2010

OPTICAL MEASUREMENT OF ENVIRONMENTAL URANIUM USING POROUS SILICA MATERIALS

Chien-Cheng Chen
Virginia Commonwealth University

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OPTICAL MEASUREMENT OF ENVIRONMENTAL URANIUM USING POROUS SILICA MATERIALS

A Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering at Virginia Commonwealth University.

by

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Acknowledgement

First and foremost, I would like to thank my advisor, Dr. Gary C. Tepper. He provided me sufficient support both in my research and student life. He is my mentor and he teaches me in establishing my research foundation as well as the positive thinking attitude. He has so much patience and a wisdom mind whenever I made mistakes and he always guided me move toward the right track. I enjoyed the time discussing my research idea and results with him. He can always give me quick responses no matter what questions I encountered. Under his guidance, I learned how to do research step by step. In addition, because of his patience and fully support, I was able to pass through the biggest challenge in my life when my father passed away during my doctorate period. I appreciate two things I learn from him: “Family first” and “Always move forward.” He is the most respectful person in my doctoral student life.

I am grateful to another important advisor, Dr. Dmitry Pestov. I would like to express my sincere thanks to him. He has a brilliant mind and a very gentle heart. He provided me fulfilled technical support in my research and also gave me many good advices not only in professional life but in personal life. Whenever I felt hesitate in trying new experiment that I have never done before, he always told me, “Go ahead, why not.” He always encouraged me to think further and to explore in my study field. Whenever I stocked somewhere because of complicated experimental data or hypothesis model, he
taught me that “We have what we have,” and we always need to respect the results. He inspires me in learning the possible mechanism behind an experimental phenomenon. As such, I learn different aspects between an engineer and a scientist.

In addition, I would like to give my humble thanks to all my committees, Dr. Supriyo Bandyopadhyay, Dr. Kenneth J. Wynne, Dr. James T. McLeskey, and Dr. Hooman V. Tafresh. Their patience and good advices help me to have my dissertation more completely. I also thank the funding support for this research from a DOE NA22 grant (DE-FG52-06NA27491). Moreover, I would like to thank our project associates, Dr. Jean Nelson and Dr. John Anderson of VCU department of Biology. With their assistance and guidance during the preliminary studies, I was able to gain more understanding in the background of uranyl. Also, because of their supply of natural soil and the soil analysis, this research was able to complete the simulation of the environmental application.

I enjoyed in studying in the department of Mechanical Engineering at VCU. I would like to thank my directors of graduate studies, Dr. Ramana M. Pidaparti, and Dr. Karla M. Mossi regarding their assistance and guidance during my doctoral study life. With their administrative help, I was able to settle in well at the time I first came to study in the U.S. and also I could finish all my academic requirements smoothly. In addition, I have many wonderful memories with all my colleagues and friends in this department. I would like to give my special thanks to my classmate and laboratory colleague, Dr. Ezzat Elshazly. We shared similar goal to have our doctoral degree accomplished. He is like my
elder brother and he provided me a lot of encouragement and assistance during my research journey. Also, I want to thank my other classmates and friends, Yingfeng Shan, Dr. Chunya Wu, Dongshan Yu, Ping-Nan Chen, Sukhada Sanjay Kulkarni, and Jan Uecker for their friendship and support. Because of their assistance and accompany ship, I would never feel alone in this journey. My appreciation is also extended to Dr. Garry P. Glaspell of VCU Department of Chemistry and the writing center of VCU, especially Jake Ziemba. I deeply appreciated their help in editing my English writing.

Furthermore, I would like to thank many Taiwanese students studying in VCU. Because of their help and friendship, I was able to adjust smoothly when studying abroad. I also thank especially the Fu’s family, Wayne Fu, and Chun-Chieh (Anna) Lin, and the former chief leader at the Taiwanese student association at VCU, Shang-Cheng (Sunt) Lin. Their enormous help and accompany are all the way from the first week I came to the U.S. to I completed my study.

My appreciation also goes to my pastor’s family, Robert and Donna Burris, who married my wife and me. Their greatest friendship and guidance helped my family as we explored American culture and American life. They are our spiritual mentor. Besides, I would like to thank Donna for editing my English grammars throughout this work.

Finally, I would like to express my greatest gratitude and appreciation to my family for their endless source of love and support, especially to my wife, Hui-Min (Esther), and my parents. The primary motivation for me to pursue my doctoral degree in
VCU is to accompany my wife in studying aboard and to fulfill our dream. During this journey, we explored this new world together. Although we encountered many difficulties, she always encouraged me keep moving forward when I got frustrated. I will never accomplish this great work without her. In addition, during this period, my dearest father passed away. I would like to thank my Mom (Yuei-Tao Ho) and my two sisters, (Bao-Hui Chen and Shu-Yan Chen) for their help in getting everything well on the right track. With their support, I was able to return to school and finish this dissertation smoothly. Finally, I would thank God for giving me strength, patience and perseverance whenever I needed.
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Abstract

OPTICAL MEASUREMENT OF ENVIRONMENTAL URANIUM USING POROUS SILICA MATERIALS

By Chien-Cheng Chen

A Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering at Virginia Commonwealth University.

Virginia Commonwealth University, 2010

Major Director: Gary C. Tepper Ph.D.
Professor and Chair of Department of Mechanical Engineering

The focus of this research is on the optical measurement of uranyl in a solid matrix using fluorescence spectroscopy. Nanoporous silica-based materials were used to extract uranyl from contaminated soil and to enhance the fluorescence intensity and lifetime. The fluorescence lifetime and intensity of uranyl ions adsorbed on porous silica-based materials of varying pore size was measured as a function of pH and in the presence of fluoride. The feasibility of uranyl fluorescence detection on the top of soil by silica gel is carried out by four types of natural soil. The results show that the uranyl fluorescence intensity can be
enhanced by approximately two orders of magnitude by the silica nanoporous matrix from pH 4-12 with the greatest enhancement occurring from pH 4-7. The enhanced fluorescence lifetime can be used in time-gated measurements to help minimize the influence of background environmental fluorophores. The pH and the fluoride variation causes different uranyl speciation and results in a peak shift in the fluorescence spectrum. The mechanism of the uranyl ion on the silica nanoporous matrix was studied through 15 different silica materials with different water content ratios and various concentrations of uranium on different silica structures. The result shows that the particle size, pore size, water content and uranyl concentration on silica surfaces are all important factors for optimizing the fluorescence intensity. The spacing between silica materials, either the pore inside materials or the space between particles, causes the variety of uranyl distribution on the material surface and changes the fluorescence performance. Also, X-Ray Photoelectron Spectroscopy (XPS) is used to identify the possible uranyl surface species on silica. The fluorescence emission spectra from silica materials and the XPS results are consistent with the presence of two different uranyl compounds. The specific surface area of silica materials plays an important role on uranyl adsorption mechanism. To further enhance the sensitivity, an optical ball lens was used to preferentially direct the fluorescence signal toward the excitation source in standoff measurements. The application of the ball lens was found to increase the detection distance up to 14 times.
Chapter 1
Introduction

1.1 Uranium – A Greenhouse Gases Free Source of Energy

“The basic energy fact is that the fission of an atom of uranium produces 10 million times the energy produced by the combustion of an atom of carbon from coal,” said John McCarthy in “Frequently Asked Questions About Energy,” on Stanford's website.

Natural uranium is a common and weakly radioactive material in the environment. It naturally occurred in low concentrations about 0.3-12 PPM in water, soil, and rock. Uranium is a metal element in the actinoids series with the 92nd atomic number in the periodic table. It has three naturally occurring major isotopes: uranium-238 (99.28%), uranium-235 (0.71%), and uranium-234 (0.0054%). All these species of uranium are radioactive elements with long half lives 4.468 billion years, 704 million years, and 245,500 years respectively("Toxicological Profile for Uranium," 1999).

The repulsion between the positively charged protons causes instability in the uranium nuclei, resulting in the radioactive properties. The 1938 Nobel Prize winner Enrico Fermi and his research team proposed that the artificial radioactivity could be produced from unstable atoms by neutron bombardment (Fermi, Amaldi, D'Agostino, Rasetti, & Segre, 1934). During World War II, two German chemists, Otto Hahn and
Fritz Strassman, discovered that the bombardment of uranium by neutrons causes nuclear fission and releases the huge binding energy, which comes from the kinetic energy of these two split lightweight nuclei repelling each other (Meitner & Frisch, 1939). Based on the theory of nuclear fission energy and the control of the “Chain reaction” (Anderson, E. Fermi, & Szilard, 1939) for continuous nuclear fission, human beings have been using nuclear power since the early 1940s.

Today, considerable quantities of fossil fuel are used to generate power for daily industrial and civil consumption. The release of excess greenhouse gas from the combustion of these fossil fuels induces global warming, which may result in a tremendous ecological crisis. To reduce the greenhouse gas, there are several choices for power generation, i.e. hydraulic power, wind power, solar power, nuclear power, etc. However, some of these substitute energy sources might be restricted by natural terrain, climate, or the efficiency of power generation, therefore, not all of them can provide enough secure power for industrial and civil consumption in every country. For these reasons, nuclear power holds great promise as a clean, stable, and efficient source of energy. More than 30 countries used the power from nuclear fission to generate 2.6 trillion kWh of electricity in 2008, which is about 15% of the energy consumption of the world. For the highly industrialized countries, the “Group of Eight,” or G8, the average energy provided by nuclear power was up to 24%.

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1 Sources: Reactor data: WNA to 13/1/10
2 G8 Countries: Canada, France, Germany, Italy, Japan, Russia, the United Kingdom, and the United States.
1.2 Uranium Detecting and Monitoring

Nuclear power has supplied energy without emitting greenhouse gases and is reducing the impact of global warming. However, this powerful energy source presents some latent health threats to the human body due to inhalation or overexposure to radioactive materials which causes the variation of human globulins and albumin (Scapolan, Ansoborlo, Moulin, & Madic, 1998; Tirmarche, Baysson, & Telle-Lamberton, 2004). Elevated uranium concentrations in soil and water (above the natural background level) have been associated with activities such as uranium mining, nuclear fuel production, and depleted nuclear cell disposal (Bernhard, Geipel, Brendler, & Nitsche, 1996a; Benjamin C. Bostick, Scott Fendorf, Mark O. Barnett, Phillip M. Jardine, & Scott C. Brooks, 2002; deLemos et al., 2008; Morris et al., 1996; Riley, Zachara, & Wobber, 1992). To protect the environment in advance, continuous monitoring of the concentration of uranium in these potential contamination areas is becoming an essential routine. Currently, there are two main techniques, radiation and fluorescence detection, already being applied to detect uranium in the environment. Some uranium analysis methods, i.e. etching uranium contaminated crystal (Price & Walker, 1963), also can be used as a trace uranium detection technique. However, most of them are considered as laboratory analysis, which is not suitable for standoff detection.

Radiation detection of uranium is a very well known technique discovered in the 19th century (Rutherford, 1899). When a radioactive uranium atom decays, it emits an alpha particle and transforms into a radioactive isotope of another lightweight molecular
element. The particle keeps decaying and emitting radioactive particles until it is stable. Conventionally detecting the radioactive particles may identify the existence of uranium. However, for uranium-238, which is 99.3% of natural uranium, the sensitivity of radiation detection is too low and not sufficient to identify the uranium element out of the background noise in the field. In addition, with the intensity decreasing inversely proportional to the distance square, radiation detection cannot be applied for standoff detection. For these reasons, we have investigated the radiation detectability for uranium-238 as the preliminary reference data. The experiment of the radiation detection of uranyl nitrate can be found in appendix A.

Conversely, uranium can exist in several oxidized forms. In contact with oxygen, uranium usually transforms into the hexavalent (VI) form as uranyl ion ($\text{UO}_2^{2+}$). Uranyl is water soluble and, therefore, can readily spread through whole soil matrices (Gabriel et al., 2001). In addition, uranyl ion has the ability to characteristically emit an identifiable spectrum, so fluorescence detection can be applied to monitor natural uranyl in contaminated regions (Hostetler & Garrels, 1962; Kowal-Fouchard, Drot, Simoni, & Ehrhardt, 2004b; Langmuir, 1978).

### 1.3 Fluorescence Spectroscopy

Fluorescence technology is a highly sensitive tool able to detect extremely low concentrations. The main idea of fluorescence is the process of adsorption and emission of light which is usually illustrated by Jablonski diagrams (see Figure 1.1) depicting
electron transition. The singlet ground, first, and second electronic states are noted as S0, S1 and S2. At each of these electronic energy states, the excited electron can exist in a number of vibrational levels which are shown as 0, 1, 2, etc. The energy spacings between these vibrational energy levels lead to the characteristic peaks illustrated in the emission spectrum. Figure 1.2 shows the fluorescence emission spectrum of uranyl nitrate in DI water. Both adsorption and emission occur mostly from the lowest vibrational energy levels (Lakowicz, 2006), as 0 shown in Figure 1.1. The energy between the electron states S0 and S1 is too large for thermal energy alone. Therefore, the source to induce fluorescence is light, not heat (Lakowicz, 2006).

Fluorescence is the process of adsorbing and emitting of light. The molecule is first excited by a high energy photon, such as X ray or UV light, pumping the electron up to the excited states such as S1 or S2 containing various vibrational levels. Within a very short time, i.e. 10-12ps or less (Lakowicz, 2006), the excited molecules soon relax to the lowest vibrational level of S1 as thermal equilibrium. This very short period of time is included in the fluorescence lifetime and is called the internal conversion.

From the excited state, S1, the excited electron will return to the ground state via four possible ways: fluorescence emission, heat dissipation, phosphorescence, and quenching. Fluorescence emission is the process of excited molecules returning to the ground state and emitting a specific spectrum of light with some characteristic wavelength of peaks. These characteristic peaks are induced by the energy difference between the excited state, S1, and the spacing of vibrational levels of ground state S0. Part of the excited molecular energy is dissipated as heat. For a similar reason, quenching
is a kind of energy dissipation, which means the excited energy transfers to the nearby molecules via collision and radiation. Excited electrons in the S1 state can undergo a spin conversion to the first triplet state, T1, through the intersystem crossing.

![Jablonski diagrams](image)

**Figure 1.1 Jablonski diagrams**

Phosphorescence is the emission from triplet state, T1, to ground state S0. The wavelength of phosphorescence is generally shifted to longer wavelengths since the T1 state is lower in energy than the S1 state observed with fluorescence.

For the uranyl fluorescence spectrum, the excited electron relaxes from excited state S1 to several different vibrational energy levels of the ground state S0. Each of relaxations induces the characteristic wavelength of the uranyl spectrum. Figure 1.2 is the
emission spectrum of 0.01M uranyl nitrate solution excited by 285nm UV light source. The spectrum shows the characteristic peaks, which occur at 498nm, 519nm, 542nm, and 567nm. The uranyl spectrum may be changed by many environmental factors, i.e. the concentration of uranyl, the temperature, pH, various ions and organic matters, and different uranyl compounds. Therefore, changes in the vibrational energy levels of the uranyl are identified by the variation of uranyl spectrum peaks.

![Characteristics Peaks](image)

**Figure 1.2** Fluorescence spectrum of 0.01M uranyl nitrate solution. The arrows show the characteristic peaks of the spectrum.

**Fluorescence Lifetime**

After excitation, the time that molecules remain in the excited state before returning to the ground state is the fluorescence lifetime. In the Time-Resolved Fluorescence (TRF), the decay curve, which is obtained from the specific excitation-emission wavelength, presents the fluorescence emission intensity history of the sample. With the calculation by software, the fluorescence lifetime of the sample can be estimated.
Figure 1.3 shows the decay curve of the 0.01M uranyl nitrate solution which was excited by 285nm UV light source and the photon emission was recorded at 498nm. The decay curve shows the amount of the photons emitted from the excited state in a series of gating time after the excitation impulse. Variations in fluorescence lifetime may be utilized to identify the uranyl speciation.

![Fluorescence decay curve of 0.01M uranyl nitrate solution](image)

**Figure 1.3 Fluorescence decay curve of 0.01M uranyl nitrate solution**

**Fluorescence Enhancer**

However, the anticipated uranyl concentration in the field is so low that we may not be able to detect it from bare soil. For this reason, fluorescence enhancers may raise the detection limit. According to past investigations, phosphate (Bonhoure, Meca, Marti, De Pablo, & Cortina, 2007; Geipel, Bernhard, Rutsch, Brendler, & Nitsche, 2000; Scapolan et al., 1998) and fluoride (Kazakov, Afonichev, Khamidullina, & Kuleshov, 2001) may be used to increase the sensitivity of the detection method.

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3 In this research, the excitation pulse is has a delay of 104μs.
1987; Lehmann, Geipel, Grambole, & Bernhard, 2009) show excellent enhancement for solution samples. Nevertheless, once applied on the field, these liquid enhancers will permeate the soil. Therefore, in this investigation, we study the fluorescence enhance materials in a solid state so that it can be applied on the top of the soil. We have tested several solid state phosphate and fluoride compound in advance to observe the feasibility as an enhancer. The results can be found in appendix B.

1.4 Silica Materials

Herein we focus on solid materials which can simultaneously extract the uranyl from the environment and, in addition, accumulate the uranyl ions to a detectable amount. Multiple tests show that organic uranyl absorbers act mostly as quenchers. Different solid phosphates show good but very slow response, and such materials are not suitable for analytical applications. In the contrast, porous silica show impressive fluorescence intensity and response right after contaminating by uranyl solution. These two advantages attract our concentration on this most common compound on earth: SiO₂.

Silica materials are all around our environment, i.e. sand, stones and rocks. Most of them in the natural environment are in crystalline form and only some of them are amorphous and porous (Unger, 1979). For this reason, the total surface area of natural silica is too small to provide enough contact area to interact with uranyl ions. The uranyl ions, therefore, can migrate through ground water with low probability to interact with these environmental silica materials.
On the contrary, some research grade silica materials, i.e. colloid silica, silicon dioxide nanopowder, mesostructured hexagonal framework silica, and silica gel, have large surface area and the silanol groups, see Figure 1.4, allow these silica materials to efficiently interact with charged metal ions (H. A. Benesi, 1959).

![Figure 1.4 The silanol group on the surface of silica materials: provide hydrophilic properties and interact with positively charged metal ions](image)

However, nano size silica materials may not work properly as a fluorescence enhancer once they discharge from water. The nano size silica materials pile up compactly after drying out. Thus, the UV excitation and emitting photons cannot pass through these materials and fluorescence can be detected only on the top surface. In addition, because the interaction with uranyl starts from the bottom of the pile of silica materials when applied on the top of the soil to measure the uranyl in the soil, the ability to detect uranyl will decreases based on the reaction rate of uranyl from bottom migrating to the top surface. For these reasons, nanopowder silica materials do not suit as an enhancer of fluorescence sensor.
Accordingly, silica materials with inside framework, or with nano porous, amorphous structure (see Figure 1.5A) can be benefit in this point of view. Silica gel (see Figure 1.5B) is commonly used as a desiccating agent in industrial and home leaching systems. Silica gel has a very high adsorption rate for uranyl ions (Tran, Roddick, & O'Donnell, 1999) but the adsorption kinetics and surface speciation are very sensitive to pH (Guibal, Lorenzelli, Vincent, & LeCloirec, 1995). The optimum pH range for uranyl adsorption by silica gel is between 5 and 5.5 (Michard, Guibal, Vincent, & LeCloirec, 1996) and depends on uranyl hydrolysis (Lieser, Quandtklenk, & Thybusch, 1992), carbonate complexes and natural electrolytes (Pathak & Choppin, 2007). The silica gel porosity also influences the sorption kinetics and maximum water capacity and the uranyl fluorescence emission spectra and lifetime can be significantly enhanced due to geometrical sheltering from quenchers such as water and other quenching anions (Lopez & Birch, 1996).

