. The sample is still believed to be uranyl acetate, due to differences from uranyl peroxide found in vibrational spectroscopy and photoluminescence spectroscopy.

![Figure 2-3. Powder X-Ray Diffraction pattern of uranyl acetate hydrate (UA), with matching pattern from PDF database.](image_url)
**UO₂SO₄·2.5H₂O (US1, US2)** The uranyl sulfate hydrate (UO₂SO₄·2.5H₂O) was synthesized by dissolving UO₂O₂·2H₂O in 95.5 % sulfuric acid (H₂SO₄) and DI water. The solution was heated to dryness resulting in a green-yellow solid. The sample was not ground due to the hygroscopic nature of the compound and the propensity to deliquesce in air, and p-XRD analysis was not performed on the uranyl sulfate samples. Two different uranyl sulfate samples were made the same way.

**UO₂F₂·xH₂O (UF)** The uranyl fluoride hydrate (a mixture of two hydrates: (UO₂)F₂(H₂O)(H₂O)₀.₅₇₁ and UO₂F₂·1.₆H₂O) was taken from LANL stock. The structure and degree of hydration was confirmed using p-XRD analysis (Figure 2-4).
Figure 2-4. Powder X-Ray Diffraction pattern of uranyl fluoride hydrate (UF), with matching pattern from PDF database.

\((\text{NH}_4)_2\text{U}_2\text{O}_7\) (ADU1, ADU2, ADU3) Ammonium Diuranate \(((\text{NH}_4)_2\text{U}_2\text{O}_7)\) was synthesized by precipitation from a UO\(_2\)(NO\(_3\))\(_2\) solution. UO\(_2\)O\(_2\)-2H\(_2\)O, prepared as above, was dissolved in conc. HNO\(_3\). From this concentrated UO\(_2\)(NO\(_3\))\(_2\) solution, an excess of NH\(_4\)OH was added to precipitate \((\text{NH}_4)_2\text{U}_2\text{O}_7\). The solid precipitate was vacuum filtered, washed several times with water, and dried at 100 °C. The structure of the solid was confirmed using p-XRD analysis. Three different ammonium diuranate samples were made (Figures 2-5, 2-6, 2-7). The p-XRD patterns for the first two samples, ADU1 and ADU2, are mainly amorphous with some peaks resembling uranyl peroxide, while the third sample, ADU3, has much more
defined peaks matching uranyl peroxide. The crystalline phase of the samples most likely resembles the uranyl peroxide, while the ammonium diuranate is amorphous.

Figure 2-5. Powder X-Ray Diffraction pattern of ammonium diuranate #1 (ADU1), with matching pattern from PDF database.
Figure 2-6. Powder X-Ray Diffraction pattern of ammonium diuranate #2 (ADU2), with matching pattern from PDF database.
Na₂U₂O₇ (SDU) Sodium diuranate (Na₂U₂O₇) was synthesized by precipitation from a UO₂(NO₃)₂ solution. UO₂O₂·2H₂O, prepared as above, was dissolved in conc. HNO₃. From this concentrated UO₂(NO₃)₂ solution, an excess of NaOH was added to precipitate Na₂U₂O₇. The solid precipitate was vacuum filtered, washed several times with water, and dried at 100 °C. The structure of the solid was confirmed using p-XRD analysis (Figure 2-8).
Figure 2-8. Powder X-Ray Diffraction pattern of sodium diuranate (SDU), with matching pattern from PDF database.

\((\text{NH}_4)_4\text{UO}_2\text{(CO}_3\text{)}_3\) (AUC) Ammonium uranyl carbonate \(((\text{NH}_4)_4\text{UO}_2\text{(CO}_3\text{)}_3)\) was precipitated from a \(\text{UO}_2\text{(NO}_3\text{)}_2\) solution using an excess of ammonium carbonate \(((\text{NH}_4)_2\text{CO}_3)\). The solid precipitate was vacuum filtered, washed several times with water, and dried at 100 °C. The structure of the dried solid was confirmed using p-XRD analysis (Figure 2-9).
Figure 2-9. Powder X-Ray Diffraction pattern of ammonium uranyl carbonate (AUC), with matching pattern from PDF database.

\[(\text{NH}_4)_2(\text{UO}_2)_2(\text{SO}_4)_3\] (USA) \& \[(\text{NH}_4)_4(\text{UO}_2)_4(\text{SO}_4)_2\text{O}_4\] (AUS) Two ammonium uranyl sulfate \[(\text{NH}_4)_2(\text{UO}_2)_2(\text{SO}_4)_3\] and \[(\text{NH}_4)_4(\text{UO}_2)_4(\text{SO}_4)_2\text{O}_4\] samples were taken from LANL stock. The structure and degree of hydration for each sample was confirmed by p-XRD analysis (Figures 2-10 (AUS) and 2-11 (USA)).
Figure 2-10. Powder X-Ray Diffraction pattern of ammonium uranyl sulfate (AUS), with matching pattern from PDF database.
UO₂ (UO₂) Uranium dioxide (UO₂) was synthesized by heating UO₂O₂·2H₂O, prepared as above, in air at 400 °C for 8 hours in a Pt-lined ceramic boat to form amorphous – uranium trioxide (A-UO₃). This material was ground using a mortar and pestle, returned to Pt-lined ceramic boat and heated for 8 hours at 500 °C under H₂. The UO₂ was allowed to cool and equilibrate for 24 hours under static H₂. [39] The product was a black powder. Phase purity was confirmed by p-XRD analysis (Figure 2-12).
U₃O₈ (U₃O₈) Triuranium Octaoxide (U₃O₈) was synthesized by heating UO₂O₂·2H₂O, prepared as above, in air at 800 °C for 20 hours in a Pt-lined ceramic boat. This material was ground using a mortar and pestle, returned to a Pt-lined ceramic boat and heated, again, in air at 800 °C for 20 hours. [38] The product was a black powder. Phase purity was confirmed by p-XRD analysis (Figure 2-13).
Figure 2-13. Powder X-Ray Diffraction pattern of alpha-triuranium octaoxide (U3O8), with matching pattern from PDF database.

\[ \alpha\text{-UO}_3 \text{ (UO}_3\text{)} \] The alpha – uranium trioxide (\( \alpha\text{-UO}_3 \)) was synthesized by heating \( \text{UO}_2\text{O}_2 \cdot x\text{H}_2\text{O} \), prepared as above, in air at 400 °C for 8 hours in a Pt-lined ceramic boat to form A-UO\(_3\). This material was ground using a mortar and pestle, returned to the Pt-lined ceramic boat and heated at 485 °C in air for 96 hours. [39] The product is a tan powder. Phase purity was confirmed by p-XRD analysis (Figure 2-14).
Figure 2-14. Powder X-Ray Diffraction pattern of alpha-uranium trioxide (UO₃), with matching pattern from PDF database.

**UO₃** Uranium tetrafluoride (UF₄) was taken from LANL stock. The structure and degree of hydration was confirmed using p-XRD analysis (Figure 2-15).
Figure 2-15. Powder X-Ray Diffraction pattern of uranium tetrafluoride (UF4), with matching pattern from PDF database.

Figure 2-16. From left to right, ground powders of uranyl nitrate, uranyl fluoride, uranyl acetate, uranyl peroxide.
Figure 2-17. From left to right, samples of uranyl sulfate #1, uranyl sulfate #2, ammonium uranyl sulfate (AUS), ammonium uranyl sulfate (USA). The uranyl sulfate samples were not ground and are crystalline.

Figure 2-18. From left to right, ground powders of ammonium diuranate #1, ammonium diuranate #2, ammonium diuranate #3, sodium diuranate, ammonium uranyl carbonate.

Figure 2-19. From left to right, ground powders of uranium dioxide, uranium trioxide, triuranium octaoxide, uranium tetrafluoride.
**Instrumentation**

**Powder X-Ray Diffraction Analysis.** Powder patterns were collected on a Bruker D8 Advance diffractometer equipped with a Lynxeye 1-D silicon strip detector and unconditioned Cu Kα X-rays. Qualitative analyses were performed using JADE 9.0 search/matching and the PDF-4 + 2013 database from the International Center for Diffraction Data. [39] Samples were prepared for p-XRD measurements by grinding using a mortar and pestle. The powder was placed on a sample holder that had vacuum grease applied to it. The powder was then sprayed with hair spray to act as containment for the radioactive powder and to keep it from dispersing off of the sample holder. Broad diffraction peaks apparent at about 53° and 59° are due to the sample holder. The patterns were used to qualitatively confirm the chemical homogeneity and the degree of hydration.

**Fourier Transform Infrared Absorption Spectroscopy.** The FTIR measurements were taken using a Thermo Scientific Nicolet iS5 Spectrometer. The iS5 uses a deuterated triglycerine sulfate (DTGS) detector. The spectra were acquired from 400-4000 cm⁻¹ with a spectral resolution of 1.0 cm⁻¹. The powder samples were mixed with FTIR grade KBr (~1 % analyte) and pressed into 13 mm pellets under several tons of pressure.

**Raman Spectroscopy.** The Raman measurements were taken on a Thermo Scientific DXR 2 Smart Raman spectrometer. The DXR 2 captures a full spectral range of 3,500 to 50 cm⁻¹ using a 400 lines/mm grating and CCD. The spectrograph aperture was set to the 25 μm slit. The resulting resolution was 0.96 cm⁻¹. A 780 nm laser used as the excitation source. The powder samples were ground with a mortar and pestle and measured in 20 mL glass vials or 4 mL glass vials.
**μ-Raman Spectroscopy.** The μ-Raman measurements were taken using a Thermo Scientific DXRxi Raman Imaging Microscope. The DXRxi is equipped with a 900 lines/mm grating and a thermoelectrically cooled Electron Multiplying CCD (EMCCD). It has an average spectral dispersion of 2 cm⁻¹ per CCD pixel, and has four different apertures: 25 and 50 μm confocal pinholes; 25 and 50 μm slits. The excitation laser was a diode-pumped, solid state 532 nm laser. The data was acquired over a range of 50 to 3400 cm⁻¹, with a resolution of 5 cm⁻¹. The powder samples were ground with a mortar and pestle, placed on carbon tape on a SEM stub, sprayed with hair spray for containment, and placed in Thermo Scientific Raman Inert Transfer Cell with Quartz Window.

**Photoluminescence Spectroscopy.** The photoluminescence data (excitation, emission) were taken using Photon Technology International QuantaMaster Spectrofluorometer. The PTI uses a continuous Xenon arc lamp, or a Xenon flash lamp, as a light source, two excitation Czerny-Turner design monochromators, one emission Czerny-Turner design monochromators and two Hamamatsu R928 photomultiplier tubes (one for arc lamp use and one for flash lamp use). The excitation wavelength was varied over a range of 200 – 700 nm and the emission wavelength was varied over a range of 400 – 900 nm using monochromators, with a resolution of 2 nm. The powder sample was flame sealed in a 5 mm borosilicate NMR tube for containment for photoluminescence measurements.

**Laser Induced Breakdown Spectroscopy.** Laser Induced Breakdown Spectroscopy (LIBs) data was taken between 200 – 1000 nm using a medium resolving power echelle spectrometer from Catalina Scientific (EMU65) with a Raptor Photonics EMCCD detector. The resolving power of the spectrometer system was approximately 10,000. The laser excitation source was a Big Sky Ultra 100 pulsed Nd:YAG laser operating at 1064 nm with 8 ns pulse width and a variable attenuator producing pulse energies up to 100 mJ at 20 Hz. The laser pulses were focused onto the sample, perpendicular to the surface, using a
2.5 cm plano-convex focusing lens with a focal length of 10 cm. The plasma light was collected using a
two lens system, consisting of a 25 cm diameter focusing lens (focal length 12.5 cm) combined with a
25 cm diameter collimating lens separated by a distance of 12.5 cm. The output from this lens system
was directed to the entrance end of a broadband UV/Vis/NIR 1 meter fiber optic cable with a 400 μm
inner core diameter. For measurements under an argon atmosphere, the sample chamber was an in-
house designed cube (25 cm on each side) equipped with 5 cm UV grade optical windows. The chamber
was filled with approximately 585 Torr of argon gas, to facilitate the measurement of carbon, nitrogen,
and oxygen in the samples. The plasma emission was collected approximately 20° from the laser path
by collection optics which included two lenses coupled to a fiber optic cable approximately 2 in. from
the plasma. The samples were mixed with 1 % by weight KBr and pressed into 13 mm pellets at
approximately 10 tons of pressure for 5 minutes. [140]

Multivariate Analysis The preprocessing of the spectral data was performed using MatLab R2016b, using
scripts based on Eilers’ work. [44, 45] The multivariate analysis (Principal Component Analysis and
Hierarchical Clustering Analysis) was performed using PLS_Toolbox Version 8.2.1 from Eigenvector
Research, Inc.
Chapter 3. Vibrational Spectroscopic Signatures

Abstract

Raman and FTIR spectroscopy (see chapter 2) can provide useful information about chemical composition and vibrational structure. Molecules have characteristic vibrations that can be detected with FTIR spectroscopy, Raman spectroscopy, or both. These characteristic vibrational signatures can be used to determine the structure of an unknown uranium sample. The variation of characteristic signatures due to differences in molecular environment can be employed to differentiate between uranium compounds. Multivariate analysis of these signatures can provide useful insights into trends and patterns within the data. Advanced statistical techniques can reduce complex spectra to discrete values that can lead to clustering of the data. Clustering techniques can provide an objective method for grouping samples based on the statistical analysis of spectra.

Introduction

The vibrational signatures of uranium compounds are dominated by the linear uranyl ion, UO$_2^{2+}$. The free uranyl ion, exhibiting $D_{\infty h}$ symmetry, should have three fundamental vibrations: symmetric stretch, $\nu_1$; double degenerate bend, $\nu_2$; and antisymmetric stretch, $\nu_3$. The symmetric stretching mode typically occurs in the region 750 cm$^{-1}$ to 900 cm$^{-1}$ and is Raman active in linearly symmetric ions. The antisymmetric stretching mode typically occurs in the region 850 cm$^{-1}$ to 1,000 cm$^{-1}$ and is IR active in linearly symmetric ions. The doubly degenerate bending mode typically occurs in the region 200 cm$^{-1}$ to 300 cm$^{-1}$ and is IR active in linearly symmetric ions. Overlaps between the $\nu_2$ bending vibration and U-O equatorial vibrations are possible.

Following a lowering of symmetry from $D_{\infty h}$ to $C_{\infty v}$, $C_{2v}$, or $C_s$ all three modes, as well as combination and overtone bands, become both IR and Raman active. If all three modes are active in both IR and Raman
spectra, the intensities of \( \nu_2 \) and \( \nu_3 \) in Raman spectra are lower than that for \( \nu_1 \), and in IR spectra the intensities of \( \nu_2 \) and \( \nu_3 \) are expected to be higher than \( \nu_1 \). If the uranyl ion is linear, then the vibrations \( 2\nu_3, 4\nu_3, 6\nu_3, \text{ etc.} \) and \( 3\nu_1, 5\nu_1, 7\nu_1, \text{ etc.} \) are IR inactive and Raman active. The vibrations \( 3\nu_3, 5\nu_3, 7\nu_3, \text{ etc.} \) and \( 2\nu_1, 4\nu_1, 6\nu_1, \text{ etc.} \) are IR active and Raman inactive. [1] The combination band \( \nu_1 + \nu_3 \) is IR allowed.

The symmetry of the uranyl ion is typically D\(_{nm}\) or lower, due to the presence of \( n \) ligands in the equatorial plane and depending on the manner in which the ligands are coordinated. The selection rules for Raman and IR spectra do not change with equatorial ligation. The presence of the Raman active \( \nu_1 \) vibration in IR spectra, suggests the symmetry is reduced with a loss of the \( C_\infty \) axis. A lowering of symmetry can also lead to splitting of the \( \nu_2 \) into 2 components. [1]

Uranyl stretching and bending vibrational frequencies can be determined from force constants and masses. From these equations, the antisymmetric and symmetric stretching vibrations can be related.

The antisymmetric stretch is easy to observe and assign due to its strong intensity, while the symmetric stretch, if IR active, has a low intensity. The location of the symmetric stretch coincides with the location of oxyanion skeletal vibrations or U-OH bends, and can be incorrectly assigned. For this reason it can be useful to calculate an estimated symmetric stretching frequency from the asymmetric stretch.

It is also possible to use the symmetric and antisymmetric stretching frequencies to calculate the uranyl U-O bond distance. [1]

Although the selection rules for the symmetric and asymmetric stretch do not change with equatorial ligation, the frequencies of the shifts are affected by ligands in the equatorial plane. The relatively large intervals for the symmetric stretch (750-900 cm\(^{-1}\)) and the asymmetric stretch (850-1,000 cm\(^{-1}\)) are indicative of the fact that complexation of the uranyl ion by ligands in the equatorial plane (perpendicular to the axial O-U-O) have a profound influence on the uranyl bond distance and the
resulting vibrations. [40] The uranyl stretching frequencies tend to decrease with a move from left to right along the spectrochemical series. [40, 41, 42, 43] Ligands on the left end of the spectrochemical series are regarded as weaker ligands and a move to the right corresponds to stronger ligands. Stronger ligands, i.e. strong Lewis bases, lead to an increase in electron density, an increase in electron delocalization, and consequently a weakening of the U-O uranyl bond. The electrostatic repulsion between equatorial ligand and uranyl oxygen exacerbates the uranyl bond weakening. This weakening in the bond strength causes larger bond distances and a lower vibrational frequency. [41]

Multivariate methods have been applied to discriminate between uranium compounds. Reading et. al. applied PCA to uranium and thorium decay series gamma spectrometry data of uranium ore concentrates to determine geographical origin. [147] Several groups have used PCA applied to trace element concentrations, determined from a variety of methods, to discriminate between uranium ore concentrates. [142, 148, 149, 150, 151] Mace et. al. used Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy and PCA to determine the coordination environments of U (VI) in cements. [152] Both Ho Mer Lin [80] and Klunder [144] used PCA applied to vibrational spectroscopy to differentiate uranium ore concentrates. Ho Mer Lin used Raman spectroscopy on a set of industrial samples to group the samples by class of uranium ore concentrate. Klunder used Near-Infrared Reflectance spectroscopy to differentiate and group uranium ore concentrates, utilizing vibrations characteristic of the precipitant used to precipitated uranium ore concentrates. Similarly to Ho Mer Lin and Klunder, vibrational structure, and not elemental impurities, is used here for discriminating uranium compounds.

Experimental

Samples for FTIR measurements were prepared by mixing approximately 1 % analyte, by weight, with approximately 400 mg of spectral grade KBr. The mixing was accomplished in polystyrene vials with a
polystyrene ball and a Wig-L-Bug grinding mill (REFLEX Analytical Corporation, model 3110B). This method of mixing introduced systematic contaminants into the sample from the polystyrene materials. Absorption peaks can be seen in sample spectra from the polystyrene. The mixture was pressed (Carver model 4350.L) into a pellet under 12,000 lbs. for 10 minutes using a 13 mm cell and die (Carver catalog #3619) while pulling a vacuum. To ensure a good vacuum was created, high vacuum grease (Dow Corning) was applied to the O-ring sealing the base and top of the pellet cell. The vacuum grease was another source of contaminant in the FTIR spectra, poly(dimethyl) siloxane. A sample containing only KBr but prepared the same way as the samples containing uranium compounds was measured to determine the location of contaminant peaks. A second KBr sample containing only KBr but ground with a mortar and pestle and not milled with the Wig-L-Bug was also measured. The FTIR spectra of both samples are shown below in Figure 3-1 and 3-2, with the contaminant peaks labeled. Experimental spectra were compared with library spectra in the Thermo Fisher OMNIC software. These results suggest that the primary contaminant peaks detected in sample spectra are from the polystyrene.
Figure 3-1. FTIR spectrum of KBr pellet prepared by milling with a Wig-L-Bug. Peaks are labeled as polystyrene (PS) or poly (dimethyl siloxane) (PDMS). The peaks labeled as CO$_2$ are from over subtraction of atmospheric carbon dioxide. The water peaks are from the KBr absorbing water. The black trace is the raw data and the blue trace has been smoothed and background subtracted.

Figure 3-2. FTIR spectrum of KBr pellet prepared by mortar and pestle. Peaks are labeled as poly (dimethyl siloxane) (PDMS). The peaks labeled as CO$_2$ are from under subtraction of atmospheric carbon dioxide. The water peaks are from the KBr absorbing water. The black trace is the raw data and the blue trace has been smoothed and background subtracted.
For Raman measurements using the Smart Raman spectrometer, there was no sample preparation necessary. The measurement was taken in the same borosilicate glass vial in which the samples were stored. Fluorescence from the borosilicate glass was detected from roughly 1,200 cm\(^{-1}\) to 2,200 cm\(^{-1}\), and was seen in many of the raw spectra. Sample preparation for measurements with the \(\mu\)Raman instrument was more involved, requiring spreading a small amount of powder on an SEM stub and applying 3 coats of hair spray for containment. The stub was then placed in a Thermo Scientific Raman Inert Transfer Cell for measurement. A peak at about 2,900 cm\(^{-1}\) to 3,100 cm\(^{-1}\) was detected in each of the spectra.

Processing of both FTIR and Raman spectra was done in three parts: smoothing, baseline subtraction, and normalization. Smoothing was accomplished using a Whittaker smoother. [44] The Whittaker smoother is a penalized least squares technique that seeks to minimize the sum of \(S + \lambda R\), where \(S\) is the usual sum of squares of differences, \(\lambda\) is an input parameter by the user, which weights the influence of \(R\), the roughness of the smoother. A larger value of \(\lambda\) leads to a more smoothed function. Baseline subtraction was accomplished using an asymmetric least squares smoothing technique. [45] This method utilizes a Whittaker smoother to estimate the baseline, but weights positive deviations from the baseline much less than negative deviations. This method of baseline subtraction requires two parameters: \(p\) for asymmetry and \(\lambda\) for smoothness. The parameter \(\lambda\) is identical to the Whittaker smoother. The asymmetry parameter introduces weights for the positive deviations from the smoother. For both the smoother and the baseline subtraction, the input parameters are tuned by hand. For the Whittaker smoother values of \(\lambda\) varied from \(10^4\) to \(10^6\). For the baseline subtraction \(\lambda\) varied from \(10^7\) to \(10^9\) and \(p\) varied from \(10^{-6}\) to \(10^{-3}\). Normalization of the spectra was accomplished by normalizing the
intensity of the most intense peak to 1. The preprocessing constants, $\lambda_1$ for smoothing, $\lambda_2$ and $p$ for baseline subtraction, are shown in Table 3-1 for FTIR and Table 3-2 for Raman.

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<th>$p$</th>
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Table 3-1. Preprocessing constants for FTIR spectra. $\lambda_1$ corresponds to the smoothing function and $\lambda_2$ corresponds to the baseline subtraction process. KBr is the sample of neat KBr prepared by milling with a Wig-L-Bug and KBr2 is the sample of neat KBr prepared by mortar and pestle.
Table 3-2. Preprocessing constants for Raman spectra. $\lambda_1$ corresponds to the smoothing function and $\lambda_2$ corresponds to the baseline subtraction process.

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<td>$10^4$</td>
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</tr>
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<td>$10^{-4}$</td>
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</tr>
</tbody>
</table>

Results

*Uranyl Nitrate Hexahydrate (UN)*

The FTIR and Raman spectra of UN are shown in Figures 3-3 and 3-4, respectively. The FTIR spectrum shows many strong peaks ranging from 750 cm$^{-1}$ to 1,700 cm$^{-1}$. The strongest of these peaks are at 1,276 cm$^{-1}$ and 1,532 cm$^{-1}$ corresponding to the asymmetric stretching mode of the two single bonded O atoms in the NO$_3^-$ ion and the N-O double bond, respectively. Nitrate peaks corresponding to bending modes are seen at 742 cm$^{-1}$, 751 cm$^{-1}$, and 804 cm$^{-1}$. Nitrate stretches are observed at 1,026 cm$^{-1}$ and 1,384 cm$^{-1}$ and a nitrate combination band was observed at 1,606 cm$^{-1}$. The uranyl asymmetric stretch $v_3$ was observed at 952 cm$^{-1}$ and 960.5 cm$^{-1}$. The broad stretch at 3,576 cm$^{-1}$ was the water stretch. The FTIR peaks and assignments are shown in Table 3-3. [40, 46, 47, 48, 49, 50, 51, 52] The Raman spectrum was dominated by the peak at 864 cm$^{-1}$, corresponding to the $v_1$ symmetric uranyl stretch. The uranyl bending mode, $v_2$, was seen at 202 cm$^{-1}$. Also present in the Raman spectrum are a number of peaks
belonging to the nitrate ion (NO$_3^-$): the symmetric stretch at 1,038 cm$^{-1}$ and 1,047 cm$^{-1}$ and the bending mode at 716 cm$^{-1}$ and 750 cm$^{-1}$. The peak at 119 cm$^{-1}$ was most likely the O-U-O$_{eq}$ bend. The Raman peaks and assignments are shown in Table 3-4. [53, 54, 55, 56, 57]

Figure 3-3. FTIR spectrum of uranyl nitrate hexahydrate (UN). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Uranyl Fluoride Hydrate (UF)

The FTIR and Raman spectra of UF are shown in Figures 3-5 and 3-6, respectively. The FTIR spectrum shows a grouping of three strong peaks at 928 cm\(^{-1}\), 941 cm\(^{-1}\), and 963 cm\(^{-1}\) that correspond to the \(\nu_3\) asymmetric stretch of uranyl. The peak at 458 cm\(^{-1}\) corresponds to the U-Feq stretch and the peak at 864 cm\(^{-1}\) was the \(\nu_1\) symmetric stretch of uranyl. The sharp peak at 1,384 cm\(^{-1}\) was the NO\(_3^-\) asymmetric stretch, an impurity here to be discussed later. The peaks at 1,619 cm\(^{-1}\) and 1,629 cm\(^{-1}\) correspond to the H\(_2\)O bending mode. The peaks at 699 cm\(^{-1}\), 1,467 cm\(^{-1}\), 2,851 cm\(^{-1}\), and 2,922 cm\(^{-1}\) are contaminants from the polystyrene vials. The broad set of peaks above 3,100 cm\(^{-1}\) (3,179 cm\(^{-1}\), 3,396 cm\(^{-1}\), 3,525 cm\(^{-1}\), 3,594 cm\(^{-1}\)) are H\(_2\)O stretches. The FTIR peaks and assignments for UF are given in Table 3-3. [58, 59, 60]

The Raman spectrum of UF was completely dominated by a strong sharp peak at 863 cm\(^{-1}\) corresponding to the \(\nu_1\) symmetric stretch of the uranyl ion. Other observed peaks include U-Feq bend at 149.5 cm\(^{-1}\), the \(\nu_2\) uranyl bend at 184 cm\(^{-1}\), and a U-Feq bend at 261.5 cm\(^{-1}\). Two small peaks corresponding to NO\(_3^-\)
Impurity are seen at 751 cm\(^{-1}\) and 1,040 cm\(^{-1}\). The Raman peaks and assignments for UF are given in Table 3-4. [58, 61, 62, 63, 64, 65]

Figure 3-5. FTIR spectrum of uranyl fluoride hydrate (UF). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-6. Raman spectrum of uranyl fluoride hydrate (UF). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

_Uranyl Peroxide Dihydrate (UP)_

The FTIR and Raman spectra of UP are shown in Figures 3-7 and 3-8, respectively. The FTIR spectrum of UP shows a set of peaks at 866 cm\(^{-1}\) (shoulder), 906.5 cm\(^{-1}\), and 930 cm\(^{-1}\) (shoulder). The low energy shoulder corresponds to the peroxo O-O stretch and the higher two peaks correspond to the \(\nu_3\) asymmetric uranyl stretch. The two peaks lowest in energy at 479 cm\(^{-1}\) and 563.5 cm\(^{-1}\) correspond to U-O\(_{eq}\) stretches. The sharp peak at 1,622 cm\(^{-1}\) was the bending mode of H\(_2\)O, and the peaks at 3,103.5 cm\(^{-1}\), 3,237 cm\(^{-1}\), and 3,470 cm\(^{-1}\) are the stretches of H\(_2\)O. The FTIR peaks and assignments of UP are given in Table 3-3. [66, 67, 68] The Raman spectrum shows two strong, sharp peaks at 826 cm\(^{-1}\) and 865 cm\(^{-1}\) corresponding to the \(\nu_3\) uranyl symmetric stretch and the peroxo O-O stretch, respectively. The low energy peak at 151 cm\(^{-1}\) corresponds to U-O\(_{eq}\) bending. The peak at 182 cm\(^{-1}\) corresponds to \(\nu_2\) uranyl
bend. The peaks at 278.5 cm$^{-1}$ and 353.5 cm$^{-1}$ are U-O$_{eq}$ stretches. The Raman peaks and assignments for UP are given in Table 3-4. [68]

![FTIR spectrum of uranyl peroxide hydrate (UP).](image1)

**Figure 3-7.** FTIR spectrum of uranyl peroxide hydrate (UP). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

![Raman spectrum of uranyl peroxide hydrate (UP).](image2)

**Figure 3-8.** Raman spectrum of uranyl peroxide hydrate (UP). The black spectrum is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
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<th>(\text{UO}_2\text{(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\text{ (UN)})</th>
<th>(\text{UO}_2\text{F}_2\cdot1.6\text{H}_2\text{O}\text{ (UF)})</th>
<th>(\text{UO}_2\text{O}_2\cdot2\text{H}_2\text{O}\text{ (UP)})</th>
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<td>479</td>
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<td></td>
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<td>U-O\text{\textunderscore eq}</td>
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<td>NO\text{\textunderscore 3} \text{ bend}</td>
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<td></td>
<td>NO\text{\textunderscore 3} \text{ bend}</td>
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<tr>
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<td>\text{H}_2\text{O} \text{ stretch}</td>
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Table 3-3. FTIR peaks (cm\(^{-1}\)) and assignments for uranyl nitrate hydrate (UN), uranyl fluoride hydrate (UF), and uranyl peroxide hydrate (UP).
<table>
<thead>
<tr>
<th></th>
<th>UO₂(NO₃)₂·6H₂O (UN)</th>
<th>UO₂F₂·1.6H₂O (UF)</th>
<th>UO₂O₂·2H₂O (UP)</th>
<th>Assignment</th>
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<td></td>
<td>U-F bend</td>
</tr>
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</tr>
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<td></td>
<td></td>
<td>NO₃⁻ stretch</td>
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Table 3-4. Raman peaks (cm⁻¹) and assignments for uranyl nitrate hydrate (UN), uranyl fluoride hydrate (UF), and uranyl peroxide hydrate (UP).

*Uranyl Acetate Dihydrate (UA)*

The FTIR and Raman spectra of UA are shown in Figures 3-9 and 3-10, respectively. The strongest feature in the FTIR spectrum was the peak at 908 cm⁻¹ with a shoulder at 931 cm⁻¹ corresponding to the ν<sub>3</sub> uranyl asymmetric stretch and C-C stretch, respectively. The peak at 495 cm⁻¹ corresponds to the U-O<sub>eq</sub> stretch. The two peaks at 606.5 cm⁻¹ and 679 cm⁻¹ correspond to the CO₂ rock and bend, respectively. The set of peaks at 1,018 cm⁻¹ and 1,052 cm⁻¹ are CH₃ rocking vibrations. The peaks at 1,344.5 cm⁻¹, 1,408.5 cm⁻¹, and 1,446.5 cm⁻¹ correspond to CH₃ bending vibrations. The two peaks at 1,470 cm⁻¹ and 1,537 cm⁻¹ correspond to the symmetric and asymmetric C-O double bond stretches, respectively. The H₂O bend was observed at 1,622 cm⁻¹ and the H₂O stretches at 3,086 cm⁻¹, 3,237 cm⁻¹, and 3,462 cm⁻¹. The FTIR peaks and assignments for UA are given in Table 3-5. [69. 70, 71, 72] The Raman spectrum was dominated by two sharp peaks at 827 cm⁻¹ and 863 cm⁻¹, assigned to the ν<sub>1</sub>
uranyl symmetric stretch and C-C stretch, respectively. The peaks at 122 cm\(^{-1}\) and 155 cm\(^{-1}\) are assigned to uranyl and U-O\(_{eq}\) bending, respectively. The \(v_2\) uranyl bending mode was observed at 213 cm\(^{-1}\) and the U-O\(_{eq}\) stretches are seen at 276 cm\(^{-1}\) and 353 cm\(^{-1}\). The sharp peak at 681 cm\(^{-1}\) corresponds to a COO bending mode. The peak at 1,353 cm\(^{-1}\) was assigned as a CH\(_3\) bending vibration, as was the broad peak at 1,439 cm\(^{-1}\). The Raman peaks and assignments for UA are given in Table 3-6. [43, 73, 74, 75]

![FTIR spectrum of uranyl acetate dihydrate (UA). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.](image-url)
Ammonium Uranyl Carbonate (AUC)

The FTIR and Raman spectra of AUC are shown in Figures 3-11 and 3-12, respectively. The most intense peak in the FTIR spectrum of AUC was assigned as a NO$_3^-$ impurity at 1,384 cm$^{-1}$. The peak at 464.5 cm$^{-1}$ corresponds to the U-N$_{eq}$ stretch. The group of peaks at 707 cm$^{-1}$, 730.5 cm$^{-1}$, and 830 cm$^{-1}$ are assigned to CO$_3^{2-}$ bending vibrations. The peak at 903 cm$^{-1}$ was the $\nu_3$ uranyl asymmetric stretch. The CO$_3^{2-}$ symmetric stretching vibration was assigned to the peak at 1,052 cm$^{-1}$. The peak at 1,545 cm$^{-1}$ was assigned to a CO$_3^{2-}$ stretch. Peaks belonging to ammonium, NH$_4^+$, vibrations are observed at 1,398 cm$^{-1}$ (bend), 1,644 cm$^{-1}$ (bend), and 3,130 cm$^{-1}$ (stretch). At 3,575.5 cm$^{-1}$, the H$_2$O stretch was observed. The FTIR peaks and assignments for AUC are given in Table 3-5. [76, 77, 78, 79] The Raman spectrum of AUC shows a set of strong sharp peaks at 830 cm$^{-1}$ and 838 cm$^{-1}$ corresponding to the $\nu_1$ uranyl symmetric stretch and a CO$_3^{2-}$ bend, respectively. The peaks at 143.5 cm$^{-1}$ and 208 cm$^{-1}$ are assigned to uranyl and...
The $v_2$ uranyl bend was observed at 233 cm$^{-1}$. The peaks at 707 cm$^{-1}$ and 725.5 cm$^{-1}$ correspond to CO$_3^{2-}$ bends, as does the peak at 918 cm$^{-1}$. The peak at 1,046 cm$^{-1}$ corresponds to a NO$_3^-$ impurity and the 1,369 cm$^{-1}$ peak to the CO$_3^{2-}$ asymmetric stretch. The Raman peaks and assignments for AUC are given in Table 3-6. [76, 80, 81]
Figure 3-12. Raman spectrum of ammonium uranyl carbonate (AUC). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
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<th></th>
<th>UO$_2$(CH$_3$COO)$_2$·2H$_2$O (UA)</th>
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<th>Assignment</th>
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Table 3-5. FTIR peaks (cm$^{-1}$) and assignments for uranyl acetate dihydrate (UA) and ammonium uranyl carbonate (AUC).
### Table 3-6. Raman peaks (cm⁻¹) and assignments for uranyl acetate dihydrate (UA) and ammonium uranyl carbonate (AUC).

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<td>NO₃⁻ stretch</td>
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<td>CO₃²⁻ stretch</td>
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<td>CH₃ bend</td>
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**Ammonium Diuranate (ADU1, ADU2, ADU3)**

The FTIR and Raman spectra for each of the three ADU samples are very similar and will be discussed together. The FTIR and Raman spectra for ADU1 are shown in Figures 3-13 and 3-14, respectively, Figures 3-15 and 3-16, respectively for ADU2, and Figures 3-17 and 3-18, respectively for ADU3. In the FTIR spectra the ν₃ uranyl asymmetric stretch was observed in all three ADU samples, at 905 cm⁻¹ for ADU1, at 904 cm⁻¹ for ADU2, and split into two peaks at 906 cm⁻¹ and 926 cm⁻¹ for ADU3. At lower wavenumbers, ADU3 has a peak at 482 cm⁻¹ corresponding to a U-N(eq) stretch. All three samples exhibit a U-O(aq) stretch at 539 cm⁻¹ for ADU1, 528 cm⁻¹ for ADU2, and 539 cm⁻¹ for ADU3. Several peaks assigned to either NH₃ or NH₄⁺ are observed in all three spectra: an NH₃ bend at 1,317 cm⁻¹ for ADU2; an NH₄⁺ bend at 1,400 cm⁻¹ for ADU1, 1,403 cm⁻¹ for ADU2, and 1,401 cm⁻¹ for ADU3; an NH₃ bend at 1,657 cm⁻¹ for ADU2 and 1,646 cm⁻¹ for ADU3; an NH₃ stretch at 3,131 cm⁻¹ for ADU1, 3,184.5 cm⁻¹ for
ADU2, and 3,185 cm\(^{-1}\) for ADU3; and an NH\(_4^+\) stretch at 3,362 cm\(^{-1}\) for ADU2 and 3,237 cm\(^{-1}\) for ADU3. All three ADU samples show a NO\(_3^-\) contaminant peak at 1,384.5 cm\(^{-1}\) for ADU1 and ADU3 and 1,385.5 cm\(^{-1}\) for ADU2. An H\(_2\)O bend was observed at 1,622 cm\(^{-1}\) for ADU1, 1,632 cm\(^{-1}\) for ADU2, and 1,621 cm\(^{-1}\) for ADU3 and an H\(_2\)O stretch was observed at 3,490 cm\(^{-1}\) for ADU1, 3,487.5 cm\(^{-1}\) for ADU2 and 3,462 cm\(^{-1}\) for ADU3. Polystyrene contaminant peaks are also observed in all three samples at 699 cm\(^{-1}\) and at \(\sim1,460\) cm\(^{-1}\) and \(\sim1,493\) cm\(^{-1}\). The FTIR peaks and assignments for the three ADU samples are given in Table 3-7. [77, 82, 83, 84, 85] The Raman spectra of all three ADU samples are dominated by the \(\nu_1\) uranyl symmetric stretch found at 819 cm\(^{-1}\) for ADU1, 823 cm\(^{-1}\) for ADU2, and 831 cm\(^{-1}\) and 869 cm\(^{-1}\) for ADU3. All three ADU samples show a stretch that could be attributed to a U-OH bend, at 743 cm\(^{-1}\) for ADU1 and ADU2 and at 737.5 cm\(^{-1}\) for ADU3. Uranyl hydroxide (UO\(_2\)(OH\(_2\))\(\cdot\)xH\(_2\)O) is an intermediate in the precipitation of ADU and could suggest the presence of a mixture of uranium species. This peak could also have contributions from the NO\(_3^-\) impurity which would have peaks around 757 cm\(^{-1}\). At low wavenumbers, all three ADU samples show the \(\nu_2\) uranyl bend at 186.5 cm\(^{-1}\) for ADU1, 185 cm\(^{-1}\) for ADU2, and 190 cm\(^{-1}\) and 280.5 cm\(^{-1}\) for ADU3. Peaks belonging to U-O\(_{eq}\) vibrations are seen in all three ADU samples: 352 cm\(^{-1}\) for ADU1; 355 cm\(^{-1}\) for ADU2; 357 cm\(^{-1}\), 453 cm\(^{-1}\), 555.5 cm\(^{-1}\) for ADU3. Another peak attributed to the NO\(_3^-\) impurity was assigned at 1,045 cm\(^{-1}\) for ADU1, 1,042 cm\(^{-1}\) for ADU2, and 1,047 cm\(^{-1}\) for ADU3. The Raman peaks and assignments for all three ADU samples are given in Table 3-8. [62, 80, 81]
Figure 3-13. FTIR spectrum of ammonium diuranate #1 (ADU1). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-14. Raman spectrum of ammonium diuranate #1 (ADU1). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-15. FTIR spectrum of ammonium diuranate #2 (ADU2). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-16. Raman spectrum of ammonium diuranate #2 (ADU2). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-17. FTIR spectrum of ammonium diuranate #3 (ADU3). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-18. Raman spectrum of ammonium diuranate #3 (ADU3). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Table 3-7. FTIR peaks (cm⁻¹) and assignments for the three ammonium diuranate samples (ADU1, ADU2, ADU3).