Figure 1.5 A- amorphous porous silica diagram: silica network with random distribution⁴; B- silica gel with particle size 60-120μm, and pore size 60Å

1.5 Retro-Refraction

In the field, the common fluorescence sensor can be degraded by environmental and geometric factors. This is because the fluorescence light is distributed randomly over $4\pi$ even if the excitation is made with a parallel beam, i.e. laser. Therefore, only a small fraction of the emitted light actually reaches a detector. (see Figure 1.6A) To increase the signal from the fluorescence source, the Directed Fluorescence (DF) method can be applied as illustrated in Figure 1.6B. The DF returns the fluorescence signal back to the excitation source using glass beads (5) coated with the fluorescence enhancer layer (3).

Figure 1.6 Optical schemes for regular (A) and Directed Fluorescence System (B). 1-UV excitation source, 2 - signal receiver and analyzer, 3 - sensor polymer, 4 - tested soil, 5 - glass or polymer transparent bead, covered with sensitive polymer.
To emit light with high efficiency the device should be optimized. The focal point for the ball lens is given by equation 1-1 and 1-2:

\[
\text{Effective focal length: } \quad \text{EFL} = \frac{nD}{4(n - 1)} \quad (1-1)
\]

\[
\text{Back focal length: } \quad \text{BFL} = \text{EFL} - \frac{D}{2} \quad (1-2)
\]

Where \( n \) is the index of reflection, \( D \) is the diameter of the ball lens. The sketches of the optical device are shown in Figure 1.7.

![Figure 1.7 Schematics for the ball lens. A – UV excitation, B – emission is directed back. (Greathouse & Cygan, 2006): The green bar represents fluorescent material and is placed in the focal length of the ball.](image)

If fluorescent material is placed within the focal length of the ball lens, it will show the highest efficiency for the directed fluorescence. Therefore, if the fluorescence material is applied very close to the ball lens as a layer of coating, the index of reflection should be as close to 2 as possible. However, lenses with higher index of reflection usually stop the UV light from exciting the fluorescence material. Based on these considerations, the sapphire ball lens, which has a reflective index of 1.77 and a diameter of 6.35mm that result in a small back focal length of 0.47mm, could be a viable solution.
1.6 X-Ray Photoelectron Spectroscopy (XPS)

To optimize the efficiency of the fluorescence enhancer, there are mainly two important parameters: the different species of the uranyl-silica compounds and the forming mechanism near the top surface. To characterize chemical composition of the surface, we rely on X-Ray Photoelectron Spectroscopy (XPS).

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is one of the most sensitive surface analysis techniques today, which combine chemical state analysis with the quantities of the target atom. It can detect all elements except hydrogen and helium, and the samples can be gaseous, liquid, or solid. The sample depth of the solid material varies from the top 2 atomic layers to 15-20 layers, therefore, smooth and flat samples are preferred. It is the least destructive of all the electron or ion spectroscopy techniques, for this reason, it has relatively poor spatial resolution compared with electron-impact and ion-impact techniques.

The basic principle of XPS is that the X rays bombard a sample material and cause electrons to be ejected, as shown in Figure 1.8. The kinetic energy (KE) of these photoelectrons can be recorded and, with the excitation energy of the X ray photon (hν), can be converted into the binding energy (BE) of the particular electrons of the concerned atoms by Einstein photoelectric law as shown in Equation (3):

\[
BE = h\nu - KE
\]  

Identification of the elements present in the sample can be determined from the binding energies of these ejected electrons from the scan spectrum. On a finer scale it is
possible to identify the chemical state of the elements present from small variations in the determined binding energies. The relative concentrations of elements can be calculated from the measured photoelectron intensities.

Figure 1.8 Schematic of the components of XPS system

In this research, for the study the surface properties of the silica – uranyl interface, we focus on the silicon, oxygen, and uranium elements to investigate the chemical state and the atom compositions from the distribution of the binding energy spectrum on different silica samples. The results can be found in Chapter 6.

1.7 Research Motivation

Mentioned in this chapter, the global warming situation is getting more and more serious and, therefore, the development of greenhouse gas free substitution energy source is vital and urgent. Among these power sources, nuclear power by uranium is the most reliable and the most efficient choice. However, the potential radiation from the nuclear fuel and waste materials may cause disease and gene mutation. Therefore, the directly remote monitoring of uranium in the field is necessary to avoid the possible toxic and radiation contamination.

For uranium detection methods, the sensitivity of both radiation and fluorescence detection is insufficient because of the limit of the amount of uranium contamination. Fluorescence detection method can be very sensitive for characterizing uranium element from the solution of the uranium-contaminated samples with some enhancers, i.e. phosphate and fluoride. Nevertheless, when we apply on the field, these enhancers will permeate the soil and lost function. To elevate the detectability of uranyl in soil, we need a material which can extract the uranyl from the soil and, meanwhile, can provide the ability of fluorescence enhancement. For these requirements, in this investigation, we employed several nanoporous silica materials and an optical device to study the enhancement of the detectability by fluorescence technique.
Chapter 2
Literature Review

2.1 Technique for evaluating the identification of uranium fluorescence

Fluorescence spectroscopy for uranium detection is a highly sensitive technique due in part to the induction of lasers as an excitation source (Campen & Bachmann, 1979; Robbins, 1978). Combining the application of electronic gating to separate the long-lived uranium fluorescence from the organic compounds emitted from the natural environment, and the employment of FLURAN as a buffer to maintain optimum pH for fluorescence enhancement, the detection limit of uranium can reach 100 ppb (Robbins, 1978). However in this scheme uranyl is found by quenching the other fluorescence dyes present. Formation of uranyl complexes in a solution at low concentrations, the detection limit of uranyl is reduced to 60nM (Nivens, Zhang, & Angel, 2002). Aqueous uranyl ions examined with a pulsed-lamp excitation source, to reject interference from organic fluorescence, the detection limits approach 10 parts per trillion (Brina & Miller, 1993; Kaminski, Purcell, & Russavage, 1981).

However, for the laser induced fluorescence of uranium on solid state substances, i.e. uranyl remote sensing directly from rocks, minerals and soils, the detection limit ranges from 15 to 3000 ppm of uranyl on the surface (Deneufville, Kasdan, & Chimenti, 1981).
The detection limit difference between aqueous and solid samples results directly from the measurement depth. The excitation light which penetrates deeper in an aqueous state, rather than on the surface of a solid state, provide more chances for UV photons to interact with uranyl ions. This phenomenon also denotes that the increasing of uranyl concentration can increase the probability of the emission of fluorescence signal. Therefore, finding a medium which can raise uranyl concentration on the top surface is the paramount to improving the detection limit of uranyl on natural soil (see Figure 2.1).

![Diagram showing the medium to concentrate the uranyl on the top of soil](image)

**Figure 2.1 Schematic of the medium to concentrate the uranyl on the top of soil**

Silica gel materials can absorb approximately 400 to 1,000 times the uranium concentration of the solution from which it forms (Zielinski, 1980). Therefore, nanoporous silica materials have a high potential to explore trace uranium in the environment. One example is the detection of uranium in sea water by using a silica gel column. Silica gel was applied as a sensor for uranium in brines with a high iron concentration. By sorption on an activated silica gel column, the detection limit of uranyl ions is precise up to 1.4 ng (Depablo et al., 1992). However, it takes approximately 20 minutes to complete the analysis. Similar experiments were also done using ion exchange (Collins, Lu, Abubeker,
& Vajs, 2002), and the adsorption interaction (Lopez & Birch, 1996). The sensitivity of applying colloidal silica in uranium-contaminated solution can detect the uranyl concentrations down to 0.02 ppb (Lopez & Birch, 1996). In addition, a similar method, photo-acoustic spectrometry, was also successfully carried out to detect the trace uranyl by the application of QAE- Sephadex gel in solution state(Yamada & Yoshimura, 1992). Furthermore, a system combining the adsorption of uranium from aqueous solutions and detecting by fluorescence method can also be applied on the water purification system to monitor the total contamination of uranium (Murray, Jenkins, Bzhelyansky, & Uy, 1997).

### 2.2 Uranium extraction from the Environment

Silica gel materials have a large surface area (from 300-800 m²/g, depending on the pore size) and silanol groups on their surface. These two properties allow silica gel to adsorb water and metal ions efficiently (H. A. Benesi, 1959). The silanol groups on silica gel surfaces act as an ion exchanger of the weakly acid type (Ahrland, Grenthe, & Noren, 1960). For a mono-valence cation the exchange reaction can be written schematically in the chemical formula (2-1),

\[ \equiv \text{SiOH} + \text{Me}^+ \rightleftharpoons \equiv \text{SiOMe} + \text{H}^+ \]  

(2-1)

Sorption of heavy metal ions on silica gel is strongly correlated to their ionic strength (Pathak & Choppin, 2006a, 2006b). A higher sorption rate is caused by the lower ionic strength. The change of pH value in a natural solution can be related to the ionic strength as well. A decreasing in pH level will cause the increasing in ionic strength, and
simultaneously affect the ion-exchange mechanism in the sorption process. An investigation shows that the sorption of uranyl ions on silica gel is a function of pH, and also in strong relation to the carbonate content (see figure 2.2) (Lieser et al., 1992). For the solutions with an absence of carbonate (curve a)), the sorption ratio (Rs) increases with the increase of pH range between 2 and 6.5 (due to the formation hydrolysis of uranyl ions, UO$_2$OH$^-$), and reaches the highest Rs around the neutral pH range. At a pH value higher than 7, the Rs decreases again. For the solutions which contain carbonate, the sorption ratio has a similar trend in an acid condition between the pH values 2 and 5.5. When the pH elevates to neutral value or higher, the Rs shows an early and very significant drop compared with carbonate free samples.

Figure 2.2 Sorption ratio (Rs, ml/g) of uranyl ions on silica gel as a function of pH. a) in absence of carbonate, b) in presence of 10-3 mol/l of total carbonate. Adapted from (Lieser et al., 1992).
Therefore, for the uranyl solutions with an absence of carbonate and the pH range between 3 and 5, the ion exchange formula on the surface of silica is shown as (2-2),

\[
\equiv \text{SiOH} + \text{UO}_2^{2+} \rightleftharpoons \equiv \text{SiOUO}_2^+ + \text{H}^+ \quad (2-2)
\]

For the higher pH values in weakly acid solutions, between pH 5-7, the formula of chemisorptions (hydrolytic adsorption) on silica surface are shown as (2-3) and (2-4),

\[
\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+ \quad (2-3)
\]

and

\[
\equiv \text{SiOH} + \text{UO}_2\text{OH}^+ \rightleftharpoons \equiv \text{SiOUO}_2^+ + \text{H}_2\text{O} \quad (2-4)
\]

For the pH values higher than 7 in weak alkaline solution, the sorption of uranyl on silica gel is formulated as (2-5) with higher hydrolysis uranyl ions,

\[
\equiv \text{SiOH} + (\text{UO}_2)_3(\text{OH})^- \rightleftharpoons \equiv \text{SiO(UO}_2)_3(\text{OH})_6^- + \text{H}_2\text{O} \quad (2-5)
\]

For the higher pH values in strong alkaline solutions, because of the higher concentration of hydroxide groups in the solution, the formula is shown as (2-6),

\[
\equiv \text{SiO}^- + (\text{UO}_2)_3(\text{OH})^- \rightleftharpoons \equiv \text{SiO(UO}_2)_3(\text{OH})_6^- + \text{OH}^- \quad (2-6)
\]

Eventually, at higher pH values between 13-14, the Si-O-Si bonds in silica gel are broken and dissolution begins (Lieser et al., 1992).

In addition, for higher uranyl concentration solutions, two possible phenomena in the sequence of the adsorption process might occur (Guibal et al., 1995) as shown in Figure 2.3. First, when the hydrolyzed uranium ions contact with the silanol groups, rapid adsorption will occur instantaneously and this reaction will reduce the uranyl concentration in the solution. The second phenomenon following the rapid adsorption is the surface precipitation. Based on the adsorption layer, the hydroxides and hydrous oxides form a
network structure near the silica surface by oxygen bridges between the metal atoms. Because this surface precipitation layer shows a good ion exchange property (Ahrland et al., 1960), the layer has the ability to adsorb continuously until it reaches chemical equilibrium status.

![Figure 2.3 The schematic diagram of silica gel surface precipitation model for the sorption of uranyl ions. Adapted from (Guibal et al., 1995)](image)

Uranyl ions also can be adsorbed on uranyl ion imprinted sol-gel glasses (Dai, Shin, Barnes, & Toth, 1997) and uranyl imprinted polymers (Bae, Southard, & Murray, 1999). The silica matrix with imprinted uranyl ion cavities shows a significant increase in affinity (Dai et al., 1997) and selectivity (Caprasse et al., 2002) of uranyl ions compared with silica gel, which has the same surface areas (Dai et al., 1997). These imprinted silica materials can be employed for uranyl ions concentration and also, simultaneously, the removal of uranyl ions from aqueous solution prior to spectroscopic investigation. The detection limit of uranium by this application can reach to $10^{-8}$ (M) (Metilda et al., 2007).

Considering the intra-structure of the porous materials, the increase of adsorption capacity is due to several factors, i.e. the large surface area induced by the surfactant template synthetic method, the high concentration of silanol surface functional ligands, and
the large pore openings of the materials allowing for access to the inner pore surfaces (Shin, Burleigh, Dai, Barnes, & Xue, 1999).

Finer porous silica materials have better sorption kinetic properties for uranyl ions. Compared with microporous materials, the sorption kinetics curve of mesoporous materials is faster. The adsorption equilibrium of mesoporous silica can reach within less than 15 min (see Figure 2.4) (Shin et al., 1999). On the other hand, uranyl also has better sorption kinetics than the other common heavy metals in the environment. The adsorption rates of the metal ions are $\text{UO}_2^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ (Tran et al., 1999).

In addition, acid solutions are reported as effective agent to remove uranium. The desorption efficiency can reach up to 90%, which is eight times the acid to uranium mole ratio in the solution. The silica materials therefore can be reused by desorption process (Michard et al., 1996).

![Figure 2.4](image)

**Figure 2.4** The adsorption kinetics on mesoporous and microporous materials. Adapted from (Shin et al., 1999).
Uranyl adsorption in soil

Soil accumulates many heavy metal ions mostly by adsorption. The reaction interfaces for heavy metal ions adsorbed in soils are mainly inorganic colloids, i.e. clays, metal oxides, and hydroxides. Some organic colloidal matter, i.e. humic matter, also provides interfaces for heavy metal adsorption (Bradl, 2004). On the other hand, the sorption and desorption mechanism of heavy metal ions still can be represented by thermodynamic analysis of two major factors about the ion distribution in the soil: the carbonate concentration and the function of pH values (Arkhipov, Medvedev, Grishina, & Fedorova, 1985).

Similar to the adsorption of heavy metal ions in soil, uranium adsorption in natural environments is strongly influenced by groundwater chemistry, especially pH, total dissolved carbonate concentration (Gabriel, Gaudet, Spadini, & Charlet, 1998; Morrison, Tripathi, & Spangler, 1995), and the uranyl concentration in the media (Greathouse & Cygan, 2006). The sorption ratio (Rs) of uranium in soil varies with no significant effect on soil texture or organic matter (Echevarria, Sheppard, & Morel, 2001). The pH values in soil is linearly correlated with “Log Rs,” and also correlated with the uranyl complexes; therefore, the existence of uranyl complexes shows various affinities for the soil as a function of pH in soil (Echevarria et al., 2001). The sorption of uranium in clay increases with the increase of the pH level and reaches a maximum in the range of near-neutral pH values. At a pH level higher than the neutral range, the sorption decreases due to the presence of aqueous uranyl carbonate complexes (Payne, Davis, Lumpkin, Chisari, & Waite, 2002).
For the uranyl desorption properties of soil, Dody has simulated the equivalent of 7,000 mm of rainfall percolated through the uranium-contaminated sandy soil. The result shows that there is only about 1/3 of uranyl desorption from the soil in a weak acid environment (Dody, Sapheir, Weiner, & Berant, 2006). On the other hand, there are many possible uranyl complexes in the texture of natural soil, i.e. uranyl hydroxide complexes, uranyl carbonate complexes, and uranyl phosphate complexes (B. C. Bostick, S. Fendorf, M. O. Barnett, P. M. Jardine, & S. C. Brooks, 2002). Among these surface complexes, the uranyl phosphate and uranyl carbonate complexes are highly disordered, and therefore they can contribute to the reversible sorption properties (B. C. Bostick et al., 2002).

In addition, for a detail expression, uranium is commonly found naturally as stable complexes with organic ligands in the form of organic colloid particles, and organic coating on quartz grains. For a higher pH level, some uranium is found on humic colloids as the potential mobile part of uranium (Sheppard & Thibault, 1992). When the pH value of humic containing soil lower than 5, the humic matter will attach on the reactive surface of quartz grains and become the immobile uranium in the soils (Crancon & van der Lee, 2003). Sheppard has used weak organic acids to leach uranium from soil (Sheppard & Thibault, 1992). However, they are unable to remove the uranyl from the coating surface. On the other hand, the humate is also reported as a factor which affects the adsorption of uranium on clay and is strongly pH dependent. The presence of humate can elevate the adsorption of uranium at pH 4-7.5 (depending on the concentrations of clay and humate) and suppress it at pH 8-12. (Benes, Kratzer, Vlckova, & Sebestova, 1998)
2.3 Uranium Fluorescence in solution

The photochemical reaction mechanism of uranyl fluorescence in aqueous solutions is known to involve the photoreduction process of uranyl ions from $\text{UO}_2^{2+}$ to $\text{UO}_2^+$ by reductants, and following the disproportionation process of these reduced uranyl ions from $\text{UO}_2^+$ to $\text{U}^{\text{IV}}$ species and $\text{UO}_2^{2+}$. The latter reaction is a very fast bimolecular process involving the collision of two reduced uranyl ions ($\text{UO}_2^+$). The intermediate reduced uranyl ions is usually very difficult to detect in this transition status (Burrows & Kemp, 1974). In a uranyl fluorescence spectrum, Kato found that the variation of the emission wavelengths, showing as a function of the excitation wavelengths, indicates that the exchange reaction is carried out only by the light adsorbed by uranium(VI) (Kato & Fukutomi, 1976). The photon adsorption band includes the weak spin-forbidden visible band (maximum adsorption band around 420nm) and the spin-allowed intense UV band (maximum adsorption band around 285nm). The quantum yield appears to be complex by both excitation sources (Kato & Fukutomi, 1976). Uranyl fluorescence lifetime varies by ligand exchange and the anion rate in a solution, which can prevent the quench effect by water (Masataka Moriyasu, Yu Yokoyama, & Shigero Ikeda, 1977). Uranyl fluorescence lifetime can be increased significantly by the addition of fluoride or phosphate, and moderately by sulfate. Though the longer lifetime can provide a larger quantum yield, however, the luminescence intensity is not strictly proportional to the luminescence lifetime (Masataka Moriyasu et al., 1977).
Optional excitation sources and environmental effects

Although photons are the most common excitation source of uranyl fluorescence, they are not the only source of it. If the uranyl is excited by electron bombardment, then the emission spectrum will be different from the emission spectrum which is excited by the energy from photons. In addition, energy transfer from water to the uranyl ion and excitation by water subexcitation electrons is another possible mechanism for the photochemical reaction (Gopinath, Hart, & Stevens, 1972).