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<thead>
<tr>
<th>(NH₄)₂U₂O₇ #1 (ADU1)</th>
<th>(NH₄)₂U₂O₇ #2 (ADU2)</th>
<th>(NH₄)₂U₂O₇ #3 (ADU3)</th>
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<tr>
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Table 3-8. Raman peaks (cm⁻¹) and assignments for the three ammonium diuranate samples (ADU1, ADU2, ADU3).

<table>
<thead>
<tr>
<th>(NH₄)₂U₂O₇ #1 (ADU1)</th>
<th>(NH₄)₂U₂O₇ #2 (ADU2)</th>
<th>(NH₄)₂U₂O₇ #3 (ADU3)</th>
<th>Assignment</th>
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<td>ν₁ uranyl symmetric stretch</td>
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<td>1045</td>
<td>1042</td>
<td>1047</td>
<td>NO₃⁻ stretch</td>
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</table>

Uranyl Sulfate Hydrate (US1, US2)

The FTIR and Raman spectra for both uranyl sulfate samples will be discussed together and are shown in Figures 3-19 and 3-20, respectively for US1 and Figures 3-21 and 3-22, respectively for US2. The low wavenumber region of the FTIR spectra for the two uranyl sulfate samples consist of a number of bands
belonging to two different bending modes of the sulfate ion $\text{SO}_4^{2-}$, $\nu_2$ and $\nu_4$ modes. The $\nu_2 \text{SO}_4^{2-}$ bend was observed at 443.5 cm$^{-1}$, 465 cm$^{-1}$, and 477.5 cm$^{-1}$ for US1 and at 467 cm$^{-1}$ for US2. The $\nu_4 \text{SO}_4^{2-}$ bend was observed at 597.5 cm$^{-1}$, 625 cm$^{-1}$, 644 cm$^{-1}$, 652 cm$^{-1}$, and 662 cm$^{-1}$ for US1 and 593 cm$^{-1}$ and 654.5 cm$^{-1}$ for US2. The peak at 884.5 cm$^{-1}$ for US2 was assigned at the $\nu_1$ uranyl symmetric stretch. Both samples have the $\nu_3$ uranyl asymmetric stretch at 927 cm$^{-1}$ and 943 cm$^{-1}$ for US1 and 942 cm$^{-1}$ for US2. The sample US1 has two peaks at 1,003 cm$^{-1}$ and 1,014 cm$^{-1}$ assigned to the symmetric stretch of $\text{SO}_4^{2-}$. Both samples show the $\text{SO}_4^{2-}$ asymmetric stretch in the 1,050 cm$^{-1}$ to 1,200 cm$^{-1}$ region: 1,052 cm$^{-1}$, 1,063 cm$^{-1}$, 1,079 cm$^{-1}$, 1,114.5 cm$^{-1}$, 1,127.5 cm$^{-1}$, 1,160.5 cm$^{-1}$, and 1,201 cm$^{-1}$ for US1 and 1,054 cm$^{-1}$, 1,103 cm$^{-1}$, 1,170.5 cm$^{-1}$ for US2. Peaks at 1,241 cm$^{-1}$ and 1,255 cm$^{-1}$ for US1 and 1,239 cm$^{-1}$ could be assigned as the asymmetric $\text{SO}_4^{2-}$ stretch and could indicate uranyl sulfate species with varying amounts of water. The $\text{H}_2\text{O}$ bending peak was seen at 1,614 cm$^{-1}$ for US1 and 1,603 cm$^{-1}$ and 1,629 cm$^{-1}$ for US2. The $\text{H}_2\text{O}$ stretches are seen at 3,491.5 cm$^{-1}$, 3,517 cm$^{-1}$, and 3,615 cm$^{-1}$ for US1 and 3,395 cm$^{-1}$ for US2. The FTIR peaks and assignments for both uranyl sulfate samples are given in Table 3-9. [86, 87, 88, 89, 90, 91, 92, 93, 94] The Raman spectrum of US1 was dominated by luminescence from the sample, and was thus difficult to observe or assign any Raman peaks. The one peak that was easily observed, at 868 cm$^{-1}$ was assigned as the $\nu_1$ uranyl symmetric stretch. A peak at 1,039 cm$^{-1}$ could be assigned as the $\text{SO}_4^{2-}$ symmetric stretch, and a peak at 1,079.5 cm$^{-1}$ could be assigned as the $\text{SO}_4^{2-}$ asymmetric stretch. The spectrum of US2, however, was devoid of luminescence and possesses easily discernable peaks. The most intense peak, at 884 cm$^{-1}$ belongs to the $\nu_1$ uranyl symmetric stretch. The $\nu_3$ uranyl symmetric stretch was seen at 918 cm$^{-1}$ and 969 cm$^{-1}$ indicating a lowering of symmetry and variations the coordination environment. At low wavenumbers, the peak at 123.5 cm$^{-1}$ corresponds to uranyl, the peak at 149.5 cm$^{-1}$ to a $\text{U-O_{eq}}$ bend, and the peaks at 192 cm$^{-1}$ and 225 cm$^{-1}$ to the $\nu_2$ uranyl bending vibration. The $\text{SO}_4^{2-}$ $\nu_2$ bending vibration was present at 412 cm$^{-1}$ and 445 cm$^{-1}$, and the $\text{SO}_4^{2-}$ $\nu_4$ bending vibration was seen at 580.5 cm$^{-1}$ and 600 cm$^{-1}$. The $\text{SO}_4^{2-}$ symmetric stretch was seen at 1,044 cm$^{-1}$ and
the asymmetric stretch at 1,092.5 cm\(^{-1}\) and 1,156 cm\(^{-1}\). The Raman peaks and assignments for both uranyl sulfate samples are given in Table 3-10. [86, 88, 89, 90, 91, 92, 93, 94]

![FTIR spectrum of uranyl sulfate hydrate #1 (US1). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.](image)

Figure 3-19. FTIR spectrum of uranyl sulfate hydrate #1 (US1). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-20. Raman spectrum of uranyl sulfate hydrate #1 (US1). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-21. FTIR spectrum of uranyl sulfate hydrate #2 (US2). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Ammonium Uranyl Sulfate Hydrate (USA, AUS)

The FTIR and Raman spectra for both ammonium uranyl sulfate samples will be discussed together are shown in Figures 3-23 and 3-24, respectively for USA and Figures 3-25 and 3-26, respectively for AUS. The FTIR spectrum of USA was very similar to that of US1 with the addition of peaks assigned to NH₄⁺, and the FTIR spectrum of AUS was very similar to US2, with the addition of the NH₄⁺ peaks. Both USA and AUS show the ν₂ and ν₄ SO₄²⁻ bending modes: ν₂ at 443.5 cm⁻¹, 464 cm⁻¹, and 477 cm⁻¹ for USA and at 465 cm⁻¹ for AUS; ν₄ at 598 cm⁻¹, 624 cm⁻¹, 643.5 cm⁻¹, 651 cm⁻¹, and 661 cm⁻¹ for USA and at 583 cm⁻¹ and 628 cm⁻¹ for AUS. The ν₁ uranyl symmetric stretch was visible for AUS at 886 cm⁻¹. The ν₃ uranyl asymmetric stretch was assigned to peaks at 927 cm⁻¹ and 940 cm⁻¹ for USA and at 919 cm⁻¹ for USA. Only USA has a peak corresponding to the SO₄²⁻ symmetric stretch at 1,002 cm⁻¹. Both samples show the SO₄²⁻ asymmetric stretch, at 1,056 cm⁻¹, 1,078 cm⁻¹, 1,128 cm⁻¹, 1,160 cm⁻¹, and 1,202 cm⁻¹ for USA and
1,079 cm\(^{-1}\) and 1,164 cm\(^{-1}\) for AUS. Peaks at 1,235 cm\(^{-1}\) and 1,252 cm\(^{-1}\) for USA could be assigned to the asymmetric SO\(_4^{2-}\) stretch, indicating species with varying amounts of water. The NH\(_4^+\) bend can be seen at 1,400.5 cm\(^{-1}\) for USA and 1,400 cm\(^{-1}\) for AUS. The NH\(_4^+\) stretch was observed at 3,125 cm\(^{-1}\) for USA and 3,126.5 cm\(^{-1}\) for AUS. The H\(_2\)O bend was assigned to a peak at 1,613.5 cm\(^{-1}\) for USA and 1,637 cm\(^{-1}\) for AUS. The H\(_2\)O stretch was seen at 3,492.5 cm\(^{-1}\), 3,528 cm\(^{-1}\), and 3,614 cm\(^{-1}\) for USA and at 3,533 cm\(^{-1}\) for AUS. The FTIR peaks and assignments for both ammonium uranyl sulfate samples are listed in Table 3-9. [86, 88, 89, 90, 91, 92, 93, 94] The Raman spectra of both samples are very similar, although USA shows more luminescence. Both spectra are dominated by \(\nu_1\) uranyl symmetric stretch at 861 cm\(^{-1}\) for USA and 802 cm\(^{-1}\) and 824 cm\(^{-1}\) for AUS. The \(\nu_3\) uranyl asymmetric stretch was also visible in USA at 925.5 cm\(^{-1}\). At low wavenumbers, AUS shows a U-O\(_{eq}\) bend at 146 cm\(^{-1}\), the \(\nu_2\) uranyl bend at 202 cm\(^{-1}\) and 258 cm\(^{-1}\), and U-O\(_{eq}\) stretches at 333 cm\(^{-1}\) and 405 cm\(^{-1}\). The \(\nu_2\) uranyl bend was seen at 186.5 cm\(^{-1}\) for USA. Both SO\(_4^{2-}\) bends are seen for AUS, \(\nu_2\) at 427 cm\(^{-1}\) and 452 cm\(^{-1}\) and \(\nu_4\) at 551 cm\(^{-1}\). The SO\(_4^{2-}\) symmetric stretch was observed at 1,009 cm\(^{-1}\) for AUS and 1,030 cm\(^{-1}\) for USA. The asymmetric SO\(_4^{2-}\) stretch was observed at 1,071 cm\(^{-1}\) for USA and 1,096 cm\(^{-1}\) for AUS. The Raman peaks and assignments for both ammonium uranyl sulfate species are listed in Table 3-10. [86, 88, 89, 90, 91, 92, 93, 94]
Figure 3-23. FTIR spectrum of ammonium uranyl sulfate hydrate (USA). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-24. Raman spectrum of ammonium uranyl sulfate hydrate (USA). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-25. FTIR spectrum of ammonium uranyl sulfate hydrate (AUS). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-26. Raman spectrum of ammonium uranyl sulfate hydrate (AUS). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
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<thead>
<tr>
<th>UO₂SO₄·2.5H₂O #1 (US1)</th>
<th>UO₂SO₄·2.5H₂O #2 (US2)</th>
<th>(NH₄)₂(UO₂)₂(SO₄)₃·5H₂O (USA)</th>
<th>(NH₄)₄(UO₂)₄(SO₄)₂O₂·5H₂O (AUS)</th>
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Table 3-9. FTIR peaks (cm⁻¹) and assignments for the two uranyl sulfate samples (US1, US2) and two ammonium uranyl sulfate samples (USA, AUS).
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<th>UO₂SO₄·2.5H₂O #1 (US1)</th>
<th>UO₂SO₄·2.5H₂O #2 (US2)</th>
<th>(NH₄)₂(UO₂)₂(SO₄)₃·5H₂O (USA)</th>
<th>(NH₄)₄(UO₂)₄(SO₄)₂O₂·5H₂O (AUS)</th>
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<td>ν₂ SO₄²⁻ bend</td>
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<td>802</td>
<td>ν₁ SO₄²⁻ bend</td>
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<td>868</td>
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<td>861</td>
<td>824</td>
<td>ν₁ uranyl symmetric stretch</td>
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<td>ν₁ uranyl symmetric stretch</td>
</tr>
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<td>ν₃ uranyl asymmetric stretch</td>
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<td>1092.5</td>
<td>1071</td>
<td>1096</td>
<td>ν₃ SO₄²⁻ stretch</td>
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<td></td>
<td></td>
<td>ν₃ SO₄²⁻ stretch</td>
</tr>
</tbody>
</table>

Table 3-10. Raman peaks (cm⁻¹) and assignments for the two uranyl sulfate samples (US1, US2) and two ammonium uranyl sulfate samples (USA, AUS).

**Sodium Diuranate (SDU)**

The FTIR and Raman spectra for sodium diuranate are shown in Figures 3-27 and 3-28, respectively. The FTIR spectrum of SDU does not show many IR absorbing peaks attributable to SDU. Small peaks ranging from 900 cm⁻¹ up to 3,200 cm⁻¹ belong to polystyrene contaminants. The sharp peak at 699 cm⁻¹ also corresponds to polystyrene. The peak at 503.5 cm⁻¹ was assigned as an U-Oeq stretch. The broad peak at 851 cm⁻¹ was assigned as ν₃ uranyl asymmetric stretch with the shoulder at 764.5 cm⁻¹ assigned as the ν₁ uranyl symmetric stretch. The broad nature of the asymmetric peak indicates the variable nature of the molecular structure of the compound. The H₂O stretch was seen at 3,506 cm⁻¹. The FTIR peaks and
assignments are listed in Table 3-11. [95, 96, 97, 98, 99] The Raman spectrum of SDU shows a strong peak at 783 cm\(^{-1}\) corresponding to the \(\nu_1\) uranyl symmetric stretch, with a shoulder at 839 cm\(^{-1}\) corresponding to the \(\nu_3\) uranyl asymmetric stretch. The peak at 112 cm\(^{-1}\) was assigned as uranyl and the peak at 288 cm\(^{-1}\) as the \(\nu_2\) uranyl bend. Two peaks assigned to vibrations between uranium and an equatorial atom are found at 357 cm\(^{-1}\) and 578.1 cm\(^{-1}\), the U-O\(_{eq}\) and U-Na vibrations, respectively. The Raman peaks and assignments are listed in Table 3-12. [91, 95, 98]

Figure 3-27. FTIR spectrum of sodium diuranate (SDU). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-28. Raman spectrum of sodium diuranate (SDU). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

<table>
<thead>
<tr>
<th>Na$_2$U$_2$O$_7$ (SDU)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>503.5</td>
<td>U-O$_{eq}$</td>
</tr>
<tr>
<td>764.5</td>
<td>$\nu_1$ uranyl symmetric stretch</td>
</tr>
<tr>
<td>851</td>
<td>$\nu_3$ uranyl asymmetric stretch</td>
</tr>
<tr>
<td>3506</td>
<td>H$_2$O stretch</td>
</tr>
</tbody>
</table>

Table 3-11. FTIR peaks (cm$^{-1}$) and assignments for sodium diuranate (SDU).

<table>
<thead>
<tr>
<th>Na$_2$U$_2$O$_7$ (SDU)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>uranyl</td>
</tr>
<tr>
<td>288</td>
<td>$\nu_2$ uranyl bend</td>
</tr>
<tr>
<td>357</td>
<td>U-O$_{eq}$</td>
</tr>
<tr>
<td>578.5</td>
<td>U-Na</td>
</tr>
<tr>
<td>783</td>
<td>$\nu_1$ uranyl symmetric stretch</td>
</tr>
<tr>
<td>839</td>
<td>$\nu_3$ uranyl asymmetric stretch</td>
</tr>
</tbody>
</table>

Table 3-12. Raman peaks (cm$^{-1}$) and assignments for sodium diuranate (SDU).
Uranium Oxide (UO2, UO3, U3O8)

The FTIR and Raman spectra of the three uranium oxides will be discussed together and are shown in Figures 3-29 and 3-30, respectively for UO2, Figures 3-31 and 3-32, respectively for U3O8, Figures 3-33 and 3-34, respectively for UO3. Both the FTIR and Raman spectra for UO2 do not show many peaks corresponding to the UO2. In the FTIR spectrum a broad peak was observed at 502 cm\(^{-1}\) and assigned as the U-O T\(_{1u}\) longitudinal optical mode with a shoulder at 438 cm\(^{-1}\) assigned as the U-O T\(_{1u}\) transverse optical mode. There was a broad peak at 899.5 cm\(^{-1}\) assigned as a combination of the broad low wavenumber peak. The other peaks in the spectrum are assigned as polystyrene contaminant or absorbed water by the KBr. The FTIR spectrum of U3O8 shows a peak at 457 cm\(^{-1}\) assigned as the Eu fundamental U-O stretch. The peak at 498 cm\(^{-1}\) was assigned as a combination of vibrations lower in wavenumber than measured here. The 541 cm\(^{-1}\) was assigned to the E\(_{g}\) fundamental U-O vibration and the 743 cm\(^{-1}\) peak to the stretching vibration in the U-O-U chains. The FTIR spectrum of UO3 exhibits several strong peaks below 1,000 cm\(^{-1}\). The lowest wavenumber peak, at 539.5 cm\(^{-1}\) has been assigned as the E\(_{u}\) fundamental vibration, and the next peak at 611.5 cm\(^{-1}\) has been conjectured to be a combination band of vibrations lower in wavenumber than observed here. The sharp peak at 699 cm\(^{-1}\) is polystyrene contaminant, but the peak it rests upon at 703 cm\(^{-1}\) has been assigned as the A\(_{2u}\) fundamental stretch. The peak at 777 cm\(^{-1}\) has been assigned as the asymmetric stretch of U-O chains. The small peak at 841.5 cm\(^{-1}\) has been assigned as the \(v_1\) uranyl symmetric stretch. The two sharp peaks at 899 cm\(^{-1}\) and 931 cm\(^{-1}\) are the \(v_3\) uranyl asymmetric stretch. The FTIR peaks and locations for all three uranium oxides are listed in Table 3-13. [100, 101, 102, 103, 104, 105, 106] The Raman spectrum of UO2 is of poor quality and assignments are difficult to make. A peak at 453 cm\(^{-1}\) was assigned as the T\(_{2g}\) U-O fundamental stretch. Two peaks at 1,332 cm\(^{-1}\) and 1,572.5 cm\(^{-1}\) are left unassigned and are most likely due to fluorescence from the sample containment. The Raman spectrum of U3O8 is of much higher
quality and displays many peaks below 900 cm$^{-1}$. The low wavenumber peaks at 85 cm$^{-1}$, 98 cm$^{-1}$, 129 cm$^{-1}$, 160 cm$^{-1}$, and 241 cm$^{-1}$ are unassigned and are most likely due to lattice vibrations and hot bands. The peak at 343 cm$^{-1}$ was assigned to the $a_{1g}$ fundamental U-O stretch, as was the peak at 482 cm$^{-1}$. The peak at 412.5 cm$^{-1}$ was assigned to the $e_g$ U-O stretch. The O-U-O-U stretch was assigned to a peak at 729 cm$^{-1}$ and the peak at 804 cm$^{-1}$ was assigned to U-O stretch. The peaks detected in the Raman spectrum of UO$_3$, 61.5 cm$^{-1}$, 113.5 cm$^{-1}$, 142.5 cm$^{-1}$, 248.5 cm$^{-1}$, 295 cm$^{-1}$, 391 cm$^{-1}$, 574.5 cm$^{-1}$, and 841 cm$^{-1}$, are left unassigned as no literature values could be used to compare. The Raman peaks and assignments for all three uranium oxide samples are given in Table 3-14. [54, 107, 108, 109, 110, 111, 112]

![Figure 3-29. FTIR spectrum of uranium dioxide (UO$_2$). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.](image-url)
Figure 3-30. Raman spectrum of uranium dioxide (UO2). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-31. FTIR spectrum of triuranium octaoxide (U3O8). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-32. Raman spectrum of triuranium octaoxide (U3O8). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 3-33. FTIR spectrum of uranium trioxide (UO3). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-34. Raman spectrum of uranium trioxide (UO3). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

<table>
<thead>
<tr>
<th>UO₂ (UO2)</th>
<th>α-UO₃ (UO3)</th>
<th>U₃O₈ (U3O8)</th>
<th>Assignment</th>
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</thead>
<tbody>
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<td>438</td>
<td></td>
<td></td>
<td>T₁u TO</td>
</tr>
<tr>
<td>457</td>
<td></td>
<td></td>
<td>e₄ U-O stretch</td>
</tr>
<tr>
<td>498</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>502</td>
<td></td>
<td></td>
<td>T₃u LO</td>
</tr>
<tr>
<td>539.5</td>
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<td>E₄ U-O stretch</td>
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<tr>
<td>541</td>
<td></td>
<td></td>
<td>e₉ U-O stretch</td>
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<td>combination</td>
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<td></td>
<td>A₂u U-O stretch</td>
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<tr>
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<td></td>
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</tr>
<tr>
<td>777</td>
<td></td>
<td></td>
<td>U-O chain stretch</td>
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<tr>
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<td></td>
<td>combination</td>
</tr>
<tr>
<td>3440</td>
<td>3439</td>
<td></td>
<td>H₂O stretch</td>
</tr>
</tbody>
</table>

Table 3-13. FTIR peaks (cm⁻¹) and assignments for uranium oxide (UO₂, UO₃, U₃O₈).
<table>
<thead>
<tr>
<th>UO₂ (UO₂)</th>
<th>α-UO₃ (UO₃)</th>
<th>U₃O₈ (U₃O₈)</th>
<th>Assignment</th>
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<tbody>
<tr>
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Table 3-14. Raman peaks (cm⁻¹) and assignments for uranium oxide (UO₂, UO₃, U₃O₈).

Uranium Tetrafluoride (UF₄)

The FTIR and Raman spectra of uranium tetrafluoride (UF₄) are shown in Figures 3-35 and 3-36, respectively. Much like the FTIR spectrum of UO₂, few peaks are observed assignable to the uranium compound. Most of the peaks belong to polystyrene. The broad peak at 427 cm⁻¹ was assigned as a U-Fₑq stretch with a shoulder at 612 cm⁻¹ assigned as a combination band of vibrations lower in wavenumber than measured here. The rest of the peaks are assumed to belong to either polystyrene or H₂O absorbed by the KBr. The FTIR peaks and assignments are given in Table 3-15. [113, 114, 115, 116, 117]. The Raman spectrum of UF₄ is of poor quality and the peaks observed (264 cm⁻¹, 914 cm⁻¹, and
1,315 cm\textsuperscript{-1}) do not match any literature values. It is possible that the peak at 914 cm\textsuperscript{-1} could belong to a uranyl stretching mode, indicating oxidation of the tetravalent uranium to a hexavalent uranyl species. The Raman peaks and assignments are given in Table 3-16. [113, 114, 118, 119]

Figure 3-35. FTIR spectrum of uranium tetrafluoride (UF\textsubscript{4}). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 3-36. Raman spectrum of uranium tetrafluoride (UF4). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

<table>
<thead>
<tr>
<th>UF₄ (UF4)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>427</td>
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</tr>
<tr>
<td>612</td>
<td>Combination</td>
</tr>
<tr>
<td>699</td>
<td>polystyrene</td>
</tr>
<tr>
<td>758.5</td>
<td>polystyrene</td>
</tr>
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Table 3-15. FTIR peaks (cm⁻¹) and assignments for uranium tetrafluoride (UF4).

<table>
<thead>
<tr>
<th>UF₄ (UF4)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td></td>
</tr>
<tr>
<td>914</td>
<td>uranyl stretch?</td>
</tr>
<tr>
<td>1315</td>
<td></td>
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</table>

Table 3-16. Raman peaks (cm⁻¹) and assignments for uranium tetrafluoride (UF4).
Vibrational spectroscopy, namely FTIR and Raman can be of great use in analyzing and identifying uranium containing compounds. The ubiquitous uranyl moiety is extremely useful in the analysis of uranium compounds using vibration spectroscopic techniques. As discussed above, the uranyl ion has three fundamental modes. The fundamental symmetric and asymmetric stretches are easily detected in Raman and FTIR spectra, respectively. The lack of these stretches in the spectrum of a uranium compound can be indicative of the lack of a uranyl structure, and possibly uranium being present in an oxidation state other than the hexavalent state. This could suggest a tetravalent compound, such as uranium dioxide or uranium tetrafluoride, or a mixed valent state species such as triuranium octaoxide.

The presence of the $\nu_1$ uranyl symmetric stretch in the FTIR spectrum or the $\nu_3$ uranyl asymmetric stretch in the Raman spectrum indicates the lowering of the symmetry of the molecule, as seen in UF, US2, AUS, USA, SDU, and UO3 above. When the uranyl containing molecule is lowered to $C_{\infty v}$, $C_{2v}$, or lower both fundamental stretching modes are active in IR and Raman. This lowering of symmetry can be caused by a distortion in the linearity of the uranyl moiety or an asymmetry in the ligation in the equatorial plane. The lowering of symmetry also leads to the splitting of the degenerate $\nu_2$ uranyl bending vibration, as seen in US2 and AUS above. This detection of the lowering of symmetry can help in the identification of an unknown species.

In a similar way, the detection of multiple vibrations assigned to the fundamental vibrations can indicate uranyl moieties in slightly different environments. This can be caused by having different uranyl species within the same sample. This was observed in samples UN, UF, UP, ADU3, US1, US2, USA, and UO3 above. These samples could have a heterogeneous character to their structure, possibly indicating varying amounts of coordinated water or possibly impurities. Knowing that an unknown sample is heterogeneous or contains multiple uranyl species could be used in identifying the sample.
Due to the effect of ligands in the equatorial plane of the uranyl molecule the frequency of the stretching modes can vary in different uranyl compounds. As discussed above, the stronger the ligand and equatorial bond, the longer the U-O$_{\text{axial}}$ uranyl bond and thus the lower the frequency of the vibration. For the samples above the $\nu_1$ symmetric stretch varies from SDU at 783 cm$^{-1}$ to US2 at 884 cm$^{-1}$ and the $\nu_3$ asymmetric stretch varies from SDU at 851 cm$^{-1}$ to UF at 963 cm$^{-1}$. While the equatorial ligand cannot be determined from just the frequencies of the symmetric and asymmetric stretches, the relationship between the frequencies of the stretches for the unknown with the corresponding frequencies for known samples can aid in the identification of the unknown.

Vibrations belonging to species other than the uranyl moiety are paramount for the identification of a possible unknown compound. Polynuclear ligands will have characteristic vibrations of their own that can be used to determine the ligand coordinated with the uranium or uranyl. In the compounds above, NO$_3^-$, O$_2$-$^2$, CH$_3$COO$^-$, CO$_3^{2-}$, and SO$_4^{2-}$ vibrations are detected by a number of stretches in both the FTIR and Raman spectra. The molecules all correspond to ligands coordinated in the equatorial plane of samples above. The ability to determine the ligand makes the ability to determine the uranium compound easy. It is also possible to determine the presence of impurities in the sample, as was seen above from NO$_3^-$ in many samples above. This will be discussed in detail below.

**Multivariate Analysis**

**FTIR Principal Component Analysis**

A principal component model was built using the FTIR data inputted as a 17 x 29,869 matrix, with the samples as rows and the absorbances as columns. To determine the optimum number of principal
components a Scree plot was made, plotting the principal component number against the eigenvalue of the principal component, shown in Figure 3-37.

Figure 3-37. Scree plot for the FTIR PCA model, showing the principal component number versus the eigenvalue.

The optimum number of PC’s will have a “knee” on the Scree plot, where the value of the eigenvalue makes a sudden jump when going from right to left. This was observed at the third principal component. A PRESS (Predictive Residual Error Sum of Squares) plot was also constructed showing the RMSECV for each additional PC, shown in Figure 3-38.
The optimum number of PC’s was determined from the RMSECV, by determining the number with the lowest RMSECV. From Figures 3-37 and 3-38, it was apparent that 3 principal components are optimum for describing the variation in the FTIR spectra.

A model was then built using 3 principal components describing 74.68 % of the variation in the FTIR spectra. The scores, which show the relationship between samples, for all three PC’s are shown in Figure 3-39. The first principal component accounted for 48.35 % of the variation and the scores on PC1 ranged from 7.5970 for US1 to 29.9268 for ADU2, as seen on the top of Figure 3-39. The second principal component accounted for 14.73 % of the variation and the scores ranged from -10.3913 for UP to 22.9171 for U3O8, as seen in the middle of Figure 3-39. The third principal component accounted for
11.60% of the variation and ranged from -10.1738 for ADU2 to 25.3689 for US2, as seen in the bottom of Figure 3-39.

The loadings of the model show how the wavenumbers relate to each other. The loadings on PC1 are plotted in Figure 3-40. From this plot the relationship between PC1 and wavenumber can be determined. It is apparent that PC1 correlates strongly in the ~900 cm\(^{-1}\) - ~950 cm\(^{-1}\) region which is where the asymmetric uranyl stretch is found. The region corresponding to the H\(_2\)O stretch at ~3,470 cm\(^{-1}\) also correlates positively with PC1, as does the regions corresponding to the H\(_2\)O bend at ~1,620 cm\(^{-1}\), the NH\(_4^+\) bend at ~1,400 cm\(^{-1}\), and the region at ~490 cm\(^{-1}\) where many U-ligand\(_{eq}\) vibrations are found. Regions associated with the polystyrene contaminant also correlate positively with PC1.

Figure 3-39. Scores for each of the three PC’s for each of the 17 samples for the FTIR model. The dotted line represents the 95% confidence level.
The loadings on PC2 are shown in Figure 3-41. From Figure 3-41, it is apparent that PC2 correlates positively with broad stretch located at ~500 cm\(^{-1}\) and ~750 cm\(^{-1}\), where most of the peaks in the spectra of UO\(_2\), UO\(_3\), U\(_3\)O\(_8\), and UF\(_4\) are located. This suggests, that the samples which do not display the traditional uranyl moiety will correlate with PC2 strongly. PC2 correlates negatively with peaks ~925 cm\(^{-1}\), ~1,079 cm\(^{-1}\), ~1,400 cm\(^{-1}\), ~1,621 cm\(^{-1}\), ~3,123 cm\(^{-1}\), and 3,474 cm\(^{-1}\), regions which correspond to the uranyl asymmetric peak, peaks associated with molecules coordinated to the uranyl ion, or water.
The loadings on PC3 are shown in Figure 3-42. It is apparent that positive correlation with PC3 is found at ~597 cm\(^{-1}\), ~1,078 cm\(^{-1}\), and ~1,236 cm\(^{-1}\), all regions which correspond to vibrations from SO\(_4^{2-}\) ligands. This indicates that PC3 correlates with the samples US1, US2, AUS, and USA, which all contain the SO\(_4^{2-}\) ligands. PC3 also correlates negatively with the region ~905 cm\(^{-1}\), corresponding to asymmetric uranyl stretches.

Figure 3-43 shows the variance captured by the model in each wavenumber. This plot shows that the model captures from ~10 % to ~95 % of the variance in all of wavenumbers, and how that variance is captured by each PC. It is apparent that PC1 captures the majority of the variance at ~2,000 cm\(^{-1}\) and above, as well as much of the variance in the region from ~1,300 cm\(^{-1}\) to 1,500 cm\(^{-1}\). PC2 greatly increases the variance captured at ~500 cm\(^{-1}\) and ~700 cm\(^{-1}\), while PC3 increases the variance captured
at ~1,000 cm\(^{-1}\) to ~1,500 cm\(^{-1}\), and at ~1,770 cm\(^{-1}\). This observation reinforces the assumption that PC2 captures the variation in the samples UO2, UO3, U3O8, and UF4, and that PC3 captures the variation in the sulfate containing samples, US1, US2, AUS, and USA.

Figure 3-42. Loadings plot for PC3 for the FTIR model, showing how PC3 varies with wavenumber.
The 3 PC model for the FTIR data captures 74.68% of the variance between the different spectra. As not all of variance is captured by the model, the Q residuals, a lack of fit statistic, can be determined to see which, if any, samples are not fit well by the model. A plot of the Q residuals is shown in Figure 3-44.
It is apparent that the model fits the sample UN the worst. The contributions to the Q residual are plotted in Figure 3-45, showing what part of the UN spectrum are not fit by the PCA model. The model does not fit sample UN well for four main regions, the N=O double bond stretch at 1,532 cm\(^{-1}\), the \(\text{NO}_3^-\) stretch at 1,276 cm\(^{-1}\), the uranyl asymmetric stretch at 952 cm\(^{-1}\), and the region from ~800 cm\(^{-1}\) to ~900 cm\(^{-1}\). These regions coincide with the regions of Figure 3-43 that have variance that are not captured at all by the 3 component model, indicating that the addition of more principal components to the model would fit the sample UN better. This is not necessarily surprising as the sample UN is the only one that has \(\text{NO}_3^-\) as a ligand and, with the exception of the 1,384 cm\(^{-1}\) peak seen in many samples, \(\text{NO}_3^-\) peaks are not and should not be observed in other samples.
Figure 3-46 shows the scores on PC1 against the scores on PC2. The biggest observation is that samples forming two groups, one with a positive PC2 score containing samples U3O8, UO2, UF4, UO3, and SDU, and the other group with a negative PC2 score containing samples AUC, UN, US1, UF, ADU1, AUS, USA, UA, UP, US2, ADU2, and ADU3. This grouping is not unexpected as PC2 correlates with regions of the FTIR spectra that contain peaks belonging to the oxides and oxide-like samples (UF4, SDU). A plot of all three PC’s is shown in Figure 3-47. This plot shows the grouping of the five oxides and oxide like samples, like in Figure 3-46. It also shows the sulfate containing US2, USA, and US1 having large scores on PC3 and grouping together. The samples ADU2 and ADU3 are shown tightly grouped, samples UP, UA, and ADU1 not far away.

Figure 3-45. Q residual contributions for the sample UN for the FTIR model.
The samples have also been grouped using a Hierarchical Clustering Analysis (HCA) method. Hierarchical clustering forms a hierarchy of clusters based on the distance between them. Each sample starts as its own cluster and at each step in the process, a cluster is formed by minimizing the total within-cluster variance. The result is a weighted squared distance between cluster centers. The input data for the HCA method was the PCA scores from the 3 PC model developed. The clustering analysis is shown as a dendrogram in Figure 3-48.
Figure 3-47. Three dimensional plot of the Scores on PC1 (perpendicular to the page) versus Scores on PC2 (horizontal on the page) versus Scores on PC3 (vertical on the page) for the FTIR model. The dashed lines represent the zero lines.
From the dendrogram shown in Figure 3-48, there are four clusters formed. A cluster containing the oxides and oxide-like samples (U3O8, UO3, UO2, UF4, SDU), a cluster containing some of the sulfate containing compounds (US2, USA, US1), a cluster containing AUS, UF, UN, AUC, and a cluster containing ADU3, ADU2, UP, UA, ADU1. This clustering of the data is fairly apparent when examining the three dimensional scores plot in Figure 3-45.

**Raman Principal Component Analysis**

Building the principal component model for the Raman spectra began by combining the data taken with the Smart Raman spectrometer (100 cm\(^{-1}\) - 3,405 cm\(^{-1}\), 6,857 data points) and the data taken with the µRaman spectrometer (50 cm\(^{-1}\) - 3,400 cm\(^{-1}\), 1,738 data points). The resulting 17 x 1,740 matrix was further truncated to a 17 x 1,714 matrix, excluding the UO2, U3O8, UO3, UF4 data from 50 cm\(^{-1}\) –
100 cm$^{-1}$. The same as for the FTIR model, the number of principal components was determined from the Scree plot and the PRESS plot, shown in Figures 3-49 and 3-50, respectively. In the Scree plot, there is not an obvious “knee” in the data. In the PRESS plot, the low value for the RMSECV is at 1 principal component. Neither processes for determining the optimum number of give way to an obvious number of principal components. Three components capture 76.67 % of the variation and are the same number of PC’s chosen for the FTIR model. For those reasons, a 3 PC model was built for the Raman data.

Figure 3-49. Scree plot for the Raman PCA model, showing how the eigenvalue changes with the principal component number.
The scores, showing the variation in the samples, for all three components are shown in Figure 3-51. The first component accounted for 47.78 % of the variation ranging from 0.5234 for UA to 7.6539 for UF4, seen at the top of Figure 3-51. The second component accounted for 19.13 % of the variation ranging from -4.6824 for UF4 to 4.7052 for ADU2, seen in the middle of Figure 3-51. The third component accounted for 9.76 % of the variation ranging from -4.0453 for UO2 to 4.2113 for UF4, seen in the bottom of Figure 3-51.
Figure 3-51. Scores for each of the three PC’s for each of the 17 samples for the Raman PCA model. The dotted line represents the 95% confidence level.