For higher density excitation sources, the saturation rate of the excitation area is higher and results in the temperature increasing in the excited volume of the sample. This is caused by the heat released in the non-radiation decay process. Meanwhile, in the emission spectrum, the intensity of a relative shorter wavelength is decreased and the vibrational structure becomes broader (Kobayashi, 1978). Also, in the decay spectrum, the lifetime decreases while the temperature increases (Kirishima, Kimura, Tochiyama, & Yoshida, 2004; Leung, 1982; Leung & Tsang, 1979), because of the structural phase transitions (Leung, Hayashibara, & Spadaro, 1999) and the bimolecular quenching of triplet excitation in the crystal (Kobayashi, 1978). Other environmental factors, i.e. the variation of pressure (0.1-40 MPa), on the fluorescence properties are invisible compared with the temperature effect (Kirishima et al., 2004).

Uranium speciation

The fluorescence properties of uranyl compounds are caused by electronic transitions from three occupied molecular orbits, which govern the formation of the
characteristic ligand of uranyl, and the deactivation of electronic excitation (Syt'ko & Umreiko, 1998). In uranyl solutions around natural pH values (pH4 - pH7), uranyl and uranyl hydroxide complexes are commonly found in four different main forms (Clark et al., 1999), which are the uranyl ion (UO$_2^{2+}$), the monomeric form (UO$_2$(OH)$^+$), the dimeric form ((UO$_2$)$_2$(OH)$_2^{2+}$), and the trimeric form ((UO$_2$)$_3$(OH)$_3^+$) (Tsushima & Reich, 2001). The distribution of each uranyl hydroxide complex species in relation to different pH values in four different temperatures are illustrated in Figure 2.5. At room temperature, the uranyl ions predominate the uranyl hydroxide complex species in the uranyl solution. With the raising of environmental temperature, the uranyl species change their distribution and population fraction under different pH values.

![Speciation diagrams](image)

Figure 2.5 Speciation diagrams of uranyl ion and its hydroxide complexes in different temperature. [U]$=5 \times 10^{-5}$M; (m, n) = (UO$_2$)$_m$(OH)$_n^{(2m-n)^+}$. Adapted from (Kirishima et al., 2004)
The most significant change of the temperature effect at higher temperatures is a raising population ratio of the monomeric form, and the decreasing of other main uranyl compounds in aqueous solutions (Eliet, Grenthe, & Bidoglio, 2000; Kirishima et al., 2004).

In aqueous solutions, uranium concentration also affects the distribution of uranyl hydroxide complex speciation. At a higher uranium concentration, the uranyl ion is the major species. When the concentration of uranyl ions decreases, it causes the increase of the hydrolysis of uranyl and results in the higher ratio of uranyl in dimeric and trimeric forms (Lopez & Birch, 1997). The uranyl in trimeric form has a similar lifetime to the uranyl in dimeric form. Both the uranyl ions in dimeric and trimeric forms have higher emission intensities than the uranyl ions. In addition, the absorption and emission spectra show a significant red-shift in both uranyl hydroxide forms. (Lopez & Birch, 1997)

In the environment, uranyl carbonate complexes $\text{UO}_2(\text{CO}_3)^{4-}$ and $\text{UO}_2(\text{CO}_3)^{2-}$ are common uranyl compounds in seepage water. Unfortunately, they are non-fluorescence species. Bernhard had a research about the interaction of calcium on uranyl carbonate complex. The calcium ion becomes a solution to detect uranyl in seepage water through fluorescence technique (Bernhard, Geipel, Brendler, & Nitsche, 1996b).

To identify the uranyl-silicate complex, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was employed to test the fluorescence of tetramethylorthosilicate (TMOS). The main fluorescence bands of the complex $\text{UO}_2\text{Si(OH)}_3^+$ are centered at 500, 521, 544 and 570 nm. Fluorescence lifetimes were obtained for two complexes: the free uranyl cation of $1.7 \pm 0.3 \ \mu s$, and the 1:1 silica-uranyl complex of $19.0 \pm 4 \ \mu s$ (Moll, Geipel, Brendler, Bernhard, & Nitsche, 1998).
2.4 Uranium Fluorescence Quenching

Although most of the uranyl complexes characteristically emit identifiable spectra, several environmental matters might quench the fluorescence. Some powerful quenchers can even eliminate all the fluorescence signals from uranyl.

These quenchers can affect the fluorescence by colliding with the excited molecules (Dynamic quenching) (Yokoyama, Mouiyasu, & Ikeda, 1976) or by forming nonfluorescent complexes with the fluorophore molecules (Static quenching) (Matsushi.R, 1972; Matsushi.R & Sakuraba, 1971; Sakuraba & Matsushi.R, 1971; Taha & Morawetz, 1971). As a result of collisions between fluorophore and quenchers, dynamic quenching causes the partial loss of fluorophore’s energy. The fluorescence intensity and lifetime of the fluorophore molecules are lower because of the loss of excited energy. The static quenching due to some of the fluorophore molecules binding to the quencher’s ligand forms nonfluorescent complexes. Because part of the fluorophore becomes nonfluorescent, the overall fluorescence intensity becomes lower. However, some of the fluorophore molecules do not interact with the quenchers; the lifetime of the fluorophore will still be the same.

The electron transfer (redox reaction) mechanism plays an important role in the aqueous fluorescence quenching process. There are not any changes in the chemical species found in the quenching process. The quenching mechanism is due to the collision followed by the electron transfer from the redox reaction process as shown in Figure 2.5.
In the beginning of the collision process, a uranyl ion (U(VI)) should be excited by a photon with specific energy (ΔE), in which one of the electrons would be pumped up to the excited state (U(VI)*) and leave a vacancy in the ground state (see Figure 2.6). With the collision of a quencher ion in the solution, the quencher (Q) would donate an electron to the excited uranyl molecule (U(VI)*) to fill in the vacancy in the ground state (U(V)), and the quencher ion itself becomes an oxide state (Q⁺). Eventually, the reduced uranyl molecule (U(V)) would give back an electron to the oxide state quencher (Q⁺) to finish the redox reaction and return to the original state (Yokoyama et al., 1976).
Uranyl fluorescence can be quenched by water molecules colliding in an aqueous solution (M. Moriyasu, Y. Yokoyama, & S. Ikeda, 1977b). The electron transfer mechanism can also explain the uranyl quenching effect involves the halide ions (i.e. Cl⁻, Br⁻, and I⁻) (Simonin et al., 2003; Yokoyama et al., 1976) and some metal ions in a lower valence state (i.e. Fe²⁺, Eu³⁺) (M. Moriyasu, Y. Yokoyama, & S. Ikeda, 1977a). Because some molecules have a higher affinity to uranyl ions and no tendency to deactivate excited uranyl ions (i.e. phosphate and fluoride ions) (Beitz & Williams, 1997), they have a high coordinating ability to surround the uranyl ions so that they can prevent the possibility of collision by water molecules. The addition of phosphate and fluoride ions to the uranyl solution increases the fluorescence lifetime significantly (Krtíl, Kuvík, & Spevackova, 1985; Yokoyama et al., 1976). For a similar reason, once a uranyl ion has formed a new compound in a solid state, i.e. doped in silica glasses through a sol-gel process, the mobility of the quencher is lower than in aqueous solutions. Therefore, the quenching
efficiency is found to be much less than that in aqueous solutions (Dai, Metcalf, DelCul, & Toth, 1996; Dai, Xu, Metcalf, & Toth, 1996).

In addition, because the possibility of collision in an aqueous solution is highly related to temperature, the fluorescence intensity and lifetime decreases significantly with the rise of temperature (M. Moriyasu et al., 1977b; Renthal & Cha, 1984). When the temperature drops to 77 degrees K or lower, the influence of the quenchers becomes negligible (Stepanov, Preobrazhenskaya, & Nikitina, 1984).

For organic compounds, uranyl fluorescence can be quenched by aromatic molecules (Matsushi.R & Sakuraba, 1971; Renthal & Cha, 1984), aliphatic alcohols (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, and s-butyl alcohols) (Sakuraba & Matsushi.R, 1971), and carbonate radicals (Meinrath, 1997). They are caused by nonelectronic-electronic energy transfer and belong to the static quenching. They form nonfluorescent complexes in the solution, and the quenching rate can be affected by the viscosity and polarity of the medium (Matsushi.R & Sakuraba, 1971; Miguel, Formosinho, & Leitao, 1986) as well as changes in the alcohol structure (the polar substituent effect) (Sakuraba & Matsushi.R, 1971).

Some of the fluorescence quenching character has been employed as a method to estimate uranyl concentration. Varineau elevated the trace uranyl concentration by using a membrane to prohibit the anionic quenchers from entering the analysis cell. The detectability over a range of $10^{-4}$ to $10^{-9} \text{M}$ in aqueous samples (Varineau, Duesing, & Wangen, 1991). On the contrary, daSilva also applied uranyl as a quencher to other fluorophores as well (daSilva, Machado, & Oliveira, 1996).
2.5 pH and Fluoride Effect on Uranium Fluorescence

In an aqueous solution, uranyl exists in different uranyl complexes in relation to the variation of the pH of the solution. It causes several species of uranyl hydroxide complexes and results in different fluorescence lifetime and spectra (Couston, Pouyat, Moulin, & Decambox, 1995; Eliet, Bidoglio, Omenetto, Parma, & Grenthe, 1995; Moulin, Decambox, Moulin, & Decaillon, 1995). At pH 1, monoexponential luminescence decay is found in the solution, which indicates that free uranyl ions predominate the uranyl species. When the pH value rises to 3, the luminescence undergoes a bi-exponential decay. The decay rate of the longer lifetime component depends on pH. The bi-exponential decay can be interpreted in terms of the deactivation of the excited uranyl aquo-ions and the hydrolysis product of uranium (Arvis, Rousseau, & Hickel, 1990). At pH 10, the signal of the fluorescence decay disappears. In this case, the quenching of the fluorescence is due to an intramolecular process (Arvis et al., 1990). For the alkaline pH range 10–12, the (1, 3) hydroxo-complex was found to predominate.(Eliet et al., 1995)

In aqueous solutions, the fluorescence from each different uranyl complex shows a different intensity. The fluorescence efficiency of the uranyl dimeric form (\(\text{UO}_2\text{O}_2\text{O}_2\text{H}^+\)) is found to be 7 to 85 times higher than the free uranyl ion (\(\text{UO}_2^{2+}\)), and also the uranyl trimeric form (\(\text{UO}_2\text{O}_2\text{O}_2\text{H}^+\)) is 3 to 4 times higher than the free uranyl ion and the monomeric form (\(\text{UO}_2\text{O}_2\text{H}^+\)) (Eliet et al., 1995). For this point of view, relatively small concentrations of uranyl species might contribute to the most fluorescent intensity of aqueous uranyl solutions.
2.6 Surface Analysis of silica-uranium interaction

Uranyl ions have a very strong affinity to interact with silica materials. On the silica material surface, the silanol groups interact with uranyl hydroxide complexes in several different forms, depending on the pH in the solution, as well as the concentration of uranyl ions and electrolytes (Glinka & Krak, 1995). Uranyl ions demonstrate different photochemical properties when they are bound to silica materials, as compared to uranyl aqueous solutions (Wheeler & Thomas, 1984). The excited cationic uranyl ions bind to the anionic silica gel network, producing electrostatic attractive or repulsive forces between the gel network and the electrolytes. The silica gel network, therefore, can provide the ability to prevent the effect from the quenchers (Thomas & Wheeler, 1985). In addition to the topographic protection, uranyl is extremely close to the silica surface, and therefore prevents quenching by water molecules (Lopez & Birch, 1996).

Uranyl silica complexes

The uranyl-silica surface complex model includes three surface species (Gabriel et al., 2001). In extremely acidic solutions (i.e. pH 1-3), silica gel is not able to adsorb uranyl ions on the surface. Under mildly acidic conditions (i.e. pH 5), the uranyl silica complexes are characterized as SiO$_2$UO$_2$. In neutral pH to mildly alkaline conditions, the complexes become SiO$_2$UO$_2$OH$^-$. Moreover, at higher pH values (i.e. pH 9) and carbonate abundant environments, a uranyl–silica–carbonate complex, SiO$_2$UO$_2$OHCO$_3$$_3^-$, may occur and predominate the surface complexes. Among these surface species, most of the uranyl
complexes show significant fluorescence, except the higher carbonate species, which were found to be nonfluorescent (Gabriel et al., 2001).

**Uranyl –silica structure by EXAFS**

Extended X-ray adsorption fine structure (EXAFS) is one of the precise methods to estimate the structure of uranyl complexes on the silica surface since 1996. The main characteristic of the uranium surface species is two oxygen coordination shells in the equatorial uranyl plane (Reich et al., 1996). From the energy analysis of a uranyl ion adsorbed on a silica surface, an investigation shows that a uranyl ion may interact with the silica surface through one or two water molecules (Glinka, Jaroniec, & Rozenbaum, 1997). Wheaton further applied the EXAFS technique on the uranyl adsorption by silica gel. The geometry optimization shows that there are two types of bridged structures for uranyl silicates: the uranyl monosilicate (UO$_2$SiO$_4$H$_2$) and the uranyl disilicate (UO$_2$Si$_2$O$_7$H$_4$) (Wheaton, Majumdar, Balasubramanian, Chauffe, & Allen, 2003). Walter also investigated the geometry of uranyl compound on silica surface. At a mildly acidic condition (i.e. pH 5.0-5.8), the monosilicate bidentate uranium(VI) surface complex has a distance of 3.09 Å between uranium and silicon, and a distance of 2.23 Å and 2.44 Å between uranium and oxygen (Walter, Arnold, Geipel, Scheinost, & Bernhard, 2005).

Molecular dynamics simulations are employed to study the structure and dynamics of the uranyl ion in solutions and interactions with hydrated quartz surfaces. The uranyl coordination shell shows pentagonal bipyramidal symmetry, with water molecules, hydroxide, and carbonate ions on the shell (Greathouse, O'Brien, Bemis, & Pabalan, 2002).
Outer-sphere surface complexes formed at the singly protonated surface are aggregated by hydrogen bonding between a coordinating water molecule and the surface. Inner-sphere surface complexes are formed at the partially deprotonated surface, with water and surface oxygen atoms equidistant to the uranium atom (Greathouse et al., 2002). The bond distances between uranium and the equatorial oxygen atoms are from 2.34 Å to 2.37 Å (Hennig, Reich, Dahn, & Scheidegger, 2002).

**X-ray photoelectron spectroscopy (XPS) study**

The electronic structure of a uranyl nitrate hydrate has been investigated by XPS (Hirata et al., 1997). Uranyl silica complexes are also investigated by XPS to identify their chemical component. By calculating the binding energy (BE), the result shows two uranyl components on the silica surface – the high binding energy component and the lower binding energy component (Kowal-Fouchard, Drot, Simoni, & Ehrhardt, 2004a). A high binding energy component, increasing in relative proportion with the rising pH from an acidic condition to the neutral condition, has U(VI) oxide hydrate character, and can be the polynuclear surface oligomers or amorphous surface precipitates. On the other hand, a lower binding energy component could be the monomeric uranyl surface complex (Froideval, Del Nero, Barillon, Hommet, & Mignot, 2003).

**2.7 Hypothesis Model**

In this research, standoff detection of trace uranyl in contaminated soil by nanoporous silica materials includes three main mechanisms: wicking effect and water
evaporation on the surface of nanoporous silica materials to pump up uranium from the soil, ion exchanging and precipitation to accumulate higher concentration of uranium on the surface of silica materials, and directed fluorescence to avoid the scattering waste of an emission signal. Among these mechanisms, the silanol group on the silica surface is the trigger to kick off the sequence of mechanisms.

**Wicking effect and water evaporation**

Nanoporous silica materials have a large surface area and, in addition, they are made with hydroxide ligands, or silanol groups, on the surface. Because the silanol group has highly hydrophilic property by the attraction of hydrogen bond, an aqueous solution can easily be sucked into the silica matrix. In a natural pH range (pH4 - pH7), though part of the uranyl is adsorbed on silica based soil, however, the uranyl still can migrate in the form of uranyl attached colloid particles and some small amount of free uranyl ions (Sheppard & Thibault, 1992). In addition, because nanoporous silica material has a very high surface area, the water in silica materials easily evaporates on each micro surface. Combined with the wicking and evaporating mechanisms, the uranyl attached colloid and free uranyl ions can be extracted from the soil by pumping out the ground water and, in advance, be accumulated on the surface of nanoporous silica materials.

**Ion exchanging**

Once the uranyl migrates from the soil onto nanoporous silica materials, the silanol group will react with the uranyl ion as an ion exchanger (Ahrland et al., 1960). This silanol
group has a very high affinity to uranyl ions and can adsorb uranyl by an ion exchange mechanism. When the hydrolyzed uranium ions contact with the silanol groups, rapid sorption occurs instantaneously. Nanoporous silica materials have a high coordinating ability to surround the uranyl ions so that they can prevent the quenching possibility by water molecules and form compounds with a longer fluorescence lifetime. In addition, because the uranyl can be continuously pumped up by ongoing evaporation and the wicking effect, these following uranyl ions start to precipitate on the silica surface as a sorption layer (Guibal et al., 1995). Based on the sorption layer, the hydroxides and hydrous oxides form a network structure near the silica surface by oxygen bridges between the metal atoms. Because this surface precipitation layer shows good ion exchange properties (Ahrland et al., 1960), the layer has the ability to adsorb continuously until it reaches the chemical equilibrium status. This layer provides high concentrated uranyl on the silica materials surface and, therefore, provides higher fluorescence detectability by efficiently elevating the fluorescence intensity.

**Directed fluorescence**

To avoid the scattering waste of a fluorescence emission signal, we need an optical device to direct the fluorescence emission from the fluorophore directly back to the photon counter. In this research, we used the sapphire ball lens, for the suitable refractive index and the transparency for UV light, to direct the emission straight back to the detector.
3.1 Experimental Design

From the hypothesis, uranyl fluorescence can be enhanced by the accumulated higher concentration of uranyl ions, anti-quenching uranyl-silica compound, and a directed fluorescence device. To study these mechanisms, this research focused on three topics: the ability of adsorption of uranyl and the enhancement of uranyl fluorescence by silica gel, the uranyl fluorescence properties from different silica materials and the surface uranyl compounds, and directed fluorescence.

The adsorption of uranyl and the enhancement of uranyl fluorescence

Nanoporous silica materials have large surface area and silanol groups on their surface. Therefore, they have very high potential to precede the adsorption of the uranyl ions through an ion exchange reaction. In the first topic, we started from the investigation of the silica gel as a solid fluorescence enhancer in a trace uranyl concentration solution in order to compare the fluorescence intensity and lifetime of the application of the silica gel. Uranyl extraction from different types of soil by silica gel was tested to investigate the pump up mechanism and the actual affinity competition to natural organic compounds with
absence of carbonate. In addition, potential uranium containing areas might associate with some change in the environment, i.e. the change in pH, and fluoride ion concentration. Therefore, we also test the silica gel in different pH and various fluoride concentrations to examine how the fluorescence properties change with environment factors.