The loadings on PC1 are shown in Figure 3-52, showing the relationship between PC1 and wavenumber. PC1 correlates strongly in the ~750 cm\(^{-1}\) to ~900 cm\(^{-1}\), corresponding to the region where the symmetric uranyl stretch occurs. The region from ~100 cm\(^{-1}\) to 600 cm\(^{-1}\) also correlates with PC1. This region corresponds to many U-ligand vibrations, as well as, the uranyl bending vibration. The peaks ~1,045 cm\(^{-1}\) corresponding to NO\(_3^-\) or SO\(_4^{2-}\) stretches also correlates with PC1. PC1 also correlates with the region where the fluorescence from the glass vials occurs, ~1,435 cm\(^{-1}\).

The loadings on PC2 are shown in Figure 3-53, showing the relationship between PC2 and wavenumber. The region corresponding to the symmetric uranyl stretch, ~750 cm\(^{-1}\) to ~900 cm\(^{-1}\), correlates strongly with PC2, as well as, PC1, as does the peaks at ~1,045 cm\(^{-1}\). The peak ~914 cm\(^{-1}\), corresponding to uranyl asymmetric stretches negatively correlates with PC2. PC2 correlates negative with much of the
structure below ~650 cm\(^{-1}\), including the peak at 224 cm\(^{-1}\) corresponding to uranyl bends or U-ligand\(_{eq}\) vibrations.

Figure 3-52. Loadings plot for PC1 for the Raman model, showing variation with wavenumber.
The loadings on PC3 are in Figure 3-54, showing the relationship between PC3 and wavenumber. PC3 correlates positively with the region from ~150 cm\(^{-1}\) to ~350 cm\(^{-1}\), and the peaks at 866 cm\(^{-1}\) and 914 cm\(^{-1}\). The region from ~350 cm\(^{-1}\) to ~700 cm\(^{-1}\) correlates negatively with PC3, as does the glass luminescence region ~1,500 cm\(^{-1}\). PC3 tends to correlate strongly with the four samples measured with the μRaman spectrometer, UO2, U3O8, UO3, and UF4.
Figure 3-54. Loadings plot for PC3, showing how PC3 varies with wavenumber.

The variance captured by the model in each wavenumber is shown in Figure 3-55, showing that the model captures from ~5% to ~95% of the variance in all of the wavenumbers, and how that variance is captured by each PC. It is evident that PC1 captures much of the variance across the whole range. PC2 increases the variance captured by 10-15% across the range. PC3 increases the variance captured at less than 500 cm⁻¹ and the range from ~1,200 cm⁻¹ to ~1,700 cm⁻¹, as well as peaks at ~900 cm⁻¹ and ~1,150 cm⁻¹. This reinforces the assumption that PC3 correlates with variation associated with the samples UO2, UO3, U3O8, and UF4.

The Q residuals, plotted in Figure 3-56, are determined to see how the model fits for all the samples, and whether or not a sample is poorly fit by the model. It is apparent that the sample UO3 is not fit well by the model, having a reduced Q residual greater than one. The contributions to the Q residual of UO3
are plotted in Figure 3-57, showing the regions of the UO3 spectrum not fit well. The model does not fit well for the stretch at \(~575\,\text{cm}^{-1}\), at \(~400\,\text{cm}^{-1}\) to \(~500\,\text{cm}^{-1}\), and the region at \(~100\,\text{cm}^{-1}\) to \(~200\,\text{cm}^{-1}\).

The sample UO3 has an unusual Raman spectrum, as it contains possible uranyl like stretches, \(~800\,\text{cm}^{-1}\) in addition to the more oxide like stretches below \(600\,\text{cm}^{-1}\). The strongest peak in the spectrum at \(~575\,\text{cm}^{-1}\), is not fit well by the model.

![Figure 3-55. Variance captured at each wavenumber for the Raman model.](image)
Figure 3-56. Q residuals for the 3 PC model of Raman Data.

Figure 3-57. Q residual contributions for the sample UO3 for the Raman model.
Figure 3-58 shows the scores on PC1 against PC2. The biggest features are the spokes sticking out from the main group. The samples ADU1 and ADU2 stick out towards the upper right, indicating high correlation with PC1 and PC2. The samples U3O8, UO3, UO2, and UF4 stick out to the lower right, indicating high correlation with PC1 and low correlation with PC2. The remaining samples are grouped towards the right of the origin, with an inner grouping of UF, USA, UN, and US2, and samples AUC, UP, UA, AUS, and ADU3 grouped to the upper right of the inner group.

An expansion of Figure 3-58, including PC3 in the z-direction is shown in Figure 3-59. This plot show sample UF4 as an outlier, with the oxide samples grouped below with negative PC3 scores and UF4 having the highest positive PC3 score. The other samples are grouped very similarly as they were comparing PC1 and PC2, as they all have scores on PC3 close to zero.
Figure 3-58. Scores on PC2 vs Scores on PC1 for the Raman model. The dotted oval is a 95% confidence interval.
Figure 3-59. Three dimensional plot of the Scores on PC1 (into the page) versus Scores on PC2 (horizontal on the page) versus Scores on PC3 (vertical on the page) for the Raman model. The dashed lines represent the zero lines.

The samples have also been grouped using a HCA model, analogous to the FTIR samples. The dendrogram for the Raman samples is shown in Figure 3-60. From the dendrogram, there are four clusters formed. The sample UF4 is in a cluster by itself. The oxides are clustered together and samples
ADU1 and ADU2 are clustered together. The remaining samples are in a cluster together, having a smaller cluster comprised of US1, US2, USA, UN, and UF, and the other comprised of SDU, UA, AUS, ADU3, UP, and AUC.

Figure 3-60. Dendrogram showing the clustering of samples resulting from PCA of Raman spectra.

Conclusions

Vibrational spectroscopy, consisting of FTIR and Raman spectrosopies, was performed on the set of 17 uranium compounds. The spectra were analyzed, assigning peaks to vibrations of the uranyl moiety, coordinated molecules, vibrations between the uranium and ligand, water, or polystyrene contaminants. The uranyl stretches prove a useful signature for detecting uranium compounds.
containing the uranyl moiety. The uranyl stretches are shown to vary in position due to the
coordination of ligands in the equatorial plane.

Multivariate analysis has been applied to both the FTIR and the Raman data sets. Principal component
models for each data set were built, consisting of three principal components each. Loading plots were
used to explain the position of samples in the score plots. A three dimensional score plot was used to
compare the samples and hierarchical cluster analysis was applied to the PCA scores to create clusters of
similar samples. The FTIR spectra were grouped into four clusters: a) U3O8, UO3, UO2, UF4, and SDU b)
US2, USA, US1 c) AUS, UF, UN, AUC d) ADU3, ADU2, UP, UA, ADU1. The Raman spectra was also
grouped into four clusters: a) UF4 b) U3O8, UO2, UO3 c) US1, US2, USA, UN, UF, SDU, UA, AUS, ADU3,
UP, AUC d) ADU2, ADU1. The multivariate analysis showed that the samples could be clustered into
groups with similar spectra, and hence, similar structure and chemical composition. The application of
principal component analysis to the vibrational spectra is useful for giving an objective and quantitative
measure for the differences and similarities in the spectra. Acquiring spectra of more uranium
compounds and adding to the model would increase the robustness of the model. The constructed
model could be used to determine if the spectrum of an unknown is similar to one of the compounds
here.
Chapter 4. Nitrate Chemical Signatures

Abstract

Signatures arising from the chemical processing of uranium compounds, process signatures, can be of great utility to nuclear forensics. The signatures may be indicative of precipitation, mixing, calcination, firing, or other physical manipulations. The pregnant liquor solution from which the uranium is precipitated from can impart impurities to the uranium compound, impurities which may be detected using spectroscopic methods. Nitrate impurities have been detected in the FTIR and Raman spectra of six uranium compounds discussed above, in six ammonium diuranate samples discussed here, and in four uranium oxide samples derived by calcination of the ammonium diuranate samples. The ammonium diuranate samples were all precipitated from nitric acid solutions. Laser Induced Breakdown Spectroscopy also showed nitrogen emission peaks. The ammonium diuranate and uranium oxide samples discussed here were used a test set for the PCA models described in Chapter 3. The test samples were used to determine the ability of the PCA models to determine the composition of uranium samples.

Introduction

After uranium has been mined and extracted from the ore, it goes through a series of concentration and purification steps. The uranium is precipitated from solution to form a uranium compound known historically as yellowcake, or uranium ore concentrate. The chemical species of the uranium ore concentrate depends on the nature of precipitant used. Uranium ore concentrates can range in composition from ammonium diuranate to uranyl peroxide. The precipitant used can lead to impurities and signatures of the processing of the uranium compound. These impurities and process signatures have been examined by many researchers and some results are discussed below. We are concerned here with signatures that can arise due to the solution from which the uranium is precipitated, the
pregnant liquor solution. These signatures can be anionic molecules such as nitrates, sulfates, or carbonates from the acidic or alkaline dissolution of the uranium ore or from the eluting from ion exchange columns. Ions such as nitrates, sulfates, and carbonates all exhibit characteristic vibrations in both the IR and Raman spectra.

Previous research of process signatures was performed using ion chromatography to measure anionic impurities in industrial uranium ore concentrates. Badaut and Keegan used an aqueous leaching technique to extract and measure fluorine, chlorine, bromine, nitrate, phosphate, and sulfate anion impurities. [141, 142] Plaue and Klunder used near infrared reflectance spectroscopy to measure industrial uranium ore concentrates. They observed common O-H and N-H combination and overtone bands, arising from the use of ammonia or hydroxide based precipitants. [143, 144] Spectral features associated with U₃O₈, magnesia, and sodium hydroxide were also observed. Varga used FTIR to analyze industrial uranium ore concentrates including ammonium uranate, uranyl hydroxides, sodium uranates, uranyl peroxides, and uranium oxides. In addition to assign many absorption bands, stretches belonging to nitrate, sulfate, and carbonate anionic impurities were observed. [77] Ho Mer Lin used Raman spectroscopy to analyze both industrial uranium ore concentrates and laboratory synthesized comparison samples. Anionic impurities such as nitrate, sulfate, and carbonate were observed and spectra were compared to Raman spectrum of pure chemicals for analysis. [80]

**Experimental**

A set of new ammonium diuranate samples were synthesized. Uranyl peroxide hydrate was dissolved in concentrated nitric acid and diluted to a nitric acid concentration of 8 M and a uranium concentration of 50 mg/mL. From this solution three aliquots were taken for precipitation. A peristaltic pump (Masterflex L/S with an Easy Load II head) was used to control the rate of ammonium hydroxide (20-
22 %) at 5 mL/min. Three different precipitations were performed with the stir rate of the pregnant liquor solution held at three different rates: 170 rpm, 280 rpm, and 400 rpm. The stir rates were taken from the stir plate (Corning PC-420D) and were not calibrated. The ammonium hydroxide was added until a pH of 8 was reached, at which point the solution was stirred for another 15 minutes. The precipitate was separated using vacuum filtration and washed with water. The precipitate was left on the filter funnel with vacuum applied overnight. At this point a portion of each sample was set aside as the “wet” sample for analysis. The remaining portion of each sample was dried overnight at 100 °C. Another fraction of the sample was set aside at this point as the “dry” sample for analysis. The rest of the ADU precipitate was fired in a tube furnace at 500 °C for 8 hours under H₂ gas for conversion to UO₂. After 8 hours the powder was removed from the furnace, stirred, and placed back in the furnace for another 8 hours at 500 °C under H₂ gas. The samples are referred to as the compound, either ADU or UO₂, the stir rate of precipitation, 170 rpm, 280 rpm, or 400 rpm, and then for the ADU “W” for wet and “D” for dry. The ADU samples are shown in Figure 4-1 and the oxide samples in Figure 4-2.
The powder of the precipitate at each stage, wet, dry, and oxide, were analyzed with p-XRD, FTIR, and Raman spectroscopy for the ADU samples. The Raman measurements were taken on the DXR Smart Raman, with a spectral range of 4,000 cm\(^{-1}\) to 400 cm\(^{-1}\) using a laser wavelength of 532 nm and a laser
power of 5mW. Sixteen 4 second exposures were averaged together for each spectrum. The FTIR measurements were taken by grinding 1% analyte into approximately 400 mg of KBr. The samples were not mixed with the Wig-L-Bug, as before, to minimize polystyrene impurities in the spectrum. The Raman and FTIR spectra were preprocessed, as before, by smoothing, baseline subtracting, and normalizing.

**Results**

The FTIR spectra for samples ADU170D, ADU170W, ADU280D, ADU280W, ADU400D, and ADU400W are shown in Figures 4-3, 4-4, 4-5, 4-6, 4-7, and 4-8, respectively. The FTIR spectra of the newly synthesized ADU samples are very similar to the original ADU samples (Figures 3-13, 3-15, 3-17), albeit without peak attributable to polystyrene from the Wig-L-Bug. The new ADU samples all exhibit a stretch at about 465 cm\(^{-1}\) attributable to U-N or U-O vibrations in the equatorial plane. The weak stretches seen in ADU170D and ADU400D at about 775 cm\(^{-1}\) could be assigned to vibrations from nitrate impurities or U-OH vibrations. The peak seen around 830 cm\(^{-1}\) corresponds to the uranyl symmetric stretch. The large broad peak around 905 cm\(^{-1}\) to 920 cm\(^{-1}\) is their asymmetric uranyl stretch. The lower intensity peak at about 980 cm\(^{-1}\) could be assigned as an asymmetric uranyl stretch indicating uranyl moieties in differing environments. The two peaks seen at ~1,318 cm\(^{-1}\) and 1,345 cm\(^{-1}\) in the ADU170D and ADU400D are most likely N-H stretches in the ammonium. The sharp peak at 1,384 cm\(^{-1}\) belongs to the nitrate impurity. A broader peak just above the nitrate peak at about 1,402 cm\(^{-1}\) is the ammonium bend. A splitting in this peak for ADU170D and ADU400D further strengthens the assumption of multiple environments in the sample. The water bending mode is observed at 1,628 cm\(^{-1}\). A broad N-H stretch is observed around 3,150 cm\(^{-1}\) to 3,230 cm\(^{-1}\) and a broad water stretch around 3,550 cm\(^{-1}\)
Figure 4-3. FTIR spectrum of ammonium diuranate precipitated at 170 rpm and dried at 100 °C overnight (ADU170D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-4. FTIR spectrum of ammonium diuranate precipitated at 170 rpm before drying (ADU170W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 4-5. FTIR spectrum of ammonium diuranate precipitated at 280 rpm and dried at 100 °C overnight (ADU280D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-6. FTIR spectrum of ammonium diuranate precipitated at 280 rpm before drying (ADU280W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 4-7. FTIR spectrum of ammonium diuranate precipitated at 400 rpm and dried at 100 °C overnight (ADU400D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-8. FTIR spectrum of ammonium diuranate precipitated at 400 rpm before drying (ADU400W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
The Raman spectra of ADU170D, ADU170W, ADU280D, ADU280W, ADU400D, and ADU400W are shown in Figures 4-9, 4-10, 4-11, 4-12, 4-13, and 4-14, respectively. The first thing to note in the Raman spectra is the presence of luminescence bands in many of the spectra. The use of a 532 nm laser is more likely to cause photoluminescence in uranyl compounds, compared to a 780 nm laser. The Raman spectra are, again, very similar to the first ADU samples characterized (Figures 3-14, 3-16, 3-18). The samples show a peak at approximately 460 cm\(^{-1}\), corresponding to U-O equatorial vibration, as does a peak at about 555 cm\(^{-1}\). The three dry samples show peaks at about 730 cm\(^{-1}\) and 760 cm\(^{-1}\), which most likely belong to a U-OH bend and nitrate rocking, respectively. These peaks are probably obscured by luminescence in the wet samples. The large peak around 830 cm\(^{-1}\) corresponds to the uranyl symmetric stretch. The nitrate impurity shows from a peak at about 1050 cm\(^{-1}\).
Figure 4-9. Raman spectrum of ammonium diuranate precipitated at 170 rpm and dried at 100 °C overnight (ADU170D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-10. Raman spectrum of ammonium diuranate precipitated at 170 rpm before drying (ADU170W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 4-11. Raman spectrum of ammonium diuranate precipitated at 280 rpm and dried at 100 °C overnight (ADU280D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-12. Raman spectrum of ammonium diuranate precipitated at 280 rpm before drying (ADU280W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 4-13. Raman spectrum of ammonium diuranate precipitated at 400 rpm and dried at 100 °C overnight (ADU400D). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-14. Raman spectrum of ammonium diuranate precipitated at 400 rpm before drying (ADU400W). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Four UO2 samples were analyzed by FTIR, one for each of the ADU samples fired for the full 16 hours and the fourth from the 400 rpm ADU sample fired for only 8 hours, labeled as UO2400h for the 8 hours and UO2400F for the 16 hours. The spectra are shown in Figures 4-15, 4-16, 4-17, and 4-18 for UO2170, UO2280, UO2400F, and UO2400H, respectively. The FTIR for the three samples fired for the full 16 hours, UO2170, UO2280, and UO2400F, show a much closer resemblance to U3O8 than UO2, as discussed above. They show peaks at about 430 cm⁻¹, about 494 cm⁻¹, about 525 cm⁻¹, and about 740 cm⁻¹, similarly to the U3O8 peaks at 457 cm⁻¹, 498 cm⁻¹, 541 cm⁻¹, and 743 cm⁻¹ above. The sample fired for only 8 hours, UO2400H, shows much more resemblance to the UO2, discussed above. This sample shows peaks at 425 cm⁻¹, 530 cm⁻¹, and 903 cm⁻¹. All four of the uranium oxide samples here, show the water bending vibration at about 1,625 cm⁻¹, the water stretch at about 3,439 cm⁻¹, and the nitrate impurity at 1,384 cm⁻¹.
Figure 4-15. FTIR spectrum of uranium dioxide fired from the ammonium diuranate precipitated at 170 rpm and dried at 100 °C overnight (UO2170). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-16. FTIR spectrum of uranium dioxide fired from the ammonium diuranate precipitated at 280 rpm and dried at 100 °C overnight (UO2280). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
Figure 4-17. FTIR spectrum of uranium dioxide fired for 16 hours from the ammonium diuranate precipitated at 400 rpm and dried at 100 °C overnight (UO2280F). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.

Figure 4-18. FTIR spectrum of uranium dioxide fired for only 8 hours from the ammonium diuranate precipitated at 400 rpm and dried at 100 °C overnight (UO2400H). The black trace is the raw spectrum. The blue trace is the spectrum after smoothing and background subtraction.
The nitrate ion in a KBr matrix exhibits an asymmetric stretching vibration at 1,385 cm\(^{-1}\), in an IR spectrum. [147] In a Raman spectrum the nitrate ion shows the symmetric stretching vibration at about 1,047 cm\(^{-1}\). [148] Both of these nitrate stretches are easily detected in FTIR and Raman, respectively.