**Uranyl fluorescence properties from different silica materials**

There are many species of nanoporous silica materials available on the market, but not all of them yield the same performance of fluorescence enhancement. In the second topic, the particle size, pore size, and the shape of some silica materials available on the market are investigated through fluorescence spectroscopy with uranium-contamination. The fluorescence intensity and decay lifetime of these uranium-contaminated silica materials are recorded to determine which kind of silica material has the best performance of the enhancement of uranyl fluorescence signals.

Except the dried status, the water which is contained inside the porosity of the silica materials is discussed for the physical effect on the uranyl fluorescence enhancement. The water contained ratio and the ability to lock the water in the porosities of silica materials is also recorded to compare the physical enhancement in different shapes.

X-Ray Photoelectron Spectroscopy (XPS) is used to identify the uranyl compounds on uranium-contaminated silica materials through the detection of the element distribution near the surface layer. In this section, we measured the binding energy (BE), the full width at half maximum (FWHM), and the atom percentage (At %) to assist the fluorescence spectroscopy to identify the uranyl-silica interface mechanism.
Directed fluorescence (DF)

In the third topic, we introduce an optical device to enhance the fluorescence emission intensity. Retro-refraction theory is applied in this investigation. Ball lenses with different refractive indexes were tested to determine the most feasible ball lens for standoff detection. The properties of the optical device are studied through 5 different conditions, including whether the uses of silica gel and the optical device or not to verify the benefit of the DF system. The angle dependence is also tested on the usage of the ball lens to learn the fluorescence intensity as a function of detecting angle.

3.2 Materials

Silica materials

Silica materials, including silicon dioxide nanopowder, nanoporous and mesoporous silica gel, and mesostructured silica, are investigated in this study (see Table 3.1). Silicon nanopowder is obtained from Sigma-Aldrich with the particle size in the range of 5-15 nm and a large surface area (about 640 m²/g). It is made with a nonporous structure as a control in this research. Silica gel materials have an amorphous structure obtained either from Acros Organics or Sigma-Aldrich with the particle size varying from 5 μm to 650 μm, the average pore size varying from 22 Å to 150 Å, and a various surface areas ranging (from 300 m²/g to 800 m²/g). These silica gel materials are commonly found for column chromatography purpose with ultrapure grade. Mesostructured silica materials are obtained from Sigma-Aldrich with a powder form. These materials have unique shape with an unit
cell size varying from 4.5 - 11.6 nm, and an average pore size different from 23 Å to 71 Å. Because the mesostructured silica materials have the smallest particle size, they have relatively largest surface area, in the range from 750 m²/g to 1000 m²/g, among these silica materials.

**Table 3.1 Physical properties of silica base materials**

<table>
<thead>
<tr>
<th>Item No.</th>
<th>Company</th>
<th>Description</th>
<th>Particle Size</th>
<th>Pore Size</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sigma-Aldrich</td>
<td>Silicon dioxide, nanopowder, 99.5% metals basis</td>
<td>5-15 nm</td>
<td>N/A</td>
<td>640</td>
</tr>
<tr>
<td>2</td>
<td>Acros Organics</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>5-15 μm</td>
<td>60 Å</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>Acros Organics</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>40 Å</td>
<td>600</td>
</tr>
<tr>
<td>4</td>
<td>Acros Organics</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>60 Å</td>
<td>550</td>
</tr>
<tr>
<td>5</td>
<td>Acros Organics</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>150 Å</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 10180, 70-230 mesh</td>
<td>63-200 μm</td>
<td>40 Å</td>
<td>750</td>
</tr>
<tr>
<td>7</td>
<td>Acros Organics</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>60-200 μm</td>
<td>60 Å</td>
<td>515</td>
</tr>
<tr>
<td>8</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 7734, 70-230 mesh</td>
<td>63-200 μm</td>
<td>60 Å</td>
<td>550</td>
</tr>
<tr>
<td>9</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 10184, 70-230 mesh</td>
<td>63-200 μm</td>
<td>100 Å</td>
<td>300</td>
</tr>
<tr>
<td>10</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 923, 100-200 mesh</td>
<td>75-150 μm</td>
<td>30 Å</td>
<td>480</td>
</tr>
<tr>
<td>11</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Davisil®, Grade 644, 100-200 mesh</td>
<td>75-150 μm</td>
<td>150 Å</td>
<td>300</td>
</tr>
<tr>
<td>12</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 12, 28-200 mesh</td>
<td>75-650 μm</td>
<td>22 Å</td>
<td>800</td>
</tr>
<tr>
<td>13</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Davisil®, Grade 636, 35-60 mesh</td>
<td>250-500 μm</td>
<td>60 Å</td>
<td>480</td>
</tr>
<tr>
<td>14</td>
<td>Sigma-Aldrich</td>
<td>Silica, Mesostructured, MCM-41</td>
<td>4.6-4.8 nm</td>
<td>23-27 Å</td>
<td>1000</td>
</tr>
<tr>
<td>15</td>
<td>Sigma-Aldrich</td>
<td>Silica, Mesostructured, MSU-H</td>
<td>11.6 nm</td>
<td>71 Å</td>
<td>750</td>
</tr>
</tbody>
</table>
Uranyl

Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from American Master Tech Scientific at A.C.S. Reagent grade and was used without further purification.

Others

- Sulfuric acid solution was obtained from Fisher Scientific.
- Sodium hydroxide was obtained from Acros Organics in pellet form at 97+% purity.
- Poly(vinyl alcohol) $M_w$ 89,000-98,000 was purchased from Sigma-Aldrich; according to it has about 1% of residual acetyl groups.
- Sea sand was obtained from Fisher Scientific and was used as is.
- The ball lens was obtained from Edmund Optics which has 6.35 mm in diameter. Sapphire material for the ball lenses was used for its excellent UV transparency.
- Indium foil from Sigma Aldrich.
3.3 Instruments

3.3.1 Quanta Master spectro-fluorometer

Fluorescence spectra are recorded by Quanta Master spectro-fluorometer (see Figure 3.1) obtained from Photon Technology International (PTI). It has 4 optional functions: fluorescence steady state excitation scan, fluorescence steady state emission scan, fluorescence decay scan, and timebased fluorescence steady state measurements.

**Fluorescence measurement for liquid samples**

The instrument is equipped with a xenon flash lamp (1), L4633, as the excitation source. The wavelength of excitation light is controlled by a single monochromator (3) and assisted by a series of shortpass filter lens (7). The shortpass filter lens can stop the longer wavelengths light and allow only the controlled shorter wavelength light to pass through. After the light passing through the excitation monochromator, a tube (4) (PMT, R1527P by

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6 2 filters in series from Edmund Optics, Inc., TS shortpass filter 450nm, and 500nm.
HAMAMATSU) is set up for the signal compensation. The resolution and the quantity of passing photons depend on the slits (2) which are controlled manually by a micrometer\textsuperscript{7}. The light then passes through a focusing lens (8) and gets into liquid sample (9). The sample holder is a 10 X 10 mm cuvette holder equipped with a variable speed stirrer. Liquid sample is put in a quartz cuvette and the fluorescence reaction would proceed within nano seconds. The emission light would pass a focusing lens (8) and a longpass filter lens\textsuperscript{8}. The longpass filter lens is employed to stop the shorter wavelength light scattered by the liquid sample from the excitation source, because the scattered light may cause the doublet or triplet effect on the emission spectrum and misleading the results. After another set of monochromator (11), the emission photon is collected by a photomultiplier tube (12) (R928P by HAMAMATSU). The component parts of the Quanta Master for solution fluorescence detection as shown in Figure 3.2.

**Fluorescence measurement for solid samples**

For solid samples measurement, we use the same excitation source, monochromator sets, and sensor devices comparing with measurement of liquid samples. In addition, because light cannot pass through solid samples, we use the optical fibers to guide the light. When the excitation light passes through the liquid sample holder (9), the light passes

\textsuperscript{7} 0.25 mm of the reading is equal to 1 nm of the slit opening mechanically.

\textsuperscript{8} 4 optional Longpass filters from Edmund Optics, Inc.

<table>
<thead>
<tr>
<th>Part No.</th>
<th>Stopband Limit λ_s (nm)</th>
<th>Cut-Off Position λ_c (nm)</th>
<th>Passband Limit 1 λ_p1 (nm)</th>
</tr>
</thead>
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<td>NT46-421</td>
<td>300.00</td>
<td>315±6</td>
<td>365.00</td>
</tr>
<tr>
<td>NT46-424</td>
<td>370.00</td>
<td>400±6</td>
<td>475.00</td>
</tr>
<tr>
<td>NT45-063</td>
<td>410.00</td>
<td>455±6</td>
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<tr>
<td>NT45-064</td>
<td>470.00</td>
<td>515±6</td>
<td>570.00</td>
</tr>
</tbody>
</table>
through a series of focusing lenses (8), shortpass filter (13), and excitation fiber light guide (14) and reach to the solid sample. After the fluorescence emitting from the solid sample, the light passes through the emission fiber light guide (15), the longpass filter (16). Finally, the light passes through the monochromator (11) and detected by PMT (12).


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9 Hoya U-330 from Edmund Optics, Inc.
10 3 optional Longpass filters from Edmund Optics, Inc.

<table>
<thead>
<tr>
<th>Part No.</th>
<th>Stopband Limit $\lambda_s$ (nm)</th>
<th>Cut-Off Position $\lambda_c$ (nm)</th>
<th>Passband Limit $\lambda_{p1}$ (nm)</th>
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<td>280.00</td>
<td>320±6</td>
<td>470.00</td>
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<tr>
<td>NT46-580</td>
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<td>380±5</td>
<td>430.00</td>
</tr>
<tr>
<td>NT46-425</td>
<td>360.00</td>
<td>420±6</td>
<td>530.00</td>
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</tbody>
</table>
Chapter 4
Environmental Uranyl Adsorption on Silica Gel

4.1 Introduction

Uranium is a ubiquitous, naturally occurring element but elevated (above natural background) uranium concentrations in soil and water have been associated with activities such as uranium mining, nuclear fuel production and disposal (Bernhard et al., 1996a; Benjamin C. Bostick et al., 2002; deLemos et al., 2008; Morris et al., 1996; Riley et al., 1992). Uranium can exist in several oxidized forms but in contact with oxygen, uranium usually occurs in the hexavalent (VI) form as the uranyl ion (UO$_2^{2+}$). Uranyl is water soluble and, therefore, can readily spread through soil matrices. In addition, uranyl ion shows a very characteristic fluorescence spectrum once irradiated by UV light. Therefore, the optical, fluorescence-based method can be used for uranyl detection. However, uranyl detection in soil by fluorescence method has a detection limit and needs some fluorescence enhancement strategies. In this chapter, we used silica gel as a solid-state fluorescence enhancer which can be applied on the surface of a contaminated soil where it adsorbs and accumulates uranyl and enhances the fluorescence signal intensity.
In this chapter, we study the possibility to use silica gel as an enhancer to uranyl fluorescence from contaminated soil through some fluorescence experiment results. The experiment starts from the adsorption and enhancement test by dropping small amount of silica gel into uranyl solution. In this preliminary test, the silica gel was demonstrated the strong adsorption ability and powerful enhance ability which can enhance both the intensity and lifetime. In addition, because of the persistence of vision effect of human eyes, the uranyl compound which has longer lifetime provides much more enhancement when use bare eye to observe the experiment.

pH can affect the adsorption ability of silica gel and the forming of uranyl compound on the surface of silica gel. We measured the uranyl fluorescence spectrum on nanoporous silica gel between pH 1-13 by titrating sulfuric acid and sodium hydroxide with the absence of carbonate. The results showed that the uranyl ions can be adsorbed on the silica gel surface when pH higher than 3 and in lower ionic strength environment. The uranyl compound on silica gel surface strongly depends on pH value. The fluorescence intensity and the peak positions in relation to pH are discussed. We showed that silica gel is a very good enhancer for pH 4-6.5, which is the common range for natural soils.

Uranium hexafluoride UF$_6$ is used in nuclear cell enrichment processes and can react with water to form uranyl fluoride and hydrofluoric acid (see formula 4-1) which has high potential to reduce the soil pH$^{11}$:

$$\text{UF}_6 + 2\text{H}_2\text{O} \rightarrow \text{UO}_2\text{F}_2 + 4\text{HF}$$  \hspace{1cm} (4-1)

$^{11}$ DUF6 Management: What happens if a cylinder of uranium hexafluoride leaks?  
http://web.ead.anl.gov/uranium/faq/storage/faq21.cfm
Here we studied the effect of fluoride in uranium-contaminated solution and silica gel matrix through the fluorescence emission intensity and lifetime. The result indicated that the presence of fluoride ions significantly increases the lifetime of uranyl fluorescence both in solution and in silica gel. Fluoride ions in the mixture also produce well defined vibronic spectra with some red shift. The specific effects of fluoride on the uranyl emission spectra may help to identify the presence of fluoride contamination with uranyl.

Silica gel has been employed as a passive sensor material on uranium detection in contaminated sand (Pestov, Chen, Nelson, Anderson, & Tepper, 2009). However, the feasibility of silica gel for detecting uranium from contaminated natural soil is not investigated yet. We used nanoporous silica gel to extract uranyl ions from 4 natural soil samples, including clay, silt (organic matters), and sand, which are contaminated with 100ppm of uranyl. It is shown that silica gel can be used to extract water containing dissolved uranyl from contaminated natural soils and results in significantly enhanced fluorescence intensity and lifetime. Because uranyl fluorescence is depended on pH, we also developed laboratory protocol for soil surface pH measurement.

**4.2 Experimental process**

**4.2.1 Test of silica gel adsorbing uranyl ions**

**Uranyl solution preparation.**

Uranyl solution was prepared by 3mL of deionized (DI) water and 6 μL of 0.01M uranyl nitrate in a quartz cell as $2 \times 10^{-5}$ M concentration.
Adsorption test.

Silica gel #7 in Table 3.1 was first put in DI water to wet the silica and prevent further breakage of silica amorphous structure, which may form silica colloid in solution. After 30 minutes of silica particles settlement, we took out 321.5mg of silica – water mixture (actual silica gel 135mg) and put into the cell which is containing 3mL of $2 \times 10^{-5}$ M uranyl solution. The cell was well mixed and then we left the silica particles to settle down for one day. Finally, we took out the bottom silica gel and the middle layer uranyl solution, and put them in separate Petri-dishes as fluorescence test samples.

Fluorescence measurement.

Fluorescence spectra were recorded with the Quanta Master spectrofluorometer (see Chapter 3.3). All tests were performed at an excitation wavelength of 285nm. Emission spectra were recorded in the range from 400 - 650nm. Decay-curve was recorded by the excitation wavelength at 285nm and the emission wavelength at the highest peak position from former emission results. Decay curves were calculated and transferred into lifetime by PTI FeliX32.

4.2.2 Test of pH effect

Sample preparation

Titration samples were prepared by mixing 10mL of deionized water, 500mg of silica gel #3 (see Table 3.1), and 0.55mL 0.01M (1.5mg UO$_2^{2+}$) uranyl nitrate in a 15ml PP beaker. After careful mixing, the samples were sealed and aged for 1 day to allow uranyl to interact with the silica gel.
pH measurement

pH was adjusted by titrating sulfuric acid or sodium hydroxide. pH values were measured through Orion 3-Star pH-meter and by Orion 8103BN ROSS combination pH electrode. The samples were mixed carefully and held for 1 minute to settle the silica gel before measuring the pH value.

Fluorescence measurement.

Fluorescence spectra were recorded with the Quanta Master spectrofluorometer (see Chapter 3.3) 5 minutes after pH measurements. All tests were performed at an excitation wavelength of 285nm. Emission spectra were recorded in the range from 400 - 650nm.

4.2.3 Test of fluoride effect

Uranyl nitrate solution with potassium fluoride (KF).

3mL 0.01M uranyl nitrate and 10.44 mg of potassium fluoride were placed into a quartz cell to simulate the final compounds of uranium hexafluoride hydrolysis: a molar ratio of uranyl to fluoride as 1:6. Addition of potassium fluoride to uranyl solution increases the pH. To obtain solutions at pH 1.4-5.4 sulfuric acid was added as indicated in Table 4.1. pH values were measured by Orion 3-Star pH-meter equipped with Orion 8103BN ROSS Combination pH Electrode.

Preparation of uranyl and KF contaminated sand samples.

Silica. 3mL of DI water and 420 µL 0.01M uranyl nitrate were placed in plastic Petri dishes and well mixed. 25.2 µL or 126 µL of 1M KF were placed in the Petri dishes as 1:6 and 1:30 in proportion of uranyl to fluoride. 10 grams of sand was then added into the
Petri dishes to produce a contamination equivalent to 100ppm of uranium. After careful mixing, the samples were aged for 3 days in hermetically sealed Petri dishes to let uranyl interact with the sand. Before fluorescence test, 5mg of silica gel #3 (see Table 3.1) was added on the top surface of the contaminated sand sample and then keep 30 minutes for adsorption mechanism.

<table>
<thead>
<tr>
<th>pH</th>
<th>Concentration of used H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Amount of H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; is added to 3ml</th>
<th>Total mole of H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>0.02M</td>
<td>40 μL</td>
<td>0.8x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>4.5</td>
<td>1M</td>
<td>2.5 μL</td>
<td>3.3 x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.8</td>
<td>1M</td>
<td>6 μL</td>
<td>9.3 x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.7</td>
<td>1M</td>
<td>50 μL</td>
<td>5.9 x10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.0</td>
<td>1M</td>
<td>100 μL</td>
<td>1.6 x10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.4</td>
<td>1M</td>
<td>500 μL</td>
<td>6.6 x10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

**Fluorescence measurement.**

Fluorescence spectra were recorded with the Quanta Master spectrofluorometer (see Chapter 3.3). All tests were performed at an excitation wavelength of 285nm. Emission spectra were recorded in the range from 400 - 650nm. Decay-curve was recorded by the excitation wavelength at 285nm and the emission wavelength at the highest peak position from former emission results. Decay curves were calculated and transferred into lifetime by PTI FeliX32.
4.2.4 Test of uranyl ions extracted in natural soil by silica gel

Preparation of uranium-contaminated soil samples.

Two natural clay and silt samples were collected around Richmond VA. Dry sea sand was obtained from Fisher Scientific. Sand samples were prepared by wetting dry sand with 13% of DI water. Table 4.2 is a list of the soil and sand samples tested in this research. Original soil samples were placed in plastic Petri dishes and 42µL 0.01M uranyl nitrate was added per 1 gram of soil. After careful mixing, the samples were aged for 1 day in covered Petri dishes to allow uranyl to interact with the soil. 5mg of silica gel #3 (see Table 3.1) was then placed on the surface of the sample. Soil pH measurements were performed using an Orion 3 star with ROSS electrode 81-35BN from Thermo Electron Corporation.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Soil texture</th>
<th>Color</th>
<th>Sample Collection Location</th>
<th>Typical condition</th>
<th>Environmental neighboring</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- UC</td>
<td>54% Sand 17% Silt 29% Clay *Sandy Clay Loam*</td>
<td>dark tan</td>
<td>Eastern Piedmont soil, Montpelier VA Upland area Est. soil penetration: 6 in</td>
<td>dry zone</td>
<td>wooded area</td>
</tr>
<tr>
<td>2- SF</td>
<td>48% Sand 31% Silt 21% Clay *Loam*</td>
<td>brown</td>
<td>Eastern Piedmont soil, Montpelier VA Semi-permanent flood zone Est. soil penetration: 6 in</td>
<td>wet zone</td>
<td>wooded area</td>
</tr>
<tr>
<td>3- JA</td>
<td>44% Sand 45% Silt 11% Clay *Loam*</td>
<td>dark brown</td>
<td>James River stream bed Hopewell VA Bottom of a shallow channel Est. soil penetration: 1 ft</td>
<td>submerge d</td>
<td>nature preserve, downriver from industrial area</td>
</tr>
<tr>
<td>4- SC</td>
<td>Sand</td>
<td>light tan</td>
<td>Fisher Scientific (Sea Sand standard)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
**Fluorescence measurement.** Fluorescence spectra were recorded with the Quanta Master spectrofluorometer. All tests were performed at an excitation wavelength of 285nm. Emission was recorded in the area of uranyl fluorescence at 400 - 650nm.

**pH measurement on soil samples.** We measure pH by Orion 3 star with ROSS electrode 81-35BN from Thermo Electron Corporation. The electrode has a flat bottom surface and pH was measured with slight pressure on the soil surface. We compared our data with a commonly used protocol for soil pH measurement: samples are diluted with DI water in 1:5 proportions, shaken for 2 minutes then allowed to settle for 2 minutes. As depicted in Table 4.3, both methods showed similar results with a deviation of less than 0.2 pH units for clay and silt samples. Our measurements show that the addition of 100ppm uranyl does not change the pH of the soil samples, but does change the pH of the sand sample. A much larger deviation in pH for the sand sample is observed due to its low buffer capacity. The pH of clay and silt samples was tested in a collaborating lab. That lab diluted the sample with DI water and used a centrifuge to separate water content from the solid part of the sample. The difference in pH measured in the two labs is about 0.3-0.6 pH units and is acceptable for pH soil tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Direct measurement of the original soil</th>
<th>Protocol with DI water dilution 1:5</th>
<th>Adding uranyl 100PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.32</td>
<td>4.46</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>4.01</td>
<td>3.90</td>
<td>3.98</td>
</tr>
<tr>
<td>3</td>
<td>7.19</td>
<td>7.24</td>
<td>7.22</td>
</tr>
<tr>
<td>4</td>
<td>4.96</td>
<td>5.85</td>
<td>4.28</td>
</tr>
</tbody>
</table>

**Table 4.3 pH measurement of soil samples.**
4.3 Uranyl fluorescence enhancement by silica

4.3.1 Fluorescence spectra of uranyl nitrate in different concentration

Uranyl has a very significant spectrum. Figure 4.1 shows the fluorescence spectrum in different uranyl concentration prepared by mixing uranyl nitrate and DI water. The fluorescence intensity is higher in more concentrated uranyl solution. In addition, because of the different uranyl concentration, the ratio of hydrolyzed uranyl ions in solution varies. This result shows in the variation of the characteristic peaks in the fluorescence spectra. In higher concentration, there are less hydrolyzed uranyl ions in the solution. Therefore, the characteristic spectrum can be identified by 4 characteristic peaks, which are 498nm, 519nm, 542nm, and 567nm. On the contrary, higher ratio of uranyl ions hydrolyze in lower uranyl concentration and form different uranyl-hydroxide compounds. Therefore, the fluorescence spectrum is mixed by several fluorescence signals from different uranyl compounds.

![Figure 4.1 Uranyl fluorescence spectra in different uranyl concentration solution](image)

Figure 4.1 Uranyl fluorescence spectra in different uranyl concentration solution
4.3.2 Fluorescence enhancement by silica gel

The schematic diagram shows the adsorption of uranyl ions on the silica gel surface (see Figure 4.2). Silica gel has an excellent ion exchange property for heavy metal ions. Therefore, uranyl ions can be adsorbed on silica gel surface by ion exchange mechanism.

Figure 4.2 Schematic diagram of Silica gel effect in Uranyl nitrate 2x10^{-5} M solution

Figure 4.2 also shows the effect through the addition of silica gel into the uranyl nitrate solution. The fluorescence intensity of the solution decreases more than 90% after adding silica gel. On the other hand, the silica gel adsorbs most of the uranyl ions, and produces a significant fluorescence signal (see Figure 4.3). In addition, the lifetime test (see Figure 4.4) shows that the silica gel has more than 10 times lifetime of the 2 x 10^{-5} M uranyl nitrate solution. Because human eyes can accumulate the fluorescence emission light in a short period of time (by the persistence of vision effect), the fluorophore which has longer lifetime can provide higher visible signal for direct observation by human eyes. For this aspect, we tested the fluorescence through two integration time (see Figure 4.3).
Figure 4.3 Fluorescence emissions of $2 \times 10^{-5}$ M uranyl nitrate solution and uranyl-contaminated silica gel through different integration time

Figure 4.4 Fluorescence lifetime of $2 \times 10^{-5}$ M uranyl nitrate solution and uranyl-contaminated silica gel
In the result of 1μs integration time (Int. 1μs), silica gel has 6 times fluorescence intensity of 2 x 10^{-5} M uranyl nitrate solution. On the contrast, silica gel has 25 times fluorescence intensity of 2 x 10^{-5} M uranyl nitrate solution in Int. 50μs. This result shows that the longer lifetime fluorophore can overall yield more photons through the accumulation of the fluorescence photons in a period of time

From these results, we conclude that the silica gel which adsorbs and accumulates the uranyl ions on its surface and has longer lifetime can emit more photons than uranyl solution. Based on these two reasons, nanoporous silica materials are great enhancer for the fluorescence detection of uranium.

4.4 pH Effect

4.4.1 pH effect on uranyl fluorescence intensity

Beakers containing silica gel in uranyl nitrate solution at different pH levels are shown in Figure 4.5 under UV excitation (254 nm). The silica gel solid phase is located at the bottom of the beaker. At the low pH (i.e. pH 1–3) the silica gel does not show significant fluorescence. In this pH range the uranyl is not hydrolysed and the silica gel has limited adsorption ability. Therefore, the observed weak fluorescence is from bare uranyl ions in the water above the silica gel (Michard et al., 1996). Uranyl hydroxylation initiates near a pH of 3 and the silica gel demonstrates excellent fluorescence enhancement until about pH 12 after which the fluorescence intensity decreases due to chemical decomposition of the silica gel.
Figure 4.5 Silica gel (500mg) with uranyl (1.5 mg) at different pH. Excitation by 254nm UV light.

Figure 4.6 shows the intensity of the characteristic fluorescence peak near 500nm as a function of pH at two different gating times (110μs and 150μs). Figure 4.7 shows the fluorescence intensity of the 500nm peak at pH 5 as a function of time in solution and within the porous silica gel. For pH 1-3, the emission intensity taken with a 150μs gating time is very low because the uranyl fluorescence lifetime in solution is short as shown in Figure 4.7. For pH 8-11, the intensity is approximately the same for the two gating times because the dominant uranyl-silica complexes within this pH range have a lifetime long in comparison to the 150μs gating time. In the near neutral pH range (pH=4.5-7) the signal intensity is largest and there is a measurable (about 15%) difference in the emission intensity at the two gating times as expected based on the lifetime data of Figure 4.7 which was obtained at pH 5.
Figure 4.6 Fluorescence intensity of silica gel – uranyl mixture at different pH. Intensity calculated as the height of the 500nm peak in the emission spectrum.

Figure 4.7 The normalized decay curve of uranyl fluorescence from silica gel and uranyl solution at pH5.
4.4.2 pH effect on uranyl fluorescence peak position

Figure 4.8 shows the uranyl fluorescence emission spectra at different pH values. The emission spectrum at each pH value shows two strong characteristic peaks near 500nm and 520nm. The characteristic peak wavelength increases monotonically (red shifts) with pH as shown in Figure 4.9. However, the peak spacing, a measure of the uranyl ground state vibrational energy, does not monotonically vary with pH. From pH 1-3, the characteristic peak separation is 22nm. From pH 4-7 the characteristic peak separation is 18nm and for pH values higher than 10 the characteristic peak separation is 20nm. Each characteristic peak in the emission spectrum represents radiative recombination to a different ground state vibrational mode of the uranyl complex and the vibrational energy spacing of the ground-state mode is influenced by the uranyl complexation (Lakowicz, 2006).

Figure 4.8 Emission spectra of uranyl solution with silica gel at different pH. Arrow shows the two peaks used for intensity calculations.
A narrower peak separation represents a lower ground state vibrational energy. Bare uranyl ions in solution (pH < 3) have the broadest ground state vibrational energy while uranyl/silicate compounds between pH 4-7 have the narrowest spacing corresponding to the lowest ground state vibrational energy.

Figure 4.9 Positions of the uranyl fluorescence emission peaks which are close to 500nm (peak 1) and 520nm (peak 2) by different pH values

4.5 Fluoride Effect

4.5.1 Fluorescence spectra of uranyl solution with and without KF.

To reject background fluorescence the delay time for the emission spectra was set at 110 µs. The normalized emission spectra are shown in Figure 4.10 for the uranyl solution and in Figure 4.11 for the uranyl solution with potassium fluoride. The uranyl solution without fluoride addition shows fine vibronic spectra only at low pH 0.8 - 2.4. For pH higher than 3.3, the uranyl solution does not show definite vibronic spectra presumably due
to speciation in solution (Moulin et al., 1995). By contrast, the spectra of uranyl solution with potassium fluoride show fine vibronic emission spectra at all pH levels.

**Figure 4.10** The normalized spectra of 0.01M uranyl nitrate in different pH

**Figure 4.11** Normalized spectra of 0.01M uranyl nitrate with 0.06M potassium fluoride in different pH.
Figure 4.12 Peak positions in emission spectra of 0.01M uranyl nitrate solution at different pH.

Figure 4.13 Peak positions in emission spectra of 0.01M uranyl nitrate solution with KF at different pH.
The influence of pH on the peak positions for both solutions is shown in Figure 4.12 and Figure 4.13. The curves in Figure 4.12 indicate that the fluorescence peaks have a significant red shift from pH 2 to pH 3 and some peaks broaden at pH 2 to pH3 and pH4 to pH5. On the other hand, Figure 4.13 (the solution with KF) exhibits a gradual red shift between pH1 to pH3 and without peak broadening. The data of Figure 4.12 and Figure 4.13 support the idea that the uranyl ion forms complexes in water solutions at higher pH levels and that these complexes can be modified by the addition of fluorine.

4.5.2 Fluorescence lifetime of uranyl solution with and without KF.

Fluorescence decays (intensity versus time) were recorded with 285 nm excitation using the second peak in the emission spectrum. Decays of pure uranyl nitrate solution and uranyl nitrate solution with potassium fluoride are shown in Figures 4.14 and 4.15. The fluorescence lifetime of the pure uranyl solution is less than 10μs for solutions between pH 1.4-3.0, and is about 20 μs for the higher pH levels. The uranyl solutions with KF show similar behavior with pH less than 3.0. At pH higher that 3 this solution demonstrates fluorescence with very long lifetime (up to 140μs). Such significant difference in fluorescence lifetime at different pH can be explained by the formation of hydrofluoric acid at pH levels near 3.2(Ayotte, Hébert, & Marchand, 2005). Below pH 3.2 fluoride ions mostly react with protons, and do not influence the uranyl ion. At pH higher that 3.2 the uranyl ions complex with fluoride producing an increase in the fluorescence lifetime.
Figure 4.14 Fluorescence decay curve of 0.01M uranyl nitrate solution in different pH.

Figure 4.15 Fluorescence decay curve of 0.01M uranyl nitrate solution with KF in different pH.
4.5.3. Fluorescence test in uranyl-contaminated sand by the existence of fluoride

Fluorescence spectra and decay curves were obtained with silica gel placed on top of the contaminated sand. Sand samples had 100ppm of uranyl and fluoride in the molar ratio of 1:6 or 1:30. Emission spectra and decay curves are shown in the Figure 4.16 and 4.17. The spectra show a significant red shift for the fluoride sample with 1:30 uranyl to fluoride ratio. The sample with 1:6 ratio does not show considerable spectral difference in comparison to the sample without fluoride. On the other hand, the lifetime of the fluoride-containing samples is notably longer than the sample with uranyl only. We conclude that the uranyl ion adsorbed on silica material can also interact with the fluoride ion causing longer fluorescence lifetimes. The interaction between the solid and liquid is very complex and these changes could also be caused by other factors such as pH changes or the exchange of other anions with fluoride.

Figure 4.16 Normalized emission spectra of silica gel on the top of uranyl and fluoride contaminated sand
4.6 Uranium adsorption from soil and enhancement

4.6.1. Uranyl extraction by Silica gel from contaminated natural soil

Figure 4.18 shows the fluorescence intensity obtained from the four different soil samples contaminated with 100 ppm of uranyl nitrate and enhanced with silica gel. The natural soil samples did not show significant fluorescence without the addition of the silica gel enhancer, whereas the sea sand standard showed some weak uranyl-associated fluorescence. In all four samples the fluorescence intensity was significantly enhanced by the silica gel, typically by over two orders of magnitude. The sand sample showed the fastest kinetics and uranyl fluorescence was detected immediately after the silica gel was applied. Samples # 1 and 2 required about 2-4 hours before the signal was observed. By
contrast, Sample # 3 showed the slowest kinetics and weakest overall fluorescence, probably due the following reasons: 1) sample # 3 was characterized by relatively higher concentrations of organic matter and iron, known quenchers of uranyl fluorescence, and 2) this soil sample was characterized by a near-neutral pH (see Table 2) where uranyl species are known to be more tightly bound to soil particles in comparison to lower pH conditions.

Figure 4.18 Comparison of fluorescence intensity for different soils. Excitation at 280nm, emission at 498nm with gating time 150μs.

Figure 4.19 shows optical images of the fluorescence enhancement for silica gel applied to the surface of the four soil samples shown in Figure 4.18. The left image is under ambient light and the right image is under the illumination of a mercury hand lamp (254 nm). The sand sample(# 4) exhibits the highest intensity while Sample # 3 exhibits the lowest intensity.
Figure 4.19 Fluorescence enhancements with silica gel after 5 days of aging. Sample numbers corresponded to the samples in Table 1. Left – under ambient light; right – under 254nm UV irradiation.

4.6.2. Kinetics of uranyl extraction by Silica gel from contaminated natural soil

For the environmental soil samples, the kinetics of uranyl migration into the silica gel is relatively slow in comparison to the pure sand sample. Figure 4.20 shows the fluorescence emission spectra immediately after the deposition of the silica gel onto the surface of soil sample # 2 in comparison to the same spectrum taken four hours later and then five days later. A detailed investigation of the kinetics of uranyl migration in the various soil types is beyond the scope of this study, but our results confirm that the kinetics will vary significantly depending on various soil features.
Figure 4.20 Fluorescence spectra of the sample #2 recorded at three different times: 1 – immediately after silica gel deposition, 2- four hours later, 3 – five days later.

Previously we showed that uranyl adsorbed in silica gel has a longer fluorescence lifetime than uranyl dissolved in water. For soil samples, background fluorescence is caused mostly by organic compounds present in the soil and also by some naturally occurring fluorescent minerals. The fact that uranyl adsorbed onto silica gel has a fluorescence lifetime longer than 100 µs can be used for background discrimination. Organic compounds typically have a short fluorescence lifetime (nanoseconds). Fluorescent minerals have longer luminescence lifetimes, but their emission spectra do not usually overlap with the uranyl spectrum. Figure 4.21 shows the effect of background rejection with longer gating time for the silt sample. The silt sample has a high organic content and background rejection is essential for trace uranyl detection.
Figure 4.21 The fluorescence spectrum of the silt sample (#3) recorded with different gating: 1 – 110 µs, 2 – 150 µs

Figure 4.22 Low levels uranyl detection in the contaminated sand samples.
4.6.3. Lowest detect level of uranium by Silica gel from uranium-contaminated sand

We have prepared several sand samples which have different uranyl concentrations and used silica gel to extract and detect uranyl from these samples. The results show that we can increase sensitivity from ppm level to ppb level. Figure 4.22 shows that uranyl signal can be easily recognized at 100 ppb level. In this experiment background fluorescence was rejected by gated fluorescence measurements. Uranyl levels less that 100 ppb show some detectable fluorescence, but requires further technique improvement.

4.7 Discussions and Conclusions

In this chapter, we demonstrate the uranyl fluorescence enhancement by silica gel, the pH and fluoride effect to the uranyl fluorescence on silica gel and the detectability of uranyl in soil by silica gel through fluorescence technique.

Because silica gel has very good ion exchange ability, it can adsorb and accumulate uranyl ions on its surface as a uranyl concentrating condition. Also, a silica gel can interact with a uranyl ion to form a compact compound, which can avoid the dynamic quenching caused by free water molecules. This compound effectively increases the uranyl lifetime so that more photons can be emitted than in uranyl solutions. Based on these two reasons, nanoporous silica materials are great enhancer for the fluorescence detection of uranium.

Uranyl fluorescence is very sensitive on pH variation. The pH was shown to affect the fluorescence intensity and lifetime as well as the peak position and peak separation. Generally, the silica gel can enhance the uranyl fluorescence at a pH range from 3 to 12.
addition, the silica gel has a best adsorption ability at pH 6.5 (Lieser et al., 1992), therefore the uranyl fluorescence shows the best emission intensity in pH ranging from 4-7, which is the common range for natural soils. However, a limitation of the usage of a silica gel may occur due to chemical decomposition of the silica gel at a pH higher than 12. The uranyl fluorescence on silica gel has a Bathochromic shift through the increasing pH values of the uranyl solution because of the formation of different uranyl-silica compounds, which are also identified by the different gaps of the energy vibration levels. Among these uranyl species, the narrowest peak separation, associated with the lowest ground state vibrational energy, occurred in the neutral soil pH region where the silica gel exhibited the best fluorescence enhancement.

In addition to the advantage from silica gel, uranyl fluorescence can also be enhanced by fluoride ions. Fluoride ions in the mixture also produce well defined vibronic spectra with some red shift. Also, it can significantly increase the uranyl fluorescence lifetime. The specific effects of fluoride on the uranyl emission spectra may help to identify the presence of fluoride contamination with uranyl. Development of a sensor for standoff detection of uranyl with fluoride can increase the overall value of our standoff sensor.

The feasibility of uranyl fluorescence detection on the top of soil by silica gel is carried out by 4 types of natural soil. All types of soil show good fluorescence through the using of silica gel at 100ppm of uranium-contamination. In addition, we obtained uranyl fluorescence through the usage of background rejection with longer gating time. The uranyl fluorescence signal can be recognized at 100 ppb level. Silica gel, applied to the soil
surface significantly enhanced (by approximately 2 orders of magnitude) the fluorescence
intensity in comparison to the fluorescence of the bare soil.