The nitrate stretches are detected in all of the FTIR spectra for the second set of ADU compounds and corresponding uranium oxides. The symmetric nitrate stretch is also detected in all of the Raman spectra for this set of ADU samples. The nitrate asymmetric stretch was also detected in many of the uranium compounds discussed in Chapter 3, samples UN, UF, AUC, ADU3, ADU2, and ADU1. The corresponding symmetric stretch was also detected in the Raman spectra of these samples. Shown in Figure 4-19 is a comparison of the FTIR spectra for the six uranium compounds analyzed in Chapter 3, showing the nitrate asymmetric stretch. In Figure 4-20, the six ADU compounds and four uranium oxide compounds synthesized and discussed in this chapter are shown to highlight the nitrate asymmetric stretch. The Raman spectra for the six uranium compound discussed in Chapter 3 are shown in Figure 4-21, highlighting the nitrate symmetric stretch at about 1,045 cm\(^{-1}\). The Raman spectra of the six ammonium diuranate discussed in this chapter are shown in Figure 4-22, highlighting the nitrate symmetric stretch at about 1,045 cm\(^{-1}\). Of the three ADU samples precipitated at varying stir rates, the sample precipitated at the slowest stir rate had the least intense relative nitrate peak, both before and after drying and in both the IR and Raman spectra. The ADU precipitated at the middle stir rate, 280 rpm, had the largest relative nitrate peak, both before and after drying, and in both spectra. The relative intensities of nitrate peaks in the IR spectra of the UO2 samples follow the same trends as the spectra of the respective ADU samples, albeit at a lower intensity.
Figure 4-19. FTIR spectra for the six uranium compounds discussed in Chapter 3, showing the 1,384 cm$^{-1}$ nitrate asymmetric stretch. This figure shows the smoothed and background subtracted spectra.

Figure 4-20. FTIR spectra for the ten uranium compounds discussed in this chapter, showing the 1,384 cm$^{-1}$ nitrate asymmetric stretch. This figure shows the smoothed and background subtracted spectra.
Figure 4-21. Raman spectra for the six uranium compounds discussed in Chapter 3, showing the 1,045 cm$^{-1}$ nitrate symmetric stretch. This figure shows the smoothed and background subtracted spectra.

Figure 4-22. Raman spectra for the six ammonium diuranate compounds discussed in this chapter, showing the 1,045 cm$^{-1}$ nitrate symmetric stretch. This figure shows the smoothed and background subtracted spectra.
The six samples discussed in Chapter 3 and the six ADU samples discussed here were all precipitated from concentrated nitric acid solutions. During the precipitation, nitrate ions were incorporated into the agglomerate of the precipitating uranium compound. These nitrate ions persisted within the uranium compound after washing with water and again after drying the compounds at 100 °C. Even more so, the nitrate ions were detected in the uranium oxide samples fired from the ammonium diuranate samples. The ammonium diuranate samples were fired for a total of 16 hours at 500 °C under a reducing H₂ gas. Concentrated nitric acid boils at a relatively low 121 °C and would be expected to volatilize off during the firing of the uranium oxides. The presence of nitrates in the uranium compounds and the secondary uranium oxides fired from the uranium compounds could prove to be an effective process signature of liquor solution used.

The sample UF is the only sample, either from Chapter 3 or discussed here, that has nitrate vibrations in its vibrational spectrum but does not contain nitrogen in its chemical form. Laser Induced Breakdown Spectroscopy, as discussed in Chapter 5, can detect nitrogen but is unable to differentiate between nitrogen present as ammonia and nitrogen present as nitrate. The LIBS spectrum of sample UF shows nitrogen emission lines at 818.8 nm and 822.3 nm, as shown in Figure 4-23, supporting the detection of nitrate impurities form the FTIR and Raman spectra (Figures 3-5 and 3-6, respectively).
Figure 4-23. Nitrogen emission lines in LIBS spectra of sample UF. The different colors show the four different replicates taken for the sample.

**Application of PCA models**

The Principal Component models built in Chapter 3 using the FTIR and Raman spectra from the set of 17 uranium compounds have been applied to the FTIR and Raman spectra acquired here from 6 ammonium diuranate samples and 4 uranium oxide samples. The ammonium diuranate and uranium oxide samples synthesized here are used as a test set of samples, showing how the PCA models work for other samples of known composition. Shown in Figure 4-24 is the Q residuals for the FTIR model, including the test set of samples. The test set of samples are labeled as ADU1 [D or W], ADU2 [D or W], ADU3 [D or W] on the figures for aesthetic reasons, but correspond to samples ADU170 [D or W], ADU280 [D or W], and ADU400 [D or W], respectively, for both the FTIR and Raman PCA models.
Figure 4-24. Q residuals of FTIR PCA model, including the test set of 10 samples. The original set of samples are shown in gray and the test set in red.

From this figure it is apparent that samples ADU170D and UO2400H, from the test set are not well fit by the PCA model, having reduced Q residuals greater than one. Observation of the Q residual contributions, shown in Figure 4-25 for ADU170D and Figure 4-26 for UO2400H, reveal the spectral regions of each sample that are not well fit. It is clear that the peak at 465 cm\(^{-1}\) and the group of peaks in the region 1,300 cm\(^{-1}\) to 1,400 cm\(^{-1}\) are not modeled well. The absence of strong water stretches and polystyrene impurity peaks are also contributing to the poor fit. The water stretches have a lower relative intensity due to drying the samples at 100 °C overnight. The model was built with samples that were milled with a Wig-L-Bug and thus have polystyrene impurities. The test set of samples were all ground with mortar and pestle and do not have polystyrene impurities, further contributing to the Q residuals. The Q residual contributions for UO2400H arise from the large water stretch and U-O stretch at about 500 cm\(^{-1}\). The relatively large water stretch is due to the normalizing of the spectra from the
strongest absorption, in this case the water stretch. Again, the lack of polystyrene contaminants contributes to the Q residuals.

Figure 4-25. Contributions to the Q Residual for sample ADU170D for the FTIR PCA model.
The three dimensional plot of the three principal components for the FTIR model is shown in Figure 4-27, analogous to Figure 3-47, with the 10 samples of the test set. It is clear that the three uranium oxide samples fired for 16 hours group consistently with the original uranium oxide samples. The uranium oxide sample fired for only 8 hours, on the other hand, groups closer to the original samples ADU1, ADU2, ADU3, UA, and UP as well as the samples ADU170D, ADU170W, and ADU400D from the test set. The remaining ammonium diuranate test samples, ADU280D, ADU280W, and ADU400W, are grouped with samples UN, UF, AUC. This grouping is presumed to be caused by the relatively strong intensity of the peak attributable to the nitrate impurity.
Figure 4-27. Three dimensional plot of the Scores on PC1 (perpendicular to the page) versus Scores on PC2 (horizontal on the page) versus Scores on PC3 (vertical on the page) for the FTIR model. The dashed lines represent the zero lines. The original set of samples are shown in gray and the test set in red.

The Q residuals for the Raman PCA model are shown in Figure 4-28. This figure indicates that the six samples in the test set are all fit well by the Raman PCA model. Analogously to Figure 3-59, the three principal components of the Raman PCA model are show in Figure 4-29, with the inclusion of the test set of samples.
From Figure 4-29, it is clear that the six ammonium diuranate samples of the test set group off similarly to the samples ADU1 and ADU2 from the original set of samples, although with a lower score on PC3.

The more negative score on PC3 is most likely due to the Raman peaks between 400 cm\(^{-1}\) and 600 cm\(^{-1}\), which trend negatively with PC3.
Conclusions

Ammonium diuranate samples were precipitated at three different stir rates and fired to uranium dioxide, after drying. Vibrational spectroscopy was used at each step to determine composition and detect impurities. The spectra showed evidence of a nitrate impurity indicative of the nitrate nature of the pregnant liquor solution. The nitrate impurity persisted in the ammonium diuranate compounds after drying at 100 °C and was even present in uranium oxide samples fired at 500 °C for a total of 16
hours. Nitrate impurities were also detected in six compounds discussed in a previous chapter, also precipitated from a nitrate solution. The sample UF also exhibits nitrogen emission lines in its LIBS spectra, definitively from a nitrate impurity and not the sample itself. The pregnant liquor solution can impinge signatures on the uranium compound as discussed here. The nitrate asymmetric stretch in IR spectra and symmetric stretch in Raman spectra are present in the spectra discussed above and could be a chemical signature of the processing of the uranium compounds.

The set of ammonium diuranate and uranium oxide samples synthesized here were used as a test set for the FTIR and Raman PCA models built in Chapter 3. The FTIR PCA model was applied to the ten FTIR spectra described here and the Raman PCA model to the six Raman spectra described here. The samples of known composition were used to test the ability of the models to determine composition. The FTIR model showed the three uranium oxide samples fired for 16 hours grouping with the original uranium oxide samples, the samples ADU170D, ADU170W, ADU400D, and UO2400H grouping with samples ADU1, ADU2, ADU3, UA, and UP, and the samples ADU280D, ADU280W, and ADU400W, are grouped with samples UN, UF, AUC. The Raman model showed the ammonium diuranate samples of the test set grouped with the samples ADU1 and ADU2.
Chapter 5. Electronic Spectroscopic Signatures

Abstract

Photoluminescence spectroscopy and Laser Induced Breakdown Spectroscopy (LIBS) can give insights to the electronic structure and elemental composition of a sample, respectfully. Both techniques can be conducted remotely and with minimal to no sample preparation. Photoluminescence spectroscopy has been shown to be selective having minimal interferences from potential impurities. The uranyl structure emits a characteristic banded luminescence pattern, with high quantum efficiencies. Laser Induced Breakdown Spectroscopy has proven to be a valuable technique for semi-nondestructive elemental analysis for a wide variety of samples both in and out of the laboratory environment. Uranium is shown to have a multitude of atomic emission lines that could be useful detection and possible chemical determination. It is possible to use the ratio of intensity lines between uranium and oxygen to differentiate between uranium oxide compounds.

Introduction

The UV-Visible absorption of the uranyl ion results from excitations from the $\sigma_u$ bonding U-O molecular orbital to the non-bonding, empty, d-type $\delta_u$ and f-type $\phi_u$ orbitals. [120, 121] This transition occurs on the blue edge of the visible spectrum, around 420 nm. The absorption spectra can be resolved into many different bands, corresponding to vibrational levels of the excited state. These bands can be assigned into three different levels of the excited triplet state, $^3\Delta_g$. [120, 121] The exact energy of the absorption band depends on the nature of the equatorial ligands.
The transition from the triplet $^3\Delta_g$ excited state to the singlet $^1\Sigma^+_g$ ground state is parity forbidden. The emission is facilitated by magnetic dipole interactions with vibronic levels in the ground state. The emission has commonly been referred to as fluorescence in the literature, but is a phosphorescence decay. The excitation of uranyl compounds in the 345 – 500 nm range produces a characteristic banded emission in the 450 – 600 nm range, built on the vibronic structure of the ground state, typically with four to six different emission bands observed. [123] The emission bands are associated with ground state vibrations built upon the symmetric uranyl stretch. The emission pattern is essentially the same.
for different excitation wavelengths or equatorial ligands, with variation in intensity, bandwidth, and wavelength.

Measuring uranium samples using LIBS can be a difficult and complex task. Ablating and vaporizing a radioactive material, such as uranium, can prove difficult from a radiological containment and safety aspect. Added to the logistical difficulties provided by uranium, is the presence of more than 100,000 spectral lines reported to belong to uranium. [124, 125, 126] The density of emission lines leads to broad continuum from about 250 nm to almost 750 nm. This continuum is the result of Bremsstrahlung emission and recombination events, but also from the unresolved lines of uranium.

Many previous LIBS measurements on uranium samples have detected uranium or determined limits of detection (LOD) in various matrices [125, 126, 127], measured isotopics [128, 129], or determined impurities. [124] A double pulse LIBS combined with PCA was used by Klus et. al. for chemical mapping of uranium in uranium ores. [153] Sirven et. al. used LIBS and chemometric models to determine the geographic origin of industrial uranium ore concentrates. The intensity of emission lines from eleven elements were used to discriminate between samples using Principal Component Analysis and Soft Independent Modeling of Class Analogy. [130] Campbell et. al. used LIBS to discriminate between different uranium oxides using of the intensities of uranium and oxygen emission lines, selecting uranium lines that have been shown to be concentration dependent. Campbell determined the uranium lines at 591.639 nm and 682.692 nm provide the greatest discrimination between uranium oxides. [131] The use of intensity ratios to differentiate uranium compounds of similar composition is expanded here utilizing nitrogen, sulfur, fluorine, hydrogen, and carbon lines. A PCA model was built to differentiate between uranium compounds utilizing the entire spectral region, in contrast to literature results which employ elemental impurities to differentiate between uranium compounds.
Experimental

Photoluminescence measurements were taken in two different methods for each sample. Method 1 monitored the same emission range, 450 – 650 nm, while changing the excitation wavelength successively in each scan, starting at an excitation wavelength of 200 nm, stepping 5 nm each scan, until an excitation wavelength of 425 nm was achieved. This method resulted in 45 scans. During each scan the emission wavelength was monitored in 0.5 nm steps integrated for 0.5 seconds each. Method 2 stepped both the emission and excitation wavelengths each scan. The monitored emission range started at 450 – 900 nm, with the start of the range increasing by 5 nm with each successive scan until an emission range starting wavelength of 750 nm was reached, while the end of the range stayed at 900 nm. The excitation wavelength started at 400 nm and was stepped by 5 nm each successive scan up to 700 nm. This method resulted in 61 scans. During each scan the emission wavelength was monitored in 0.5 nm steps integrated for 0.5 seconds each. The entrance and exit slit widths for the first excitation monochromator were kept constant at 3.0 mm, and the entrance slit widths for the second excitation monochromator were kept constant at 3.0 mm, while the exit slit widths varied from 0.2 mm for strong luminescence, to 1.0 mm for weak luminescence. The entrance slits for the emission monochromator varied from 0.2 mm to 1.0 mm and the exit slits were held constant at 0.1 mm. The slit widths at the PMT (emission monochromator exit) lead to a bandpass of ~0.42 nm.

As stated above, the samples were ground with a mortar and pestle and flamed sealed in borosilicate NMR tubes. The borosilicate tube showed luminescence at ~710 nm, when excited with ~690 nm light, shown in Figure 5-2.
For LIBS measurements, the laser energy was attenuated 45% corresponding to an energy of 26 mJ, and focused to a spot approximately 350 μm in diameter on the sample. The height of the sample was carefully controlled to ensure sampling of the same region of the plasma. The control of sample height was accomplished by measuring the thickness of the sample and using a set of washers to maintain the same distance from the top surface of the sample to the sample stand. The gate delay and gate width were held constant at 100 ns and 500 ns, respectively. The laser was rastered across the surface of the pellet, and each spectrum is the average of 500 laser shot, with three to five replicates acquired for each sample. [131]

The LIBS spectra were first corrected using a crosstalk suppression algorithm and stray light removal algorithm, built into the Raptor Photonics software. The crosstalk suppression algorithm works to limit cross talk between different diffraction orders of the spectrometer in the CCD due to the size of the
pixels. The stray light removal algorithm removes the stray light between orders caused by the unavoidable grating scatter in an echelle grating. It does this by averaging and subtracting background between orders. The spectra are then corrected using an instrument response function generated from a calibrated lamp source, correcting for the response of the entire system from the optical fiber to the gratings and the CCD.

Emission lines for each element in every sample were selected based on relative intensity, transition probability, and energy levels of the transmission listed in the NIST data base. [132] For uranium, the lines used for analysis are 591.539 nm and 682.692 nm. [126, 131] The oxygen triplet line at 777.194 nm, 777.417 nm, and 777.539 nm were used for oxygen analysis. [131] The nitrogen lines used were 818.802 nm and 822.314 nm, as the nitrogen lines normally used for LIBS analysis at 742.364 nm, 744.229 nm, and 746.831 nm were not observed and possibly obscured by the uranium line at 742.550 nm. The fluorine line at 685.603 nm was used, but had low intensity. [133, 134] The sulfur emission lines at 921.287 nm and 923.754 nm were used for sulfur analysis. [135, 136] The carbon was analyzed using the emission line at 247.856 nm [137, 138] and the hydrogen using the emission line at 656.272 nm. [138, 139]

Background subtraction was applied to the lines of interest. From each data point of the emission line, a local minimum, within 1 nm of the line, was subtracted. The points of the peak were summed to determine an integrated line intensity. [131] The 591 nm uranium line was integrated from 591.42 nm to 591.62 nm and the 682 nm uranium line was integrated from 682.58 nm to 682.76 nm. The oxygen triplet at 777 nm was integrated together from 777.1 nm to 777.64 nm. The 818 nm nitrogen line was integrated from 818.74 nm to 818.86 nm and the 822 nm line from 822.2 nm to 822.38 nm. The 685 nm fluorine line was integrated from 685.5 nm to 685.76 nm. The 921 nm sulfur line was integrated from
921.18 nm to 921.48 nm and the 923 nm line from 923.7 nm to 923.88 nm. The hydrogen 656 nm line was integrated from 656.08 nm to 658.14 nm and the 247 nm carbon line from 247.82 nm to 247.92 nm. The integrated line ratios were then used to calculate ratios of uranium to oxygen line intensities, uranium to nitrogen line intensities, uranium to fluorine line intensities, uranium to sulfur line intensities, uranium to hydrogen line intensities, and uranium to carbon line intensities. In order to compare intensity ratios between samples, measurements would need to be taken on the same day to ensure that the plasma light collection and experimental setup was identical. For this reason, samples ADU, AUC, AUS, UN, US, and USA LIBS measurements were taken on two different days. Spectra names are denoted with an a and b to differentiate between measurements on the different days.

Results

Photoluminescence

The photoluminescence results can be divided into two groups, compound that do not produce detectable photoluminescence and compounds that do produce detectable photoluminescence. Of the 15 compounds evaluated (samples ADU2 and ADU3 were not measured), photoluminescence was observed for seven compounds. The three uranium oxide samples, UO2 in Figure 5-3, UO3 in Figure 5-4, and U3O8 in Figure 5-5, did not exhibit any luminescence.
Figure 5-3. Photoluminescence spectra of uranium dioxide (UO2). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.

Figure 5-4. Photoluminescence spectra of uranium trioxide (UO3). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.
Figure 5-5. Photoluminescence spectra of triuranium octaoxide (U3O8). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.

The samples ADU1 (Figure 5-6), AUC (Figure 5-7), SDU (Figure 5-8), and UF4 (Figure 5-9) do not exhibit any luminescence. The sample UP did not exhibit any luminescence (Figure 5-10), although the similar uranyl complexes did. In each of these spectra, a peak around 470 nm was observed. This peak is believed to be a Raman scattering peak as it shifted in location parallel to the excitation wavelength changing.
Figure 5-6. Photoluminescence spectra of ammonium diuranate #1 (ADU1). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.

Figure 5-7. Photoluminescence spectra of ammonium uranyl carbonate (AUC). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.
Figure 5-8. Photoluminescence spectra of sodium diuranate (SDU). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The black trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.

Figure 5-9. Photoluminescence spectra of uranium tetrafluoride (UF4). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.
Figure 5-10. Photoluminescence spectra of uranyl peroxide hydrate (UP). The black trace shows a scan from method 1 with an excitation wavelength of 420 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 420 nm. The large peak at 840 nm is second order scattering of the excitation light.

The samples UA (Figure 5-11), UF (Figure 5-12), UN (Figure 5-13), US1 (Figure 5-14), US2 (Figure 5-15), and USA (Figure 5-16) all exhibit the typical banded uranyl luminescence. The characteristic luminescence is due to a vibrational progression in the uranyl symmetric stretch, \( I \rightarrow 0 \) and \( I \rightarrow 0 + \nu_2 + n\nu_1 \), where \( n=0, 1, 2, 3, 4 \). The locations of these peaks for the samples displaying the uranyl luminescence are given in Table 5-1. In addition to the locations of the peaks shifting slightly, the relative intensities vary depending on the equatorial ligand. The ratios of intensities of the vibrational progression to the transition to the vibrational ground state are given in Table 5-2. It is apparent that the photoluminescence of UF has emission bands that have been shifted to longer wavelengths and exhibits luminescence bands possibly attributable to other vibrational progressions (Figure 5-12). The photoluminescence of US2 also shows luminescence bands that could belong to other vibrational
progressions (Figure 5-15). The sample AUS, Figure 5-17, shows weak photoluminescence emission in the same region as the characteristic uranyl luminescence, although it does not have the banded structure, or the intensity.