Through the wicking effect and the higher evaporation due to the high surface area of
silica gel, the uranyl can migrate through water to the silica surface. However, the
evaporation speed depends on the humidity and air flow and can be slow. There is a
limitation in the kinetic of uranyl fluorescence detection.
Chapter 5

Uranium Fluorescence Enhanced by Silica Materials

5.1 Introduction

Silica is a common element in the natural environment. It is the main composition of natural rocks, stones and soils. Most of the silica materials found in the environment are in a crystalline form and only some of them are porous (amorphous structure) (Unger, 1979). A silica material may have a very good ion-exchange ability due to the high forming of silanol groups on its surface (H. A. Benesi, 1959). Because the crystalline structure is a compact stacking, it only has a small overall surface area and cannot interact with metal ions efficiently. On the contrary, some research grade silica materials, i.e. colloid silica, silicon dioxide nanopowder, mesostructured hexagonal framework silica and silica gels, have a large unit surface area to allow these silica materials to efficiently interact with charged metal ions through silanol groups and adsorb them on the silica surface. In Chapter 4, we investigated the wicking effect and the uranyl fluorescence enhancement using the nanoporous silica gel. However, this amorphous structure is not the only structure of silica materials. Other silica structures, i.e. mesostructured hexagonal framework and nano size particles, may also cause various uranyl-silica interactions and spacial effects, which may eventually affect the uranyl fluorescence enhance ability.
In this chapter, we investigate 15 different silica materials, which are available on the market, to determine the microstructure effect to the enhancement of uranyl fluorescence. The factors include the particle size, the pore size and the structure of these silica materials. These silica materials are contaminated by a uranyl nitrate aqueous solution of 100 parts per million (ppm) by weight of uranium-contamination and are interrogated with the fluorescence intensity and their associated decay lifetime. Through the fluorescence spectroscopy test, we can determine which kind of silica material has the best performance of the enhancement of uranyl fluorescence signals.

Through the uranium-contaminating process of silica materials, we found that the water content in silica materials affects the fluorescence spectra during the drying process significantly. From this phenomenon, we recorded the fluorescence spectra of uranium-contaminated silica materials with various contents of water. Through this test of water effect, we discussed the water inside the porosity of the silica material for the physical effect on the uranyl fluorescence enhancement.

Several uranyl concentrations on various structures of silica materials are also studied in this research to identify the uranyl density change in relation to the fluorescence properties. The fluorescence excitation spectra, emission spectra and the fluorescence lifetime are discussed and conclude a mechanism on the influence of uranyl concentration.

In addition, X-ray Photoelectron Spectroscopy (XPS) was performed to investigate the uranium compounds on uranium-contaminated silica material surfaces. Through the XPS spectra, the binding energy (BE), full width at half maximum (FWHM), and atom percentage (At %) are discussed.
5.2 Experimental process

5.2.1 Uranium-contaminated silica materials

There are three test sets of uranium-contaminated silica materials used in this study. The first set is a general test for the silica properties. 15 kinds of silica materials, which are available in the market for chromatography purpose, are contaminated with the same uranyl concentration. The second set is the test for uranyl concentration. Five species of silica materials, which are made in different structures, are contaminated with a different uranyl concentration. The third set is the test for silica particle size. A silica gel is ground to a smaller particle size and contaminated by a different uranyl concentration.

Materials for general testing

200 mg of silica materials was mixed well with a 8.4 μL 0.01M uranyl nitrate solution and 1mL of water resulting in 100 parts per million (ppm) by weight of uranium contamination to silica materials. Among these silica materials, the mesostructured materials have a lower bulk density; therefore, to prepare similar size samples (by volume), the amount of silica was 100 mg and 4.2 μL of 0.01 M of a uranyl nitrate solution which was added. The physical properties of silica materials are listed in Table 3.1. The samples were air-dried in covered Petri-dishes to reduce the speed of evaporation. The sample weights and the fluorescence spectra were recorded on the 1st, 2nd, 3rd, 4th, 7th and 14th days using a microbalance (Fisher Scientific accu-124), which has an accuracy of about 0.1 mg. The water content ratio was calculated by the ratio of water to silica materials.
Materials to test the effect of uranyl concentration

Silica materials item numbers 1, 4, 11, 12, and 14 (see Table 3.1) are tested in this study. The uranium to silica concentration by weight is made from 1ppm to 100,000 ppm (see Table 5.1). The samples in a wet condition are examined right after the mixing of silica materials and the uranyl solution. Therefore, some uranyl solution may remain on the top of the silica material. On the other hand, the samples in a dry condition are examined at the dried out state of silica materials. The water content ratio in these dried out samples are less than 0.5%. Among these silica materials, silica gel with the largest particle size and the smallest porosity (item #12 in Table 3.1) shows excellent water lock ability.

Table 5.1 The chart of the sample preparation in different uranyl concentrations

<table>
<thead>
<tr>
<th>Uranium Concentration</th>
<th>Uranyl Solution concentration</th>
<th>Uranyl solution Volume (μL)</th>
<th>Water volume (μL)</th>
<th>Silica weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td>$10^{-5}$M</td>
<td>42</td>
<td>378</td>
<td>100</td>
</tr>
<tr>
<td>10 ppm</td>
<td>$10^{-5}$M</td>
<td>420</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>100 ppm</td>
<td>0.01M</td>
<td>4.2</td>
<td>416</td>
<td>100</td>
</tr>
<tr>
<td>1,000 ppm</td>
<td>0.01M</td>
<td>42</td>
<td>378</td>
<td>100</td>
</tr>
<tr>
<td>10,000 ppm</td>
<td>0.01M</td>
<td>420</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>100,000 ppm</td>
<td>1M</td>
<td>42</td>
<td>378</td>
<td>90</td>
</tr>
</tbody>
</table>

Materials for the test of silica gel particle size effect

Silica gel item number 7 (see Table 3.1) is tested in this study. 100mg of silica gel is finely ground to 5-10μm in particle size using a mortar. 100, 1,000 and 10,000 ppm of uranium contamination on both original and ground silica materials are prepared to examine the effect of particle size in wet and dry conditions.
5.2.2 Fluorescence measurement.

Fluorescence spectra were recorded with a Quanta Master spectrofluorometer by Photon Technology International (PTI) equipped with a xenon pulse lamp for sample excitation (see Figure 3.1). Fluorescence measurement included 3 main tests: emission scan, excitation scan, and a fluorescence intensity decay test. All tests were started at a fluorescence emission scan. Excitation wavelength is fixed at 285nm and goes along with the assistance of a series of shortpass filter (TS-450, TS-500, and Hoya U-330). Emission spectrum was recorded in the range of 400 - 650nm with the assistance of a longpass filter, NT-419. From the emission scan, several characteristic peaks (shown as wavelength) in the emission spectrum can be identified. After the emission scan, the first characteristic peak (generally near 500nm) in the emission spectrum was chosen as the fixed emission wavelength for the excitation scan. Excitation spectra were recorded in the range of 200-450nm. Fluorescence intensity decay tests were taken place by the excitation wavelength at 285nm and the emission wavelength at the first characteristic peak (generally near 500nm) in the emission spectrum. Each spectrum was made with an average of 5 scans. Each scan was made with an average of 20 lamp pulse signals. The integration time of each signal was 1 μs. The delay time of both fluorescence emission and excitation scans was 110 μs. This specific delay time, which was chosen by the experimental experience from PTI, can provide a similar result to the identification to the human eye under a continuous light source. These fluorescence spectra were collected right after the weighting of samples. Fluorescence decay curves can be calculated and transferred into fluorescence lifetime by the software PTI FeliX32.
5.2.3 XPS measurement.

XPS spectra

Binding Energy (BE) distribution was recorded with ESCALAB 250 by Thermo Scientific (see Figure 5.1), which is equipped with a 1.5KV Al kα X-ray source. The sample scanning area is 500µm squared. XPS spectra files were recorded and analyzed by the Avantage software. The binding energy survey was recorded to discover the entire possible element on the surface of the sample. Detail detections on uranium, oxygen, silicon, and carbon elements were done by averaging 30 scanning data.

![ESCALAB 250 XPS instrument](image)

**Figure 5.1 ESCALAB 250 XPS instrument**

XPS samples.

Uranyl nitrate powder, glass slide, and the silica materials including nano powders (#1 in Table 3.1), meso-structured silica (#14), and some amorphous silica gel particles (#2-5, 7, and 12) were used in this research.
Uranyl nitrate powder was used without further purification. The glass slide was dipped in a 0.01M uranyl nitrate solution for 30 minutes and then dried by argon air. 10mg of silica materials were mixed well with 204 μL 0.01M uranyl nitrate solution as 0.2 At% uranium contamination to silica materials. The samples are air-dried in Petri-dishes. The 100 ppm silica samples in Chapter 5.2.1 were also interrogated by XPS as a control.

Samples were prepared with indium foils to provide the conductivity to the silica materials. Indium foils were cleaned by a supersonic oscillator in methanol bath for 20 minutes and then air dried. We cut the foil to a size of 3mm squared, pressed each of the uranium-contaminated silica materials on the indium surface and then cleaned the surface by argon air to prevent any loosened particles from remaining on the sample surface. Finally, we applied conductive tape between the sample holder and the indium foil to bind the sample to the holder.

<table>
<thead>
<tr>
<th>Item No.</th>
<th>Ref. No.</th>
<th>Company</th>
<th>Description</th>
<th>Particle Size</th>
<th>Pore Size</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Sigma-Aldrich</td>
<td>Silicon dioxide, nano-powder, 99.5% metals basis</td>
<td>5-15 nm</td>
<td>N/A</td>
<td>640</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>Sigma-Aldrich</td>
<td>Silica, mesostructured hexagonal framework, MCM-41Type</td>
<td>4.6-4.8 nm</td>
<td>23-27 Å</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>ACROS ORGANICS</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>40 Å</td>
<td>750</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>ACROS ORGANICS</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>60 Å</td>
<td>550</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>ACROS ORGANICS</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>40-60 μm</td>
<td>150 Å</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>ACROS ORGANICS</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>5-15 μm</td>
<td>60 Å</td>
<td>550</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>ACROS ORGANICS</td>
<td>Silica gel, for column chromat., ultra pure</td>
<td>60-200 μm</td>
<td>60 Å</td>
<td>550</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>Sigma-Aldrich</td>
<td>Silica gel, Grade 12, 28-200 mesh</td>
<td>75-650 μm</td>
<td>22 Å</td>
<td>800</td>
</tr>
</tbody>
</table>
5.3 Silica materials general test

5.3.1 Fluorescence intensity

The fluorescence intensity on the peak of each emission spectrum from different uranium-contaminated silica materials is plotted in Figure 5.2. To eliminate the influence of the physical enhancement by water, all samples are in a dry condition\textsuperscript{12}. These samples can be divided into 5 groups according to their particle sizes.

![Fluorescence intensity on silica material with different porosity](image)

**Figure 5.2 Fluorescence intensity on silica material with different porosity**

Particle size can affect the uranyl fluorescence intensity in a dry condition. Nano level silica materials, including silica nanopowder, mesostructured silica and silica molecular sieves, demonstrate a relatively low fluorescence intensity in all silica materials.

\textsuperscript{12} The water contained in the silica materials is less than 0.5%.
Silica gel materials, which have a relatively larger particle size, show higher fluorescence intensity among these silica material species. Furthermore, in silica materials, larger particle sizes can also cause higher fluorescence intensity. For instance, among these silica gels which have a pore size average of 60Å, a sample which has a larger particle size also performs with a higher fluorescence intensity. From these results, we can roughly conclude that the particle size is one of the important factors in fluorescence intensity. Among the same average pore size silica materials, larger particle size can be utilized to enhance more of the uranyl fluorescence.

Pore size can also be an important factor that relates to uranyl fluorescence on silica materials. From the fluorescence intensities of the group of silica particles size 40-200 μm, the fluorescence intensities are similar when the pore size is larger than 60 Å. On the other hand, when the pore size smaller than 60 Å, the uranyl fluorescence intensities increase along with the decrease of the pore size. However, the decrease of the pore size is limited to the amount that it can increase the intensity. The silica gel which has a pore size of 22 Å shows lower uranyl fluorescence intensity even though it has a relatively larger particle size rather than the silica gel which has a pore size of 30 Å. This phenomenon can also be demonstrated in nano level silica materials. Because of the fine stacking of nano particles, the spacing between particles is relatively small. For instance, the silica nano powder has a particle size of 5-15nm. The spacing between each particle can be less than 15 Å, whose pore size is smaller than the silica gel with a pore size of 22 Å. Because of the pore size limitation, there is no point to enhance the fluorescence once it is in a dry condition.
5.3.2 Fluorescence lifetime

The fluorescence lifetime of 15 species of silica materials, which are calculated by the software PTI FeliX32 from their fluorescence intensity decay curves, is shown in Figure 5.3. In this fluorescence lifetime analysis, we have tried one exponential lifetime and two exponential lifetimes to test the curve fitting. In these calculations, we used a Chi Square Statistic\(^ {13} \) (Chi2) for testing correlation.

![Figure 5.3 Fluorescence lifetime on different pore sizes of dry silica materials](image)

\(^{13}\)Deviations of the fit function from the real data can be characterized using the chi-square statistic. The best fit is determined when chi-square value is minimized. Good results typically produce a chi-square of 0.9 to 1.2.
These calculation results show a large bias in one exponential lifetime curve fitting. Therefore, we used two exponential lifetimes curve fittings to analyze the decay curves in this study. This result demonstrates that these fluorescence decay curves include two fluorescence decay processes. Also, this phenomenon can be explained as two species of uranyl-silica compounds on the surface of silica materials.

In section 5.2, we concluded that both the particle size and the pore size can affect the intensity of the uranyl fluorescence. Particle sizes in the range of nano meters or pore sizes less than a specific size can decrease the fluorescence intensity. For this reason, we divided the samples into three parts in this lifetime study: silica gel (pore size greater than 30Å), Nano level silica (particle size between 5-15 nm), and fine pore size silica gel (pore size of 22 Å). The result shows that the silica gel materials have a higher lifetime. Nano level silica materials show a relatively lower lifetime than silica gels, and the silica gel with a specific fine pore size shows the lowest lifetime.

Among these silica gel materials, the pore size can also slightly affect the lifetime. In this study, the lifetime of the silica gel decreases with the increase of the average pore size of the silica gel. On the other hand, silica material in the nano meter range shows a slightly increasing in fluorescence lifetime with the increase of the pore size. In addition, an enormous lifetime drop is shown between a silica pore size of 22 Å and 30 Å.

These pheromones are caused by the distribution of uranyl molecules on silica surfaces. Because the surface area and the shape of the silica materials varies, the density of the uranyl molecule on the surface of silica material and the spacial distribution of the uranyl molecules can both affect the uranyl fluorescence on silica materials.
5.4 Water effect

Water provides a very important effect on the enhancement of uranyl fluorescence by silica materials: the spacing between uranyl ions. The water content ratio of silica material is shown in Table 5.2. All of the silica materials were thoroughly mixed with the uranium-contaminated water because of the hydrophilic properties of silanol groups on the surface. However, the lower mass density meso-structured silica materials required more water to be full saturated. By comparison, the silica gel with the largest particle size and the finest pore size exhibited the lowest water adsorption ability and, therefore, the kinetics of uranyl reacting with this larger silica gel was slower than the other silica materials.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Particle Size</th>
<th>Pore Size</th>
<th>Right after</th>
<th>1st Day</th>
<th>2nd Day</th>
<th>3rd Day</th>
<th>4th Day</th>
<th>1st Week</th>
<th>2nd Week</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5-15 nm</td>
<td>N/A</td>
<td>4.815</td>
<td>4.044</td>
<td>2.445</td>
<td>0.899</td>
<td>0.678</td>
<td>0.325</td>
<td>0.055</td>
</tr>
<tr>
<td>2</td>
<td>5-15 μm</td>
<td>60 Å</td>
<td>4.822</td>
<td>4.128</td>
<td>2.346</td>
<td>0.806</td>
<td>0.570</td>
<td>0.378</td>
<td>0.048</td>
</tr>
<tr>
<td>3</td>
<td>40-60 μm</td>
<td>40 Å</td>
<td>3.971</td>
<td>3.322</td>
<td>2.496</td>
<td>0.932</td>
<td>0.647</td>
<td>0.441</td>
<td>0.052</td>
</tr>
<tr>
<td>4</td>
<td>40-60 μm</td>
<td>60 Å</td>
<td>4.833</td>
<td>4.093</td>
<td>2.569</td>
<td>1.078</td>
<td>0.814</td>
<td>0.485</td>
<td>0.049</td>
</tr>
<tr>
<td>5</td>
<td>40-60 μm</td>
<td>150 Å</td>
<td>4.876</td>
<td>4.141</td>
<td>2.537</td>
<td>1.116</td>
<td>0.781</td>
<td>0.500</td>
<td>0.046</td>
</tr>
<tr>
<td>6</td>
<td>63-200 μm</td>
<td>40 Å</td>
<td>4.859</td>
<td>4.076</td>
<td>2.609</td>
<td>0.901</td>
<td>0.600</td>
<td>0.452</td>
<td>0.132</td>
</tr>
<tr>
<td>7</td>
<td>60-200 μm</td>
<td>60 Å</td>
<td>4.850</td>
<td>4.064</td>
<td>2.625</td>
<td>1.240</td>
<td>0.798</td>
<td>0.503</td>
<td>0.007</td>
</tr>
<tr>
<td>8</td>
<td>63-200 μm</td>
<td>60 Å</td>
<td>4.886</td>
<td>4.094</td>
<td>2.550</td>
<td>1.129</td>
<td>0.802</td>
<td>0.515</td>
<td>0.093</td>
</tr>
<tr>
<td>9</td>
<td>63-200 μm</td>
<td>100 Å</td>
<td>4.825</td>
<td>4.054</td>
<td>2.662</td>
<td>1.197</td>
<td>0.934</td>
<td>0.577</td>
<td>0.030</td>
</tr>
<tr>
<td>10</td>
<td>75-150 μm</td>
<td>30 Å</td>
<td>4.864</td>
<td>4.091</td>
<td>2.722</td>
<td>1.221</td>
<td>0.699</td>
<td>0.329</td>
<td>0.166</td>
</tr>
<tr>
<td>11</td>
<td>75-150 μm</td>
<td>150 Å</td>
<td>4.849</td>
<td>4.093</td>
<td>2.587</td>
<td>1.748</td>
<td>1.115</td>
<td>0.737</td>
<td>0.001</td>
</tr>
<tr>
<td>12</td>
<td>75-650 μm</td>
<td>22 Å</td>
<td>4.860</td>
<td>4.123</td>
<td>2.677</td>
<td>1.144</td>
<td>0.662</td>
<td>0.382</td>
<td>0.302</td>
</tr>
<tr>
<td>13</td>
<td>250-500 μm</td>
<td>60 Å</td>
<td>4.900</td>
<td>4.131</td>
<td>2.679</td>
<td>1.152</td>
<td>0.785</td>
<td>0.552</td>
<td>0.036</td>
</tr>
<tr>
<td>14</td>
<td>4.6-4.8 nm</td>
<td>23-27 Å</td>
<td>9.714</td>
<td>8.227</td>
<td>6.218</td>
<td>4.027</td>
<td>3.717</td>
<td>3.402</td>
<td>0.512</td>
</tr>
</tbody>
</table>

Note: shows the maximum emission for each sample
The fluorescence intensity of the samples increased during the drying process, reached a maximum and then decreased, eventually reaching equilibrium. The time required to reach the maximum emission intensity for each sample is highlighted in Table 5.2. Smaller particles, (i.e. nano-powder) exhibited the highest intensity when the particles were surrounded by water with a water content ratio up to 4.0. When this nano material is dried out, the intensity decreases significantly as shown in Figure 5.4. Therefore, water plays a very important role for fluorescence from the nano-powder.

On the other hand, amorphous structured silica gel shows overall higher fluorescence intensity than the nano powder material, but the peak resolution of the spectra is lower than in the nano-powder material. The water content ratio for these amorphous gel materials is between 0.2 and 1.2. When these amorphous gel materials were dried out they maintained about 80 % of the maximum intensity (see Figure 5.5). For the meso-structured silica materials, the result is between the nano particles and the amorphous materials. A water content ratio between 0.5 and 1.9 exhibits the highest fluorescence intensity, and also is proportional to the pore size difference. During drying, the meso-structured materials maintain less than 40 % of the maximum uranyl fluorescence (see Figure 5.6).