It is possible to calculate the frequency of the uranyl symmetric stretch from the luminescence spectra, as the bands are spaced apart equal to the symmetric stretch frequency. The symmetric stretch for UA calculated from the photoluminescence data was 843 cm$^{-1} \pm 21.5$ cm$^{-1}$. The frequency was calculated from the average spacing between peaks, and the uncertainty is equal to the standard deviation in that measurement. The uranyl symmetric stretch for UA determined from the Raman data (Table 3-6) was 827 cm$^{-1}$, within error of the photoluminescence determined frequency. The symmetric stretch for UF calculated from the photoluminescence data was 866 cm$^{-1} \pm 25$ cm$^{-1}$, and the stretch determined from the Raman data (Table 3-4) was 863 cm$^{-1}$. The uranyl symmetric stretch for UN calculated from the photoluminescence data was 863 cm$^{-1} \pm 30$ cm$^{-1}$, compared to 864 cm$^{-1}$ (Table 3-4) from the Raman data. For sample US1 the symmetric stretch was 870 cm$^{-1} \pm 28$ cm$^{-1}$ from the photoluminescence data and 868 cm$^{-1}$ (Table 3-10) from the Raman data. The symmetric stretch for US2 was 908 cm$^{-1} \pm 32$ cm$^{-1}$ from the photoluminescence data and 884 cm$^{-1}$ (Table 3-10) from the Raman data. For sample USA the symmetric stretch from the photoluminescence data was 850 cm$^{-1} \pm 26$ cm$^{-1}$ and 861 cm$^{-1}$ (Table 3-10) from the Raman data. For each of the six samples exhibiting the characteristic banded uranyl emission, the symmetric stretch calculated from the photoluminescence data was statistically equivalent to the symmetric stretch determined from the Raman data.
Table 5-1. Peak locations for the characteristic uranyl luminescence. The peaks are given in units of nm, and the uncertainty in the peak location is ± 2nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I \rightarrow 0$ origin</th>
<th>$I \rightarrow 0 + \nu_2$</th>
<th>$I \rightarrow 0 + \nu_2 + \nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 2\nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 3\nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 4\nu_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA</td>
<td>492.5</td>
<td>511.5</td>
<td>535</td>
<td>559.5</td>
<td>587.5</td>
<td></td>
</tr>
<tr>
<td>UF</td>
<td>497.5</td>
<td>519.5</td>
<td>544.5</td>
<td>572</td>
<td>600.5</td>
<td>633.5</td>
</tr>
<tr>
<td>UN</td>
<td>487.5</td>
<td>509</td>
<td>533.5</td>
<td>559.5</td>
<td>587</td>
<td>617.5</td>
</tr>
<tr>
<td>US1</td>
<td>489.5</td>
<td>510</td>
<td>534.5</td>
<td>561</td>
<td>589.5</td>
<td>620</td>
</tr>
<tr>
<td>US2</td>
<td>493</td>
<td>514</td>
<td>540</td>
<td>566.5</td>
<td>598</td>
<td>632</td>
</tr>
<tr>
<td>USA</td>
<td>493.5</td>
<td>514.5</td>
<td>539</td>
<td>565</td>
<td>593</td>
<td>623.5</td>
</tr>
</tbody>
</table>

Table 5-2. Ratios of peak intensities relative to the transition to the vibrational ground state.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I \rightarrow 0$ origin</th>
<th>$I \rightarrow 0 + \nu_2$</th>
<th>$I \rightarrow 0 + \nu_2 + \nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 2\nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 3\nu_1$</th>
<th>$I \rightarrow 0 + \nu_2 + 4\nu_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA</td>
<td>1.00</td>
<td>1.86</td>
<td>1.32</td>
<td>0.57</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>UF</td>
<td>1.00</td>
<td>1.80</td>
<td>1.13</td>
<td>0.46</td>
<td>0.17</td>
<td>0.08</td>
</tr>
<tr>
<td>UN</td>
<td>1.00</td>
<td>1.97</td>
<td>1.32</td>
<td>0.49</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>US1</td>
<td>1.00</td>
<td>2.66</td>
<td>1.32</td>
<td>0.39</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>US2</td>
<td>1.00</td>
<td>5.07</td>
<td>2.43</td>
<td>0.79</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>USA</td>
<td>1.00</td>
<td>2.28</td>
<td>1.22</td>
<td>0.38</td>
<td>0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure 5-11. Photoluminescence spectra of uranyl acetate hydrate (UA). The black trace shows a scan from method 1 with an excitation wavelength of 430 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 400 nm. A 475 nm long pass filter was placed at the entrance of the emission monochromator, after the sample.

Figure 5-12. Photoluminescence spectra of uranyl fluoride hydrate (UF). The black trace shows a scan from method 1 with an excitation wavelength of 400 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 405 nm. The large peak at 810 nm is second order scattering of the excitation light.
Figure 5-13. Photoluminescence spectra of uranyl nitrate hydrate (UN). The black trace shows a scan from method 1 with an excitation wavelength of 340 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 400 nm. The large peak at 800 nm is second order scattering of the excitation light.

Figure 5-14. Photoluminescence spectra of uranyl sulfate hydrate #1 (US1). The black trace shows a scan from method 1 with an excitation wavelength of 345 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 400 nm. The large peak at 800 nm is second order scattering of the excitation light.
Figure 5-15. Photoluminescence spectra of uranyl sulfate hydrate #2 (US2). The black trace shows a scan from method 1 with an excitation wavelength of 380 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 400 nm. The large peak at 800 nm is second order scattering of the excitation light.

Figure 5-16. Photoluminescence spectra of ammonium uranyl sulfate (USA). The black trace shows a scan from method 1 with an excitation wavelength of 350 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 400 nm. The large peak at 800 nm is second order scattering of the excitation light.
Figure 5-17. Photoluminescence spectra of ammonium uranyl sulfate (AUS). The black trace shows a scan from method 1 with an excitation wavelength of 380 nm. The blue trace shows a scan from method 2 with an excitation wavelength of 450 nm. The large peak at 900 nm is second order scattering of the excitation light.

Laser Induced Breakdown Spectroscopy

The LIBS spectrum of a uranium compound, as discussed above, is dominated by broad continuum emission and the density of emission lines from uranium. The three uranium oxides, samples UO₂, UO₃, U₃O₈, had the highest intensity of lines as seen in Figures 5-18, 5-19, and 5-20, respectively. The negative peaks present in the spectrum are an artifact of the stray light removal process. They occur when too much background as been subtracted and tend to occur close to strong, wide peaks. Another feature of note in LIBS spectra are the spectral gaps that occur starting at approximately 670 nm and are present at longer wavelengths. These gaps are due to the design of the echelle spectrometer. The “humps” in the spectra are caused by the loss in efficiency at the edges of diffraction order. The “humps” have been mostly removed from the spectra presented below for aesthetic reasons, but were not removed in the determination of peak intensity and ratios.
Figure 5-18. Laser Induced Breakdown Spectroscopy spectrum of uranium dioxide under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UO2a.
Figure 5-19. Laser Induced Breakdown Spectroscopy spectrum of uranium trioxide under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UO₃a.

Figure 5-20. Laser Induced Breakdown Spectroscopy spectrum of triuranium octaoxide under an Ar atmosphere, taken on the first day of data acquisition. Referred to as U₃O₈a.
The other lines of note are the Ar lines present above approximately 700 nm. It is a known phenomenon in LIBS that the surrounding atmosphere is incorporated into the LIBS plasma and emits lines from the atmosphere constituents. [140] The prominent Ar emission lines detected are all from neutral Ar species at 696.543 nm, 706.722 nm, 738.398 nm, 750.387 nm, 751.465 nm, 763.511 nm, 772.376 nm, 772.421 nm, 794.818 nm, 800.616 nm, 801.479 nm, 826.452 nm, 852.144 nm, 866.794 nm, 922.450 nm, and 965.779 nm.

An intense luminescence was detected in the LIBS spectra for samples UNa (taken on the first day of data acquisition), USa, USb (second day of data acquisition), USAa, and USAb, as seen in Figures 5-21, 5-22, 5-23, 5-24, and 5-25 respectively. The luminescence appears in the same range, 470 nm to 600 nm, and has the same characteristic banded structure as the uranyl luminescence presented above. The laser used here has a wavelength in the IR region, 1064 nm, and would not be expected to be absorbed and excite the uranyl species. The excitation and resulting emission is most likely the result of multiphoton processes caused by the high irradiance necessary for LIBS. The presence of photoluminescence tends to greatly depress the LIBS emission from the sample.
Figure 5-21. Laser Induced Breakdown Spectroscopy spectrum of uranyl nitrate hexahydrate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UNa.

Figure 5-22. Laser Induced Breakdown Spectroscopy spectrum of uranyl sulfate hydrate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as USa.
Figure 5-23. Laser Induced Breakdown Spectroscopy spectrum of uranyl sulfate hydrate under an Ar atmosphere, taken on the second day of data acquisition. Referred to as USb.

Figure 5-24. Laser Induced Breakdown Spectroscopy spectrum of ammonium uranyl sulfate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as USAa.
The spectrum of sample SDU, Figure 5-26, is unique. The presence of a significant amount of Na in the sample, ~7 wt. %, leads to very strong emission lines from neutral Na at 588.995 nm and 589.592 nm. The only other sample that shows a significant intensity from the Na emission lines is UF4, Figure 5-27. The Na is present in UF4 either as a contaminant from the synthesis of the compound or as a contaminant from handling the UF4 sample or pellet.
Figure 5-26. Laser Induced Breakdown Spectroscopy spectrum of sodium diuranate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as SDUa.

Figure 5-27. Laser Induced Breakdown Spectroscopy spectrum of uranium tetrafluoride under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UF4a.
The remaining samples did not have any spectral features of note, besides showing emission lines belonging to N, S, F, C, or H depending on the sample. The spectra for these samples are shown below: ADUa in Figure 5-28, ADUb in Figure 5-29, AUCa in Figure 5-30, AUCb in Figure 5-31, AUSa in Figure 5-32, AUSb in Figure 5-33, UA in Figure 5-34, UF in Figure 5-35, UNb in Figure 5-36, and UP in Figure 5-37.

Figure 5-28. Laser Induced Breakdown Spectroscopy spectrum of ammonium diuranate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as ADUa.
Figure 5-29. Laser Induced Breakdown Spectroscopy spectrum of ammonium diuranate under an Ar atmosphere, taken on the second day of data acquisition. Referred to as ADUb.

Figure 5-30. Laser Induced Breakdown Spectroscopy spectrum of ammonium uranyl carbonate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as AUCa.
Figure 5-31. Laser Induced Breakdown Spectroscopy spectrum of ammonium uranyl carbonate under an Ar atmosphere, taken on the second day of data acquisition. Referred to as AUCb.

Figure 5-32. Laser Induced Breakdown Spectroscopy spectrum of ammonium uranyl sulfate (AUS) under an Ar atmosphere, taken on the first day of data acquisition. Referred to as AUSa.
Figure 5-33. Laser Induced Breakdown Spectroscopy spectrum of ammonium uranyl sulfate (AUS) under an Ar atmosphere, taken on the second day of data acquisition. Referred to as AUSb.

Figure 5-34. Laser Induced Breakdown Spectroscopy spectrum of uranyl acetate hydrate under an Ar atmosphere, taken on the second day of data acquisition. Referred to as UAb.
Figure 5-35. Laser Induced Breakdown Spectroscopy spectrum of uranyl fluoride hydrate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UFa.

Figure 5-36. Laser Induced Breakdown Spectroscopy spectrum of uranyl nitrate hydrate under an Ar atmosphere, taken on the second day of data acquisition. Referred to as UNb.
Figure 5-37. Laser Induced Breakdown Spectroscopy spectrum of uranyl peroxide hydrate under an Ar atmosphere, taken on the first day of data acquisition. Referred to as UPa.

Similar to the work of Campbell et. al. [131] and Colgan et. al. [141], ratios of integrated peak intensities have been calculated in an attempt to differentiate between uranium compounds. Integrated uranium intensities (591.539 nm and 682.692 nm, Figures 5-38 and 5-39, respectively) were compared to integrated intensities for oxygen lines (~777 nm, Figure 5-40), nitrogen lines (818.802 nm and 822.314 nm, Figure 5-41), sulfur lines (921.287 nm and 923.754 nm, Figure 5-42), a fluorine line (685.603 nm, Figure 5-43), a carbon line (247.856 nm, Figure 5-44), and a hydrogen line (656.272, Figure 5-45). The ratios were calculated for each of the three to five replicates taken for each sample. An average and standard deviation was calculated for each ratio. Average ratios for each sample were calculated for each uranium line to each of the other element lines for samples that contained the element. The ratios, for example, are given as U591/S923b referring to the ratio of the integrated
intensity of the uranium line at 591.539 nm to the integrate intensity of the sulfur line at 923.754, with the \( b \) corresponding to the data taken on the second day of data analysis.

As the sample pellets were prepared, pressed, and ablated under the same conditions, it is assumed the same amount of material is ablated for each sample. It is also assumed that the same fraction of elements in the sample is in the plasma. The quantitative determination of species present in the LIBS plasma is an extremely difficult task. Plasma dynamics can be affected by ionization potentials, Einstein coefficients, energy levels, or excited states. Due to the complexities of LIBS plasmas, the ratio of line intensities is expected to differ from the mass ratios of constituents, but both ratios should present the same trends.

Figure 5-38. Representative neutral uranium emission line at 591.539 nm. From the LIBS spectrum of UO2a.
Figure 5-39. Representative neutral uranium emission line at 682.692 nm. From the LIBS spectrum of UO2a.

Figure 5-40. Representative neutral oxygen emission lines at 777.194 nm, 777.417 nm, and 777.539 nm. From the LIBS spectrum of UNb.
Figure 5-41. Representative neutral nitrogen emission lines at 818.802 nm and 822.314 nm. From the LIBS spectrum of AUSb.

Figure 5-42. Representative neutral sulfur emission lines at 921.287 nm and 923.754 nm. From the LIBS spectrum of USb.
Figure 5-43. Representative neutral fluorine emission line at 685.03 nm. From the LIBS spectrum of UF4a.

Figure 5-44. Representative neutral carbon emission line at 247.856 nm. From the LIBS spectrum of UAb.
The ratio \( U591/O \) varies from 0.039 for USa, indicating a large amount of oxygen, to 1.484 for UF4a, indicating a small amount of oxygen. For \( U682/O \), the ratio varies from 0.020 for USa to 1.080 for UF4. The \( U591/O \) ratio gives a higher value than the \( U682/O \) ratio for all samples, although they follow the same trend. The \( U591/O \) ratio also tends to have a higher uncertainty. The ratios are shown for each sample in Figure 5-46. The weight % ratios have also been calculated for each sample and are shown in Table 4-3. The \( U/O \) ratio for the intensities is plotted against the \( U/O \) ratio for the mass and is shown in Figure 5-47. The intensity ratio trends with the mass ratio, as the \( U/O \) mass ratio increases, the \( U/O \) intensity increases as well in a linear fashion.
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Table 5-3. Weight percent for elements in each sample. The ratios of uranium to each constituent element, calculated from the weight percent.
Figure 5-46. Uranium to oxygen line intensity ratios for each sample, except for UF4. The error bars correspond to the standard deviation within 3-5 replicates of each sample.

Figure 5-47. Uranium to oxygen line intensity ratios as a function of uranium to oxygen mass ratio in each sample. The error bars correspond to the standard deviation within 3-5 replicates of each sample.
Ratios of uranium to nitrogen were calculated for the samples containing nitrogen, ADU, AUC, AUS, UN, and USA. Like the uranium oxygen ratios, the uranium nitrogen ratios using the 591 nm uranium give a higher value for both nitrogen lines and all samples, it also tends to give a higher uncertainty. The ratios using the nitrogen 818 nm line all have a higher ratio than the corresponding ratio using the nitrogen 822 nm line. The ratios using either nitrogen line follow the same trend between samples, for both uranium lines, as seen in Figures 5-48 (U/N818) and 5-49 (U/N22). Similarly to the uranium oxygen ratios, the uranium nitrogen intensity ratios were compared against uranium nitrogen mass ratio. Unlike the uranium oxygen ratios, the uranium nitrogen ratios, both using the 818 nm line and the 822 nm line, do not trend with the mass ratios. The uranium nitrogen mass ratios do not have the same variation as the uranium oxygen ratios. The samples ADU, AUS, and USA all have the same uranium nitrogen mass ratio, leading to the four data points for each sample (U591/N818a, U591/N818b, U682/N818a, U682/N818b, for each nitrogen line) to fall on a vertical line, as seen in Figures 5-50 (818 nm nitrogen) and 5-51 (822 nm nitrogen).
Figure 5-48. Uranium to nitrogen intensity ratios using the 818 nm nitrogen line. The error bars correspond to the standard deviation within 4-5 replicates for each sample.
Figure 5-49. Uranium to nitrogen intensity ratios using the 818 nm nitrogen line. The error bars correspond to the standard deviation within 4-5 replicates for each sample.

Figure 5-50. Uranium to nitrogen line intensity ratios as a function of uranium to nitrogen mass ratio in each sample, using the 818 nm nitrogen line. The error bars correspond to the standard deviation within 4-5 replicates of each sample.
Figure 5-51. Uranium to nitrogen line intensity ratios as a function of uranium to nitrogen mass ratio in each sample, using the 822 nm nitrogen line. The error bars correspond to the standard deviation within 4-5 replicates of each sample.

Ratios of uranium to sulfur line intensities were calculated for the samples containing sulfur, AUS, US, and USA, using a 921 nm sulfur emission line (Figure 5-52) and a 923 nm sulfur emission line (Figure 5-53). Like oxygen and nitrogen, the uranium sulfur ratios using the 591 nm line have higher values for all the samples and both sulfur lines. For both the sulfur emission lines used, the ratios for AUS were significantly higher than the other two samples and have significantly larger uncertainties. The ratios for US and USA were similar in value to each other for both sulfur lines. The uranium sulfur lines were also compared with the uranium sulfur mass ratios, shown in Figure 5-54 for the 921 nm sulfur line and Figure 5-55 for the 923 nm sulfur line. Not many conclusions can be drawn from this comparison, as the samples USA and US have very similar line intensity ratios for both sulfur lines, and AUS has significantly
larger uncertainties. The intensity ratios are further affected by the fact that both USA and US exhibit significant luminescence in their LIBS spectra. The luminescence could affect the integrated intensities of the uranium lines due to the spectral proximity to the luminescence and the overall dampening of the LIBS intensity.

Figure 5-52. Uranium to sulfur intensity ratios using the 921 nm sulfur line. The error bars correspond to the standard deviation within 3-5 replicates for each sample.
Figure 5-53. Uranium to sulfur intensity ratios using the 923 nm sulfur line. The error bars correspond to the standard deviation within 3-5 replicates for each sample.

Figure 5-54. Uranium to sulfur line intensity ratios as a function of uranium to sulfur mass ratio in each sample, using the 921 nm sulfur line. The error bars correspond to the standard deviation within 3-5 replicates of each sample.
Figure 5-55. Uranium to sulfur line intensity ratios as a function of uranium to sulfur mass ratio in each sample, using the 923 nm sulfur line. The error bars correspond to the standard deviation within 3-5 replicates of each sample.