**Water content and pore size affect the uranyl fluorescence in silica materials**

For amorphous silica gel materials and mesostructured silica, the water content ratio is a significant factor for optimization of the fluorescence performance. The relation of pore size and water content ratio to the maximum emission of each silica gel is shown in Figure 5.7. We found that the smaller pore size silica gel requires less water to produce maximum fluorescence intensity.
Figure 5.4 100ppm uranium-contaminated silicon dioxide nano-powder fluorescence emission under 285nm UV during the drying process

Figure 5.5 100ppm uranium-contaminated silica gel (40-60μm, 60 Å) fluorescence emission spectra under 285nm UV during the drying process
Figure 5.6 100ppm uranium-contaminated meso-structured silica (MCM-41) fluorescence emission spectra under 285nm UV during the drying process.

Figure 5.7 Water contained ratio in silica gel for the maximum intensity in different pore sizes.
Uranyl fluorescence peak shift in the drying process

The characteristic peaks were analyzed in the emission spectrum of each material (see Figure 5.8). In these characteristic peaks, we found that most of the silica materials showed significant red shift during the drying process. However, the peak position in the nano powder silica did not change significantly during drying. In addition, silica materials with a pore size less than 30 Å, (i.e. #1 nonporous, #12=22 Å, #14=23-27 Å) exhibited a shorter emission wavelength in the first peak compared with other silica materials. Therefore, the uranium distribution on the surface of these smaller porous materials may be different from larger porous materials when the sample is surrounded by water.

Figure 5.8 Collection of characteristic fluorescence peaks by uranyl with different silica materials
5.5 Uranyl concentration effect on silica materials

To demonstrate the uranyl molecule density effect on the uranyl fluorescence, the uranyl contaminations on various species of silica materials with different concentrations are examined. The fluorescence excitation and emission spectra are discussed in different uranyl concentrations to derive the mechanism of the uranyl fluorescence. In addition, a large particle size silica gel is ground into small particles and contaminated with different uranyl concentrations to test the silica particle size effect on the fluorescence properties.

5.5.1 Excitation spectrum

Based on quantum theory, the uranyl compound on a silica surface can absorb several characteristic energies from higher energy photons and emit lower energy photons. These characteristic energies of photons can be specified in the peaks of an excitation spectrum. The peaks with longer wavelengths show lower characteristic excitation energies. On the contrary, the peaks with shorter wavelengths demonstrate higher excitation energy. The positions of these excitation peaks for uranyl molecule on silica were at 251, 262, 275, 288, 300, 312 and 325nm for all concentrations and all species of silica materials in this investigation (see Figure 5.9).

The intensity of each excitation wavelength shows the probability of photons emitted by uranyl molecule, which absorb the photons at this energy level. The structure of an excitation spectrum can be used to identify the composition of the fluorophore on a
material. Because all uranyl compounds show the same peaks, the relative ratio of the peaks’ intensities can be an index to govern the property of uranyl fluorescence.

![Figure 5.9 Uranyl fluorescence excitation spectrum analysis of 10K ppm uranium contamination on 60 Å silica gel using fityk software.](image)

Different uranyl concentrations on various types of silica materials are examined to investigate the mechanism of the adsorption of uranyl molecule on silica materials (see Figure 5.10-17). Generally, the fluorescence intensity increases with the increase of the uranyl concentration because of the higher uranyl molecule density. However, the increase of intensity is not linearly proportional to the increase of the total amount of uranyl molecule. From the experiment results, we found that when the total uranyl amount is higher than the specific capacity of a silica material, the increase of the fluorescence
intensity was slower than lower concentration samples. Furthermore, when the total amount of uranyl on the surface of silica material exceeds the surface’s maximum capacity, the overcrowded uranyl molecules will quench each other and cause a decrease in fluorescence intensity.

Except for the overall intensity, the composition of the excitation spectrum also varies with different uranyl concentrations. In lower concentration samples, the spectra show three main peaks at 275, 288 and 300nm in silica materials. A higher uranyl concentration causes the significant increase of the intensity ratio on the peaks at 312 and 325nm. Because these two increasing peaks represent the absorption of the energies in lower vibrational level of uranyl molecules, this phenomenon shows that the uranyl concentration may cause a change in the photon absorption properties.

The intensity ratio from silica material also shows a variety in distribution. For amorphous nanoporous silica gel materials, including several pore sizes, the change of the intensity ratio is significant. Peaks at 312 and 325 nm, which are less than 40% in lower concentrations, can increase to around 100% of the highest intensity ratio. For silica nanopowder and mesostructured silica materials, the change in intensity ratio during the increase of intensity is less than 20%. Because these two materials are made in very fine particle sizes (nano: 5-15 nm; MCM-41: 4.6-4.8nm), the condensed packing of these materials will cause the surfaces of the nano materials contact to contact each other and shorten the distance between uranyl molecules. Therefore, the excitation spectra of these two silica materials show similar properties in different uranyl conditions.
Figure 5.10 Uranyl fluorescence excitation spectrum of silica nano powder contaminated by various uranyl concentrations in wet condition.

Figure 5.11 Uranyl fluorescence excitation spectrum of silica nano powder contaminated by various uranyl concentrations in dry condition.
Figure 5.12 Uranyl fluorescence excitation spectrum of silica mesostructured (MCM-41) contaminated by various uranyl concentrations in wet condition.

Figure 5.13 Uranyl fluorescence excitation spectrum of silica mesostructured (MCM-41) contaminated by various uranyl concentrations in dry condition.
Figure 5.14 Uranyl fluorescence excitation spectrum of 60 Å silica gel (40-60μm) contaminated by various uranyl concentrations in wet condition.

Figure 5.15 Uranyl fluorescence excitation spectrum of 60 Å silica gel (40-60μm) contaminated by various uranyl concentrations in dry condition.
Figure 5.16 Uranyl fluorescence excitation spectrum of 150 Å silica gel (75-150μm) contaminated by various uranyl concentrations in wet condition.

Figure 5.17 Uranyl fluorescence excitation spectrum of 150 Å silica gel (75-150μm) contaminated by various uranyl concentrations in dry condition
5.5.2 Emission spectrum

Based on the Jablonski diagram, an emission spectrum has a symmetrical distribution of peaks from its excitation spectrum because the number of a molecule’s characteristic vibrational levels will be the same both in the ground state (S0) and the first excited state (S1). In the uranyl nitrate emission spectrum, it shows seven peaks at 468, 483, 504, 527, 552, 580, and 607nm (see Figure 5.18). The peaks with longer wavelengths show lower characteristic emission energies. On the contrary, the peaks with shorter wavelength values demonstrate higher emission energy. In addition, because uranyl has more than one compound on the silica surface, the distribution of the peaks in an emission spectrum shows the combination of some different sets of peaks from various species of the uranyl compounds on the silica surface.

Figure 5.18 Uranyl fluorescence emission spectrum analysis of uranyl nitrate
Emission spectra of different uranyl concentration in various silica materials are shown in Figure 19-26. The uranyl compound, which has a higher ratio of the shorter wavelength peaks (i.e. 288 or 300nm) in an excitation spectrum, will induce a red shift in the emission spectrum. On the contrary, the uranyl compound which has a higher ratio of the longer excitation wavelength peaks (i.e. 312 or 325nm) will lead a blue shift in the emission spectrum. This phenomenon is caused by the energy loss in the excitation state during the process that an electron returns from higher vibration level to the ground vibrational level. Because the molecules which prefer to absorb stronger excitation energy can cause a higher energy loss, the emission spectrum results in a relative red shift. On the contrary, the molecules which trend to absorb lower excitation energy can induce a relative blue shift in the emission spectrum.

Different uranyl concentrations on various types of silica materials are examined to investigate the emission peaks. All the emission spectra demonstrate the combination of different uranyl compounds’ emission spectra. Amorphous nanoporous silica gel in lower uranyl concentration, which has a higher probability to absorb higher energy photons in excitation process, shows two specific peaks at 505 and 520. With the increase of the uranyl concentration, both specific peaks shift to shorter wavelengths up to 495 and 515nm due to the relative increasing intensity ratio of the lower absorption wavelength. In silica nanopowder and mesostructured silica materials, because the ratio of the lower absorption wavelength did not vary significantly, the peak position is relatively stable in various uranyl concentrations.
Figure 5.19 Uranyl fluorescence emission spectrum of silica nano powder contaminated by various uranyl concentrations in wet condition.

Figure 5.20 Uranyl fluorescence emission spectrum of silica nano powder contaminated by various uranyl concentrations in dry condition
Figure 5.21 Uranyl fluorescence emission spectrum of silica mesostructured (MCM-41) contaminated by various uranyl concentrations in wet condition.

Figure 5.22 Uranyl fluorescence emission spectrum of silica mesostructured (MCM-41) contaminated by various uranyl concentrations in dry condition.
Figure 5.23 Uranyl fluorescence emission spectrum of 60 Å silica gel (40-60μm) contaminated by various uranyl concentrations in wet condition.

Figure 5.24 Uranyl fluorescence emission spectrum of 60 Å silica gel (40-60μm) contaminated by various uranyl concentrations in dry condition.
Figure 5.25 Uranyl fluorescence emission spectrum of 150 Å silica gel (75-150μm) contaminated by various uranyl concentrations in wet condition.

Figure 5.26 Uranyl fluorescence emission spectrum of 150 Å silica gel (75-150μm) contaminated by various uranyl concentrations in dry condition
In addition, the emission spectrum also shows an indication of the remaining space on the silica material. Silica materials have a main peak at 440nm in the emission spectrum (see Figure 5.27). The fluorescence intensity of silica material on this peak decreases when the uranyl molecule interacts with the silica on the surface. Because once the site on the silica surface is occupied by uranyl compounds, the excitation photons which are absorbed by silica materials decrease and eventually result in a decreased emission of photons.

Figure 5.27 Silica characteristic peak at the uranyl fluorescence emission spectrum of 150 Å silica gel (75-150μm) contaminated by various uranyl concentrations in dry condition
5.5.3 Particle Size effect

Nano powder and mesostructured silica are very hard to mix with uranyl solutions. The same situation shows up in ground silica gel as well. The mixing of silica and uranyl solution is relatively difficult due to the large surface area of the ground silica. The surface area of ground silica gel may have some electronic charge. This static charge on the particle surface will repel each other while attempting to use an exterior force to stir.

Excitation spectrum:

Figure 5.28-29 show the absorption spectra of these two particle sizes of silica gel in different uranyl concentrations. In lower concentrations at 10ppm, the ground silica gel shows higher intensity at 251, 262, 275, and 363nm. On the contrary, large-sized silica shows higher intensity at 300 and 312nm. There is no significant variation between wet and dried samples. On the other hand, in higher concentration at 1,000 ppm, the intensity at 288, 300, and 312 are the same on two samples in a wet situation. The other characteristic peaks show higher intensity in ground silica gel. The intensity ratio of at wavelength 251, 262, and 275nm are higher in ground silica samples.

On wavelength 363, higher uranyl concentration on silica material shows higher intensity. This peak can also be found in pure silica materials in an excitation scan. With the forming of uranyl compound on a silica surface, the emission intensity on this specific excitation wavelength increases until uranyl concentration on the silica surface reaches the capacity of the silica material.
Figure 5.28 Uranyl fluorescence excitation spectrum of 60 Å silica gel contaminated by various uranyl concentrations in wet condition. - Particle size effect.

Figure 5.29 Uranyl fluorescence excitation spectrum of 60 Å silica gel contaminated by various uranyl concentrations in dry condition. - Particle size effect.
Emission spectrum

Figure 5.30-31 show the fluorescence emission spectra of these two particle size of silica gel in different uranyl concentrations. The intensities of different sizes of silica materials are similar in a wet condition. The higher uranyl concentration on silica gel surface shows the higher emission intensity. On the other hand, in dry conditions, the larger particle size samples show higher intensity than smaller particle size materials. This result demonstrates that gel structure can provide more space for light to pass through efficiently rather than nano powder particles in a dry condition. Because the small particle size materials have higher packing density once they are without water support in between particles, the light cannot penetrate deeply into the surface area, and the detector can only obtain the fluorescence on the skin layer of the silica material.

The main peak is on 501 and 521 nm for a wet condition, and 505 and 520 for dry samples. The peak positions of these two different sizes are the same either in wet or dry conditions. This result shows that there is no relation between the speciation of a uranyl compound on silica gel surfaces and the particle size of silica materials.
Figure 5.30 Uranyl fluorescence emission spectrum of 60 Å silica gel contaminated by various uranyl concentrations in wet condition. -Particle size effect.

Figure 5.31 Uranyl fluorescence emission spectrum of 60 Å silica gel contaminated by various uranyl concentrations in dry condition. -Particle size effect.
Fluorescence lifetime

Figure 5.32-33 show the fluorescence decay curve of these two particle sizes of silica gel in different uranyl concentrations. Both size materials show a short lifetime $\tau_1$ (range from 110 - 150$\mu$s) and a longer lifetime $\tau_2$ (range from 330 - 355 $\mu$s). In wet conditions, the lifetime calculation results are almost the same in all samples, because of the water on the compound surface. Once the water evaporates from the silica materials’ surface, the shorter lifetime ($\tau_1$) will decrease, and the longer lifetime ($\tau_2$) will increase during the process.

The fluorescence lifetime shows only a slight difference between these two particle sizes. The fluorescence lifetime during a drying process is found to be a more significant variation in higher concentration (1Kppm) samples. In addition, ground silica demonstrates a larger difference in the shorter lifetime ($\tau_1$). This phenomenon presents that the elimination of water can change the properties of the short lifetime species. Also, a smaller particle size causes a more serious variation in this process. Because water can be the media between two small silica particles in a wet condition, the static electronic force will separate the fine particles. When the water completely evaporates, there was no media is between the silica particles. Therefore, gravity will cause the silica materials to pile up very compactly. In addition, the uranyl compounds on the silica material in a short distance have a resonance quench effect. Based on these two reasons, some of the UV excitation energy can be dissipated by the quenching of uranyl compounds on the silica surface due to close stacking. This theory can be proved when we add some water into the uranyl-contaminated fine silica material; the fluorescence intensity will increase again.
Figure 5.32 Uranyl fluorescence decay curve of 60 Å silica gel contaminated by various uranyl concentrations in wet condition. -Particle size effect.

Figure 5.33 Uranyl fluorescence decay curve of 60 Å silica gel contaminated by various uranyl concentrations in dry condition. -Particle size effect.
5.6 Surface Modeling by XPS

Surface survey on silica gel contaminated by 0.2% atomic ratio uranium

The XPS spectrum shows the Binding energy (BE) distribution of the electrons from the elements on the surface layer (see Figure 5.34). In this survey spectrum, we detected the oxygen, silicon, and uranium as the main elements. In addition, we measured the BE of carbon for calibration purposes. Most of the materials exhibited significant BE signals except for silica gel contaminated with 100 ppm uranium. The result shows, for uranium detection, the fluorescence method has much higher sensitivity than XPS characterization.

Figure 5.34 Binding energy surveys on silica gel contaminated by 0.2% of uranium
**Binding energy (BE)**

Figure 5.35 shows the peak values of the binding energies from the uranium-contaminated silica materials. Each binding energy spectrum was calibrated with the carbon (C1S) to correct the bias position. Most of the binding energies are all the same (380.8 ± 0.1 e.V) except for the nano particle nonporous material (item No. 1, 379.4 e.V). The result shows that uranium forms the same uranyl-silica compound on the surface of the nanoporous silica materials.

![Graph showing peak values of binding energy](image)

**Figure 5.35 Peak values the binding energy from uranium 4f7 orbit**

“Binding energy” is the energy required to remove an electron from a molecule. Therefore, higher binding energy indicates that the molecule is more stable. Metal atoms in the molecule are usually in a higher valence state. When uranyl ions react with the silanol group on the silica surface, the ion exchange mechanism causes the uranyl ion to bind on the silica surface through covalent bonding. Because of this chemical bonding, the uranium atoms of the uranyl-silica compound are more stable than the uranium atoms of free uranyl ions. Therefore, the binding energies are different in these two types of samples.
**Full width at half maximum (FWHM)**

FWHM value in XPS is an indication of the possible species of compounds. Figure 5.36 shows the FWHM value of the binding energies from the uranium atoms. Most of the values are similar (4.15 ± 0.1 e.V) except item #3 which has a lower value, and items #5 and #8 which have higher values. Higher FWHM value means two or more nearby binding energy signals merge with each other and form a combination of all signals. In this result, items #5 and #8 both have higher FWHM values and minor low peak of binding energies, which indicates that at least two different binding energies merge together. On the contrary, item #3 shows the lowest FWHM value, which means the surface composition is simpler than the other samples.

![Figure 5.36 Full width at half maximum of the binding energy from uranium 4f7 orbit](image)
Item #5 is the silica sample which has the largest pore size and item #8 is the silica sample with the smallest pore size. Both of them show at least two species on the surface. This result means that there is an optimum pore size for the uranyl ion exchange mechanism on nanoporous silica surfaces. If the average pore size is either too small or too large, it will cause the decreasing of ion exchange ability with uranyl ions, and leave some free uranyl on the surface above the silica-uranyl structure.

**Atom percentage (At %)**

Surface element composition can be analyzed by atom percentage function. After calculating the oxygen, silicon, and uranium amount from the shallow layer on the surface, the uranium atom percentage from these three elements can be plotted in Figure 5.37. Because uranyl ions distribute over the whole surface area, materials with a larger specific surface area have less uranyl precipitation on the silica surface. On the other hand, materials with a smaller specific surface area have more uranyl precipitation. Therefore, in this analysis, the uranium atom percentage can be plotted as an inverse proportion to the unit surface area of silica materials.

However, not all samples show the same trend. Silica nano powder shows the lowest atom percentage of this trend. In addition, the samples were all prepared at a 0.2 % uranium atomic ratio, but on the surface silica nano powder shows only 0.05 At % in the bulk. From this phenomenon, we infer that the nano silica powder cannot provide the precipitation of uranyl ion on its surface, and therefore the binding energy shows an enormous difference from the other silica materials.
On the other hand, sample #5 has the smallest specific surface area and, for this reason, the most uranium precipitation on the surface per unit area. However, it might reach the adsorption limit, or the equilibrium of the ion exchange mechanism, and therefore a small amount of the different uranyl compound shows on the surface. This phenomenon matches the results from binding energy and FWHM values.

For large specific surface area materials, item #2 and #8, the uranyl ions can distribute equally over the whole surface, and therefore the At% is close to 0.2%. This result shows that larger specific surface areas in silica materials can provide more interaction surface to adsorb uranyl ions. In this experiment, all nanoporous silica materials show the adsorption capacity is more than 0.2 At%.
From these observations, we found that the specific surface area of silica materials plays an important role in the uranyl adsorption mechanism. The uranyl ions can be adsorbed onto the silica surface uniformly on an adequate interaction surface (with silanol group). If the amount of uranyl is larger than the sites of silanol groups, the ion exchange mechanism will continue to precipitate the uranyl ions on the structure by the oxygen bridge between the uranium atoms (Ahrland et al., 1960). As these silica materials reach their adsorption limit, uranyl will stay in the free ion state. Uranyl free ions cannot over accumulate because of the electro static on uranyl molecules repulsing each other.

5.7 Discussion and Conclusion

In this chapter, we examined the uranyl fluorescence properties on 15 different silica materials with different water content ratios, and various concentrations of uranium on different silica structures. In addition, X-Ray Photoelectron Spectroscopy (XPS) identifies possible surface species. We found that the particle size, pore size, water content and uranyl concentration on silica surfaces are all important factors for optimizing the fluorescence intensity.

The particle size can affect the uranyl fluorescence intensity. Micro meter level silica gel has a higher fluorescence intensity than nano meter level mesostructured silica and silica nano powder. Among silica gel materials which have the same pore size, larger particle sizes have higher uranyl fluorescence intensity.
The pore size can also affect the uranyl fluorescence intensity. Among micro meter level silica gel materials, the fluorescence intensities are similar when a pore size larger than 60 Å and the intensity increase with the decrease of the pore sizes which are smaller than 60 Å. Increasing the fluorescence intensity is limited by decreasing the silica pore size. The result shows in this research that the silica gel which has a pore size of 22 Å shows relative low uranyl fluorescence intensity among silica materials. This phenomenon is also demonstrated in nano level silica in dry conditions due to the compact packing of nano powders. This compact packing causes narrow spacing and reduces the equal pore size.

Also, fluorescence lifetime is affected by the spacing inside silica material. Silica gel materials show a lifetime decreasing trend when their pore size increase and is larger than 30 Å. Nano meter level particles cause a small equal pore size, and therefore the lifetime is shorter than silica gel materials. However, mesostructured silica (#15 in Table 3.1) that has a pore size of 71 Å shows a long lifetime in the range of silica gel materials. All these tests show a consistence results, the spacing between silica materials, either between amorphous or mesostructured material or between particles, can cause a change of fluorescence.

Water is a very important factor in the uranyl fluorescence sensor. Smaller particle size has a better water absorption ability, and therefore has a faster kinetic to interact with uranyl ions in the water. Water content in porous material can enhance the physical fluorescence intensity. For amorphous silica gel materials and mesostructured silica, the water content ratio is a significant factor for optimization of the fluorescence performance. We found that the smaller pore size silica gel requires less water to produce the maximum
fluorescence intensity. During the drying process from uranium-contamination, most of the silica materials show significant red shift except silica nano powder. Silica materials which have a pore size less than 30Å exhibited a shorter emission wavelength compared with other silica materials. This example shows that the uranyl distribution on silica materials can be similar in both dry and wet conditions.

The uranyl concentration on silica materials demonstrates the important influence of uranyl distribution density. For instance, a silica gel, which has a specific surface area of 500-600m²/g, contaminated by 100ppm (by weight) of uranium means that each uranyl occupies a area of 444 Å square on the silica surface. Therefore, the average distance between two uranyl molecules is 444 Å for an even distribution. For the same calculation, 1,000ppm has a distance between each uranyl molecule of 140 Å, the 10,000 ppm sample has a distance of 44 Å, and 100,000 ppm sample has a distance of 14 Å. A linear dependence occurs on the uranyl concentration and fluorescence intensity with concentrations lower than 1,000 ppm. When the concentration is higher than 1,000 ppm, the increased ratio of the fluorescence intensity is less than the increased ratio of the uranyl concentration. When concentration is 100,000 ppm, the fluorescence intensity is lower than the 10,000 ppm. This is the “Resonance Energy Transfer” which can occur over distances of 100 angstroms or more. This effect can cause the self quenching of uranyl fluorescence. This phenomenon can also be found on the excitation and emission spectrum. The increase of uranyl concentration causes the change of the profile of uranyl vibrational mode. It causes an increase in the ratio of the lower vibration level and results in a blue shift on the uranyl fluorescence emission spectrum.
From the water content analysis and the XPS characterization we conclude that the fluorescence emission spectra from silica materials are consistent with the presence of at least two different optically active uranyl compounds. The specific surface area of silica materials plays an important role on uranyl adsorption mechanism.
Chapter 6
Optical Enhancement - Directed Fluorescence

6.1 Introduction

In previous chapters, we have proved the uranyl adsorption ability of nano porous silica materials which are used on the top of uranyl-contaminated natural soils and discussed the fluorescence enhancement properties of different nano porous silica materials through their porosity, particle size, and water content. However, the fluorescence signal from a silica material which is applied to detect the uranium contamination in natural environments is limited and can be degraded by some environmental and geometric factors. This is because the fluorescence light is distributed randomly over $4\pi$ even if the excitation is made with a parallel beam (laser). For this reason, only a small fraction of the emitted light can actually reach the detector. Therefore, for standoff detection, we need a device to concentrate the emission from the fluorophore to send back directly to the detector.

In this chapter, we have studied the properties of the Directed Fluorescence (DF) method to increase the signal for detection. There are three main subjects discussed in this chapter: the requirement of an optical device in the DF method, the intensity enhancement by a DF application, and the angle limitation for a DF device. The experiment was started
with the observation of glass beads with a different refractive index to prove the retro-refraction theory. Based on the reflective index of the material which can result in a feasible focal length, and the property of the UV transmitting, we chose sapphire as a medium of the optical device.

As mention in section 1.5, the DF system is required to maintain a zero angle between excitation and emission beams. For this reason, the DF test system (see Figure 7.1) employed a 45 degree beam splitter to simulate a zero angle between a fixed vertical excitation source and a photon detector on a horizontal rail. Sea sand was the uranium-contaminated target material used to simulate natural soil. The signal enhancement ability from the usage of the DF system can be shown in a series of measurements of different distances compared with bared uranium-contaminated sand. The results demonstrate that a 200-times increase in the signal intensity, which is translated to a 14-times increase in the standoff distance through the application of directed fluorescence. The fluorescence intensity decreases significantly with the increase of the detection angle between the light source and the detector. The signal intensity decreases by 50% at a detector angle of just 5 degrees.

6.2 Experimental process

Test Station for the Directed Fluorescence Measurement.

To evaluate the effect of distance on the signal intensity in the DF system, we constructed the system shown schematically in Figure 6.1. The system consists of a ball
lens (D) coated with a layer of fluorescence enhancing material (E) that comes in contact with uranyl-contaminated sand (F), an excitation source (A), a beam splitter (C) and an emission detector (B). All mechanical components were mounted on an optical bench and the detector was mounted on a rail to allow varying distance. The beam splitter is an essential part of this system because it allows us to maintain a ‘zero’ angle between excitation and emission beams. The test system of Figure 6.1 was used to simulate typical conditions for standoff detection, where the distance between the target and detector is much longer than the geometry of the detector. With the usage of the rail and the carrier, the intensity detection can extend up to 1 meter.

Figure 6.1 Direct Fluorescence measuring system. A - Excitation Source (UV wavelength = 280nm), B - Emission detector, C - Beam splitter, D - Sapphire ball lens, E - Uranyl fluorescence enhancer, F - Uranium-contaminated sand
Preparation of uranyl-contaminated sand:

The uranium-contaminated sand was prepared by adding 210 μL of 10 mM uranyl nitrate solution to 5 g of sand and 1 ml of water. The uranium-contaminated sand was thoroughly mixed and allowed to equilibrate for two days prior to optical interrogation. These proportions produced a uranium concentration of about 100 ppm. To obtain comparable results, the area of optical interrogation was the same for all experiments and was a circular spot, 6.5 mm in diameter. Prior to each optical measurement the sand was moistened by the addition of 0.5 ml of DI water. The emission spectrum was then obtained for the bare sand and with each component of the DF sensor element while the sand was still moist. Then, each system (sand plus sensor element) was air dried for 24 hours and the peak emission wavelength was measured as a function of standoff distance as described below.

DF sensor element preparation:

1g of poly (vinyl alcohol) was dissolved in 20 ml of DI water with continuous stirring at 60 °C. One milliliter of this solution was diluted with 1ml of DI water and mixed with 1g of silica gel #3 in Table 3.1. Prior uses of the sapphire ball lenses were cleaned with acetone and immersed into 10% sodium metasilicate solution for 30 min, rinsed with DI water and dried. The above prepared paste was placed on the sapphire ball lenses and dried for 24h at room temperature. The applied composite layer has a thickness of about 0.5 mm
Fluorescence measurement.

Fluorescence spectra were recorded with the Quanta Master spectro-fluorometer (see Chapter 3.3) which was equipped with flexible liquid wave guides on its excitation and emission sides. In Figure 6.1, only distal ends of these wave guides are shown as an emitter and detector. The samples were exited with 280nm and an emission was collected at 498nm. An average of 200 points for each experiment was calculated with Felix32 Analysis software.

DF angle dependence measurement system

The DF angle dependence measurement system is set up as Figure 6.2, and the top view is illustrated in Figure 6.3. The system is mainly set up by the fixed excitation source (A) and the detector (B) on a swiveling mechanism (C). A sapphire ball lens (D) was set at the center of the swiveling mechanism and level with the excitation source (A). Because the intensity is very sensitive to the BFL, we chose a fluorophore with a flat surface to avoid the variation which may be caused by the unleveled surface. Therefore, a 3M fluorescence tape (E) was used as the fluorescence material and was cut in a round shape with the same diameter as the sapphire ball lens. The whole system was fine adjusted by a 3-axes stage (F) before fluorescence interrogation.
Figure 6.2 The schematic of the DF angle dependence measurement system. A - Fixed excitation source, B - Fluorescence detector, C - Swiveling mechanism, D - Sapphire ball lens, E - Fluorophore material, F - 3-axes stage.

Figure 6.3 Top view of the schematic of the DF angle dependence measurements.
6.3 Optical Device

Glass beads for Directed Fluorescence

Two glass beads with a relative higher refractive index (n=1.95) and lower refractive index (n=1.52) were employed in the preliminary retro-refraction test. Both species of beads have a diameter of about 100 μm. Under an optical microscope, glass beads with a higher refractive index (sample B in Figure 6.4) exhibit a uniform intensity on the whole bead surface because they can reflect light back to the camera. On the contrary, glass beads with a lower refractive index (sample A in Figure 6.4) show signals only on the center of the beads, which means that the light cannot be sent back from the beads efficiently and most of the light is scattered. From equation 1-1 and 1-2, because the fluorophore touched the ball lens, the back focal length is zero. Therefore, the index of reflection should be as close to 2 as possible. This preliminary optical test helps us to prove the influence of refractive index on DF performance (see Figure 1.7).

Figure 6.4 Retroreflectivity from glass beads with different refractive index. A - soda-lime glass beads (n = 1.52), B – High refractive index (n = 1.95) glass beads
However, higher refractive index glass beads are not transparent using short UV radiation because of the microstructure and the components of the glass material. In addition, the back focal length could govern the amount of the fluorophore which can receive the excitation source efficiently (see Figure 1.7). As a conclusion, we chose 6.5mm sapphire spherical beads to model DF system for uranyl fluorescence enhanced with silica gel. These beads have a refractive index 1.768, and their BFL is about 0.5mm. With such relatively big beads, it is easy to construct and understand optical properties of the DF system.

Figure 6.5 shows photographs of the directed fluorescence (DF) sensor element placed onto the urannium-contaminated sea sand under both ambient light and under 254nm UV irradiation. The UV excitation was applied uniformly to both the sensor and the surrounding sand in the photographs of Figure 6.5 (B). It demonstrated that the fluorescence signal from the directed fluorescence sensor element is much stronger than the signal from the bare sand, which appears as a dark background in the photograph.

![Figure 6.5 Photograph of Directed Fluorescence placed sensor onto uranyl nitrate contaminated sand. A – under ambient light, B – under 254 nm UV irradiation. The sand contamination is equivalent to 100 ppm of uranium.](image-url)
6.4 Intensity Enhancement

To evaluate the advantage of the sensor over the regular method with fluorescence detection, we recorded the signal degradation by distance for sets with the sensor and several settings without the sensor. Results are represented in Figure 6.6. The curve A in Figure 6.6 shows the signal originated from sea sand contaminated with uranyl. Due to a low signal intensity for the sand sample our spectro-fluorometer was able to pick up the signal only for a distance less than 25cm. If a ball lens without any coating was added the signal became about 10 times stronger (see curve B in Figure 6.6).

Curve C in Figure 6.6 shows that the silica gel when distributed onto the uranium-contaminated sand can increase the fluorescence signal. We also covered the sapphire ball lens with a silica gel composite material. Because pure silica gel layers prepared by the sol-gel process onto the glass surface without any additives were not stable, such layers promptly pilled off by contact with water or wet soil. Better mechanical properties can be achieved by combining silica gel with organic polymers. We found that poly (methyl methacrylate) (PMMA) and poly (vinyl alcohol) (PVA) can be combined with silica gel without serious fluorescence quenching. However, the composition material with PMMA shows a hydrophobic behavior that causes a longer time (more than 1h) to adsorb uranyl form the sand sample and detect its fluorescence. In the contrast, the composite with PVA shows good mechanical properties and fast interaction with uranyl. The prepared sapphire bids with a 5% PVA-silica gel composite layer show 200 times signal improvement over bare sand (see curve D in Figure 6.6).
Sapphire exhibits birefringence, a difference in index of refraction in orthogonal directions. The difference in index is 0.008 between light traveling along the optic axis and light traveling perpendicular to it. For the present calculations this difference is not so essential and we used data for the ordinary ray. For excitation light at 280nm sapphire refractive index is 1.824 and it is 1.774 for emission light at 498nm. That led to BFL equal to 0.339mm and 0.543mm correspondingly. Thus, we can conclude that the prepared silica composite layer is near optimum to present application.
The curve E in Figure 6.6 represents the set where the ball lens sits on silica gel powder over contaminated sand. For present tests that combination demonstrates strongest signal enhancement. This set shows the strongest signal but there was a lack of repeatable results due to inconsistency in the optical contact between the lens and silica gel layer.

Compare curves 4A and 4D in Figure 6.6, for the same signal intensity the coated sapphire ball lens shows a fluorescence response which detected a longer distance of up to 14 times than the response originated from the bare contaminated sand. This fact shows that DF is very beneficial for the remote detection of soil contaminations.

In conclusion, we demonstrated that the DF system increased the signal intensity by more than 200 times and DF can be used as a prospective method for environment monitoring. It is advantage that the beads can be stored for very long time and they are environmentally stable. This method can also be applied for the detection of other contaminates if the target element can produce a fluorescence signal when reacting with the solid reagent.

6.5 Angle depended intensity of DF

Although the DF system has the advantage to be able to enhance the uranyl fluorescence signal from natural environments, the detection method has a limitation in the effective observation angle. In this section, we investigated and plotted the dependence of the fluorescence intensity on the angle between irradiation and emission beams of the DF system (see Figure 6.7). The result shows that this system only allows a narrow angle
range of light to go back to the detector. The emission signal is eliminated when the included angle exceed twenty degrees. The signal intensity decreases by 50% with a detector angle of just 5 degrees.

![Figure 6.7 Emitted light intensity vs. angle between emission and excitation source (a) for the DF system with the polymer fluorescent material.](image)

6.6 Discussions and Conclusions

We have developed and demonstrated a DF sensor element for the standoff detection of uranium in soil. Our results show that the DF sensor element can be used to increase the signal intensity by 200-times and the maximum standoff distance by 14-times. The DF sensor is based on the integration of a nanoporous silica gel fluorescence enhancement matrix and a spherical ball lens, which provides additional optical signal enhancement. The DF sensor element can be easily modified for the detection of other fluorescent molecules simply by changing the properties of the coating material.
Literature Cited


Geipel, G., Bernhard, G., Rutsch, M., Brendler, V., & Nitsche, H. (2000). *Spectroscopic properties of uranium(VI) minerals studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS).*


APPENDIX A

The Radiation Detection of Uranyl Nitrate

Gamma radiation measurements are considered as a competitive and somewhat more conventional method for uranium detection. Uranium itself undergoes α-decay and spontaneous fission, but its daughter products produce gamma radiation which can be detected in commercial scintillation detectors. The gamma radiation from a uranyl nitrate sample was measured with a scintillation detector (Bicron 2M2/2_P-14) and a universal counter HP 53132A was used to measure the gamma-ray emission intensity as a function of distance. Five samples containing 1, 2, 5, 10 and 20g of uranyl nitrate were prepared and counts were measured as a function of distance for each sample from 7 to 40cm. These results are shown in Fig 6. The lower detection limit (LDL) was calculated for an 18cm distance. To calculate the LDL we adopted a technique described by Sowder and coworkers\textsuperscript{14}. The value of the LDL was experimentally determined as 3 times the standard deviation of replicate measurements near the detection limit. For the gamma-ray measurement the calculated LDL is about 6.7g of uranyl nitrate at 18cm. To calculate the LDL for the DF technique we used the fact that 5.02\times10^{-5} g of uranyl nitrate produces

detectable signal at 18 cm and even much longer distances (Figure A.1). Thus, the relative sensitivity of the DF method over conventional technique can be estimated as \( 6.7 : 5.02 \times 10^{-5} = 1.3 \times 10^5 \). This is an estimation value and is for unshielded material. However, it clearly shows that, for unshielded material, the DF method is more sensitive than conventional gamma radiation methods by more than 5 orders of magnitude.

![Figure A.1](image-url)" Figure A.1 Uranium detection by gamma-radiation (scintillation detector). X-Axis shows the distance between uranyl nitrate sample and the radiation detector. Each color represents amount of uranyl nitrate was taken for the experiment.
APPENDIX B

Test of Uranyl Fluorescence Enhancers

To choose the best material of fluorescence enhancer for this study, we have tried several phosphate, fluoride, and silica compounds in solid states (see Table B.1). Each sample was contaminated with 3mL, $10^{-5}$M uranyl solution for 1Day. The result of the fluorescence enhancement is shown in Figure B1.

We found the silica gel shows the best fluorescence signal in both UV wavelengths (254nm and 365nm by UV lamp). Phosphate compounds also show fluorescence signal as well, however, the intensity is lower than silica materials and only can be observed by the shorter wavelength (254nm). On the other hand, fluoride compound cannot show any fluorescence in this experiment.

In addition, the material response time was roughly noted. We found that the silica material can react with diluted uranyl solution instantly and show very promised fluorescence signal. On the contrary, phosphate compounds showed a slow kinetic response, which increased the fluorescence intensity gradually in couple days.

In conclusion, silica gel shows higher enhancement ability for uranyl fluorescence than other compounds, and it was chosen as the target material in this study.
Table B.1 Candidate enhancers for uranyl fluorescence

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Brand</th>
<th>Part Number</th>
<th>Fluorescence</th>
<th>Possible UV wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cellulose Phosphate</td>
<td>SIGMA</td>
<td>C2258-100G</td>
<td>White</td>
<td>365</td>
</tr>
<tr>
<td>2</td>
<td>β-tri-Calcium Phosphate</td>
<td>Fluka</td>
<td>21218</td>
<td>Green</td>
<td>254</td>
</tr>
<tr>
<td>3</td>
<td>Polyacrylic Acid (Gel form)</td>
<td>SIGMA</td>
<td>D7416-50G</td>
<td>White</td>
<td>365</td>
</tr>
<tr>
<td>4</td>
<td>Calcium Hydroxyphosphate</td>
<td>ALDRICH</td>
<td>574791-5G</td>
<td>Green</td>
<td>254</td>
</tr>
<tr>
<td>5</td>
<td>Calcium Fluride</td>
<td>ALDRICH</td>
<td>23,794-9</td>
<td>N/A</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>Silica Gel</td>
<td>ACROS</td>
<td>360062500</td>
<td>Green</td>
<td>365/254</td>
</tr>
</tbody>
</table>

Figure B.1 Solid uranyl fluorescence enhancers exposed under 254nm UV lamp
VITA

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