Uranium to fluorine intensity ratios were calculated for the two samples containing fluorine, UF and UF4, using the 685 nm fluorine emission line (Figure 5-56). The uranium to fluorine ratios were higher for both samples using the 591 nm uranium line. The sample UF had a higher value than UF4 for both uranium lines, as well as higher uncertainty. The intensity ratios were compared to the mass ratios in Figure 5-57. With only two samples, strong conclusions are difficult to draw, although the uranium fluorine ratios seem to trend with the mass ratio.
Figure 5-56. Uranium to fluorine intensity ratios using the 685 nm sulfur line. The error bars correspond to the standard deviation within 4-5 replicates for each sample.
Figure 5-57. Uranium to fluorine line intensity ratios as a function of uranium to fluorine mass ratio in each sample, using the 685 nm fluorine line. The error bars correspond to the standard deviation within 4-5 replicates of each sample.

The ratio of uranium to hydrogen intensity was calculated for all samples in which hydrogen was present, excluding SDU, UO2, UO3, U3O8, and UF4, shown in Figure 5-58. The hydrogen emission line at 656 nm was used for the ratios. As with the other elements, the ratio with the 591 nm uranium line had a higher value than the corresponding ratio with the 682 nm uranium line for all the samples. The U591/O ratio had a low value of 0.03 for sample US on the first day of data acquisition and a high value of 0.43 for sample ADU on the second day of testing. The ratio using the 682 nm uranium had a low and high value at the same samples, as the ratios with either uranium line showed the same trend. The line intensity ratios were compared with the uranium hydrogen mass ratios in Figure 5-59. Once again it is
hard to draw conclusions due to samples ADU, AUS, and UP having the same uranium hydrogen mass ratio, and form a vertical line on the plot. The ratios using hydrogen are further confounded due to the large variable emission peak of hydrogen.

Figure 5-58. Uranium to hydrogen intensity ratios using the 656 nm hydrogen line. The error bars correspond to the standard deviation within 3-5 replicates for each sample.
Figure 5-59. Uranium to hydrogen line intensity ratios as a function of uranium to hydrogen mass ratio in each sample, using the 656 nm hydrogen line. The error bars correspond to the standard deviation within 3-5 replicates of each sample.

Uranium to carbon intensity ratios were calculated for the two samples containing carbon, AUC and UA, using the 247 nm carbon emission line, shown in Figure 5-60. The uranium carbon ratios show high uncertainty and no clear trend. The comparison with the uranium to carbon mass ratio shows no clear trend either (Figure 5-61). The 247 nm carbon line does not have high signal to noise and shows a large amount of variance between spectra.
Figure 5-60. Uranium to carbon intensity ratios using the 247 nm carbon line. The error bars correspond to the standard deviation within 4-5 replicates for each sample.
Figure 5-61. Uranium to carbon line intensity ratios as a function of uranium to carbon mass ratio in each sample, using the 247 nm carbon line. The error bars correspond to the standard deviation within 4-5 replicates of each sample.

**Multivariate Analysis**

*LIBS Principal Component Analysis*

A principal component model was built using the first replicate of each sample from both days of data acquisition. The LIBS data was inputted as a 20 x 38,051 matrix, with the samples as rows and the intensities as columns. The optimum number of principal components was determined using a Scree plot, Figure 5-62, analogous to the PCA models built for the FTIR and Raman data. The Scree plot here has plotted the log of the eigenvalue against the principal component number to better accentuate the “knee.” The “knee” of the plot is observed at the third eigenvalue. A PRESS plot is shown in Figure 5-63, showing the RMSECV for each PC. Three principal components gave a local minimum in the PRESS plot,
the lowest value of RMSECV for a reasonable number of principal components. The model was built using three components, as determined from the Scree and PRESS plots.

Figure 5-62. Scree plot for the LIBS PCA model, showing the principal component number versus the log of the eigenvalue.
Figure 5-63. PRESS plot for the LIBS PCA model, showing the RMSECV for each additional principal component.

The model with 3 principal components described 99.03% of the variation within the LIBS spectra. The scores, showing the relationship between the samples, are shown in Figure 5-64 for all three PC’s. The first principal component accounted for 95.87% of the variation, and the scores ranged from $1.41 \times 10^7$ for USA1a to $3.83 \times 10^8$ for UO21. The second principal component accounted for 2.16% of the variation, with scores ranging from $-3.68 \times 10^7$ for U3O81 to $2.99 \times 10^7$ for AUS1a. The third principal component account for just 1.00% of the variation, with a low score of $-3.10 \times 10^7$ for AUS1a and a high of $2.83 \times 10^7$ for UN1b.
Figure 5-64. Scores for the three principal components for all 20 spectra in the model. Scores on PC1 are shown in the top frame, PC2 in the middle frame, and PC3 in the bottom frame. The dotted lines represent the 95% confidence level.

The loadings show how the wavelengths relate to each other in the model. The loadings on PC1 are shown in Figure 5-65, on PC2 in Figure 5-66, and on PC3 in Figure 5-67. The loadings on PC1 show that the first principal component correlates positively with the continuum and the density of uranium lines present. It also correlates with the argon lines at higher wavelength. The first principal component correlates with the overall shape and intensity of a LIBS spectrum of a uranium compound. The loadings on PC2 show a strong correlation with higher wavelength lines, including those of argon. There is not much of a correlation with the overall continuum, or many uranium lines. There appears to be a negative correlation with spectra showing luminescence. The second principal component correlates with the hydrogen line at 656 nm and the sodium lines at 588 nm and 589 nm. The loadings on PC3 show no correlation with the continuum and a negative correlation for many of the strong uranium lines. The third principal component shows a positive correlation to luminescence in the LIBS spectra.
and to the 656 nm hydrogen line. Many of the longer wavelength lines show a positive correlation with PC3.

Figure 5-65. Loadings plot for PC1 of the LIBS model, showing how PC1 varies with wavelength.
Figure 5-66. Loadings plot for PC2 of the LIBS model, showing how PC2 varies with wavelength.

Figure 5-67. Loadings plot for PC3 of the LIBS model, showing how PC3 varies with wavelength.
The variance captured by the model for each wavelength is shown in Figure 5-68. The plot shows that the model captures between 100% and ~5% of the variance in all the wavelengths, except for the data gaps present at about 700 nm and up. The first principal component captures much of the variation from about 220 nm to about 650 nm while PC2 captures the rest of the variation from about 220 nm to about 400 nm. The third principal component captures much of the variation that is missed by the first two at the longer wavelengths.

![Figure 5-68. Variance captured at each wavelength for the LIBS model.](image)

The Q residuals, showing what samples do not fit the model well are shown in Figure 5-69. It is apparent that both US1b and SDU1 do not fit the model well, both having reduced q residuals above 1. The contributions to the Q residual for US1b are shown in Figure 5-70 and Figure 5-71 for SDU1. It is obvious from Figure 5-70 that the model does not fit the strong luminescence of US1b. The luminescence bands...
at about 500 nm contribute the most to the Q residuals. The largest contributions to the Q residuals for SDU1 are the strong sodium emission lines. The sample SDU is the only sample that contains sodium and the model does not account for sodium lines.

Figure 5-69. Q residuals for the 3 PC model of the LIBS data.
Figure 5-70. Contributions to the Q residual for sample US1b for the LIBS PCA model.

Figure 5-71. Contributions to the Q residuals for sample SDU1 for the LIBS PCA model.
The scores of PC1 are shown plotted against PC2 in Figure 5-72. The biggest observation is the three oxides far away from the main group, having positive scores on PC1 and negative scores on PC2. The samples UN1a and US1a are separated from the main group and samples UP1, UF1, and UF41 have grouped away as well. A plot of all three PC’s against each other is shown in 5-73. This plot shows U3O81, UO31, and UO21 far away from the rest of the samples. The three samples with the most luminescence, UN1b, US1b, and USA1b have all formed a group as well. Samples USA1a, ADU1a, AUC1a, and AUS1a have grouped together having negative scores on PC3.

Figure 5-72. Scores on PC2 vs Scores on PC1 for the LIBS model. The dotted oval is a 95% confidence interval.
Figure 5-73. Three dimensional plot of the Scores on PC1 (perpendicular to the page) versus Scores on PC2 (horizontal on the page) versus Scores on PC3 (vertical on the page) for the LIBS model. The dashed lines represent the zero lines.

The samples have also been grouped using a Hierarchical Clustering Analysis method, analogous to the FTIR and Raman data. The HCA method forms a hierarchy of clusters based on the distance between them, with clusters formed by minimizing the total within-cluster variance. The input data for the HCA
method was the PCA scores from the 3 PC model discussed above. The clustering analysis is shown as a dendrogram in Figure 5-74.

![Dendrogram showing the clustering of samples resulting from PCA of LIBS spectra.](image)

Figure 5-74. Dendrogram showing the clustering of samples resulting from PCA of LIBS spectra.

From the dendrogram it is apparent the four clusters are formed. A cluster containing the three uranium oxide samples, separated the farthest from the rest. A cluster containing samples UF41, UF1, and UP1 less than half the distance as the oxide cluster. A cluster of US1a, UN1a, SDU1, and USA1a, the samples displaying luminescence and the sample with the strong sodium lines. Both the luminescence and the sodium lines tend to decrease the intensity of the continuum resulting in lower LIBS emission from uranium. The fourth cluster is comprised of 3 smaller clusters: one contains ADU1a, AUC1a, and AUS1a, one containing USA1b, UN1b, UA1b, and AUC1b, and the last containing US1b, AUS1b, and
ADU1b. This clustering is fairly apparent when examining the three dimensional scores plot in Figure 5-73.

**Conclusions**

Photoluminescence spectroscopy was performed on 15 of the uranium compounds, excluding ADU2 and ADU3. Seven of the compounds showed photoluminescence, while eight did not. The samples ADU, AUC, UP, UO2, UO3, U3O8, UF4, and SDU did not exhibit any measureable luminescence with this experimental set up. The sample AUS showed some slight luminescence in the region corresponding to uranyl emission, but did not exhibit the characteristic banded structure. The samples UA, UF, UN, US1, US2, and USA all displayed the characteristic banded uranyl luminescence. The characteristic luminescence can be used to easily and non-destructively determine the presence of uranyl in the sample. The uranyl luminescence, based on a progression in the symmetric uranyl stretch, can be used to calculate a frequency for the uranyl stretch. The calculated frequency matched the frequency for the uranyl symmetric stretch determined from the Raman data, within uncertainty.

Laser Induced Breakdown Spectroscopy was used on 14 of the uranium compounds, excluding ADU2, ADU3, and US2, to determine elemental impurities and examine the feasibility of using emission intensity ratios to differentiate between compounds. The uranium to oxygen intensity ratio showed a linear trend with the uranium to oxygen mass ratio of the compound. The uranium to nitrogen, sulfur, fluorine, carbon, or hydrogen ratios were also calculated. The ability to draw conclusions from those relationships was hindered by the poor emission lines in the spectra or from compounds having the same mass ratios.
Chapter 6. Conclusions and Future Work

The purpose of this project was to determine the feasibility to detect and differentiate uranium speciation. Spectroscopic techniques were used to observe chemical signatures of uranium speciation and a range of uranium compounds. Raman and FTIR spectroscopy were used to determine vibrational structure of uranium compounds, including the uranyl moiety. Photoluminescence spectroscopy was used to determine optical emission of the uranium compounds. Laser Induced Breakdown Spectroscopy was used to determine elemental composition and impurities and differentiate between elemental compositions. The differentiation of uranium speciation was further expanded by the use of Principal Component Analysis of spectral data to examine trends. Principal Component Analysis models were built to observe trends and discriminate between uranium compounds.

Multivariate methods have been shown to be effective for discriminating between uranium samples. Models were built using FTIR, Raman, and LIBS data. Each model showed the ability to discriminate between uranium compounds of differing chemical composition and structure. In addition to the discrimination of uranium compounds, the FTIR and Raman models were used to predict the chemical composition of samples. The models showed the ability to predict composition of uranium samples. The PCA models are shown it easily and effectively discriminate uranium compounds.

IR and Raman Spectroscopy

FTIR and Raman spectroscopy were performed on the set of seventeen uranium compounds. Supported by literature, vibrational assignments were made for prominent peaks in the spectra. The vibrational structure of the uranyl moiety was seen to provide a valuable signature for the detection of uranium compounds. In the FTIR spectra the uranyl asymmetric peak was observed to vary from 851 cm\(^{-1}\) for SDU to 963 cm\(^{-1}\) for UF, with an average frequency and standard deviation for all the compounds of
923 cm$^{-1}$ ± 25 cm$^{-1}$. The uranyl symmetric stretch was observed to vary from 783 cm$^{-1}$ for SDU to 884 cm$^{-1}$ for US2, with an average frequency and standard deviation for all the compounds of 839 cm$^{-1}$ ± 28 cm$^{-1}$. In addition to uranyl vibrations, many ligands coordinated to the uranium exhibited characteristic vibrations. These characteristic ligand vibrations aided in differentiating compounds.

Principal Component models were constructed for both the FTIR and Raman spectra. Each model consisted of 3 principal components, describing 74.68 % of the variation in the FTIR spectra and 76.67 % of the variation in the Raman spectra. The score plots for each model showed grouping between different compounds. Each model showed the uranium oxides and uranium tetrafluoride grouped together away from the rest of the samples. The sulfate containing samples also showed grouping together. The grouping of samples was also obtained objectively using Hierarchical Clustering Analysis, based on the PCA models created. The PCA models effectively showed discrimination between samples of varying composition. The groups formed consist of samples with similar sample composition and structure.

Future work with vibrational spectroscopy would include retaking the FTIR spectra without using the Wig-L-Bug to mix the sample in the KBr matrix to eliminate peaks from the polystyrene. The lack of impurity peaks would aid in the assignment of peaks arising from the sample. Further exploring the Raman spectra of the uranium oxides would lead to the ability to further discriminate between uranium compounds. The addition of more known uranium compounds would lead to a more robust model. The model constructed using the known uranium compounds can be applied to an unknown sample to help with potential identification of the sample.
The vibrational spectroscopies showed to be very useful in determining chemical signatures of uranium compounds. These signatures could be used to determine composition of unknown uranium compounds. The uranyl vibrations are suitable for detecting the presence of uranium and for differentiating between uranium compounds. The presence of coordinated ligands give further chemical signatures to differentiate between uranium compounds.

_Nitrate Signature_

Chemical signatures arising from the processing of uranium are of great use in forensics applications. These signatures could help to identify the provenance of an unknown sample. Several ammonium diuranate samples were synthesized with varying stir rates. These samples, as well as several uranium samples from the set of seventeen, exhibited signatures indicative of precipitation from a nitric acid solution. Peaks attributable to nitrate impurities were observed in both FTIR and Raman spectra. The nitrate impurity was found to persist even after drying the diuranate samples at 100 °C and after firing the ammonium diuranate to uranium oxide at 500 °C under H₂ gas for two 8 hour periods. For the one sample exhibiting nitrate peaks in both FTIR and Raman, but did not contain nitrogen in its chemical formula, nitrogen emission lines were observed in the LIBS spectrum.

The ammonium diuranate samples precipitated at three different stir rates, and respective uranium oxide samples, were used as test sets for the principal component models built from the set of 17 uranium compounds. The FTIR model showed three of the uranium oxide samples from the test set grouping with the uranium oxides from the original set. The ammonium diuranate test samples grouped with the original ammonium diuranate samples, or with the original samples that also had relatively intense peaks from the nitrate impurity. The Raman model showed the ammonium diuranate samples in the test set grouped near to the ammonium diuranate samples in the original set.
Future work for detecting signatures indicative of pregnant liquor would include analyzing uranium compounds from pregnant liquors of a sulfate, chloride, or carbonate nature. Signatures arising from the precipitant could also be explored as well as the ability to detect impurities with other methods. The ability to infer the pregnant liquor from which the uranium was precipitated is a valuable tool for attribution and determining the intended use of uranium compounds.

*Photoluminescence and Laser Induced Breakdown Spectroscopy*

Photoluminescence spectroscopy was performed on fifteen of the seventeen uranium compounds. Identical methods of scanning for luminescence were used on each sample to detect any photoluminescent emission. Seven of the fifteen samples exhibited a detectable luminescence, with six of the samples showing the characteristic banded luminescence of the uranyl moiety. The luminescence consisted of 5 to 6 bands ranging from 487.5 cm\(^{-1}\) to 633.5 cm\(^{-1}\). The bands are assigned as a transition from the first excited state to the vibrational levels in the ground state. A progression was observed based on the uranyl symmetric stretch and a frequency for the stretch was determined and compared with the symmetric stretch frequencies determined from the Raman data.

Future work with the photoluminescence spectroscopy of uranium compounds would include using a laser to excite the samples. Literature results suggest emission for some of the samples which did not exhibit luminescence here. Using a laser would allow for more intense, specific excitation of the samples. It would also permit easier filtering of the excitation light source.

Laser Induced Breakdown Spectroscopy was performed on fourteen of the uranium compounds on two days of data acquisition. Measurements were made under an Ar atmosphere to allow for the analysis of
oxygen, nitrogen, and carbon lines emitting from the sample and not the surrounding atmosphere. The resulting spectra show a large broad background consisting of Bremsstrahlung emission, recombination events, and unresolved lines. Uranium is known to have over 100,000 emission lines, and thus dominates the LIBS spectra. Five spectra showed signs of uranyl luminescence and the sodium diuranate sample showed strong sodium lines. The integrated intensities of two uranium lines, a triplet of oxygen lines, two nitrogen lines, two sulfur lines, one hydrogen line, one fluorine line, and one carbon line were used to calculate ratios of uranium to one of the other elements in the compound. The line intensity ratios were compared with the corresponding mass ratios based on the stoichiometry of the compounds. The ratio of line intensity of uranium to oxygen trended positively with the mass ratio of uranium to oxygen, with the intensity ratio increasing as the mass ratio increased. Fluorine was the only other element that showed a trend between intensity ratios and mass ratios, although there were only two data points.

A principal component model was constructed with the spectra for the fourteen uranium compounds. Three principal components were used accounting for 99.03 % of the variation within the spectra. Similarly to the models for the FTIR and Raman data, plots of the scores showed grouping within the spectra, with the main grouping coming from the oxides and the samples showing luminescence. Hierarchical Clustering Analysis was performed based on the principal component model, reflecting the grouping seen from the score plots. The PCA model built with LIBS data shows discrimination between samples.

Future work for the LIBS analysis of the uranium compounds would include optimizing the collection parameters, gate delay and width or laser energy, to better ionize detect the carbon, sulfur, fluorine, and nitrogen in the samples. This would increase the fidelity of the intensity ratios and thus lead to the
ability to draw stronger conclusions between intensity ratios and mass ratios. The measurement of more uranium compounds and inclusion in the principal component model would make for a more robust model. The model could be applied to unknown samples to aid in the determination of their composition.

Photoluminescence proves to be useful in determining the presence of the uranyl moiety in uranium compounds. The ability of calculating a symmetric stretching frequency could be used to further differentiate between uranyl compounds. Laser Induced Breakdown Spectroscopy is very useful for determining elemental composition of samples and has been shown to be able to differentiate between uranium compounds using uranium to oxygen line intensity ratios.
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