

Uranyl Soil Extraction and Fluorescence Enhancement by Nanoporous Silica Gel: pH effects

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Abstract Nanoporous silica gel was employed to extract uranyl from contaminated soil and to enhance the fluorescence intensity and lifetime. The fluorescence lifetime and intensity of uranyl ions absorbed within nanoporous silica gel was measured from pH 1–13. 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.

Keywords Uranium · pH effect · Micro porous silica · Fluorescence · Soil

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 [1–5]. 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 matrixes and new detection methods are needed in order to monitor uranyl soil concentrations [6, 7].

Uranium and its compounds are naturally radioactive and are traditionally detected through the emitted high energy radiation. However, radiation detection does not provide sufficient sensitivity for standoff measurements of trace uranium concentrations in soil and we have, therefore, been investigating optical, fluorescence-based methods for uranyl detection. Laser-Induced-Fluorescence (LIF) measurements of uranium were introduced by Robbins [8], and have subsequently been widely investigated and applied to contaminated areas [9–12]. However, the detection threshold of LIF measurements of uranyl in soil is still insufficient and fluorescence enhancement strategies applicable to soil measurements are necessary. While chemical enhancement of uranyl fluorescence in aqueous solutions has been widely reported, our work has focused on the investigation of high porosity silica gel as a solid-state fluorescence enhancer which can be applied to the surface of a contaminated solid (e.g. soil) where it absorbs and accumulates uranyl and enhances the fluorescence signal intensity.

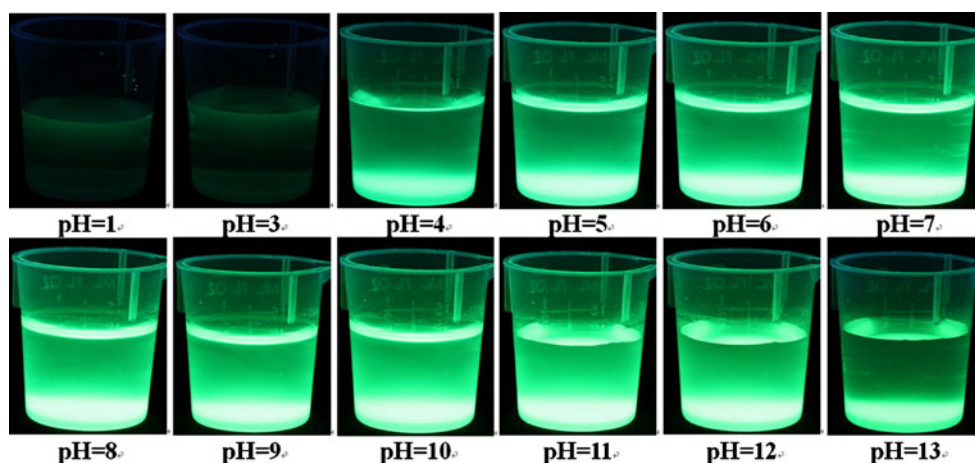
Silica gel has a large surface area (from 300 to 800 m^2/g , depending on the pore size) and the silanol groups allow silica gel to efficiently absorb water and metal ions [13]. Therefore, silica gel is commonly used as a desiccating and filtering agent in industrial and home leaching systems. A study of the adsorption of uranyl to amorphous silica as a function of pH indicates a general trend with adsorption climbing in the pH 3–5 range, leveling off in the neutral range, and dropping rapidly in the pH 8.5–9 range [14–16]. This general uranyl-silica adsorption trend with pH is very similar to that seen when uranyl sorbs to natural mineral surfaces. The optimum pH range for uranyl adsorption by silica

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Table 1 Environmental soil samples

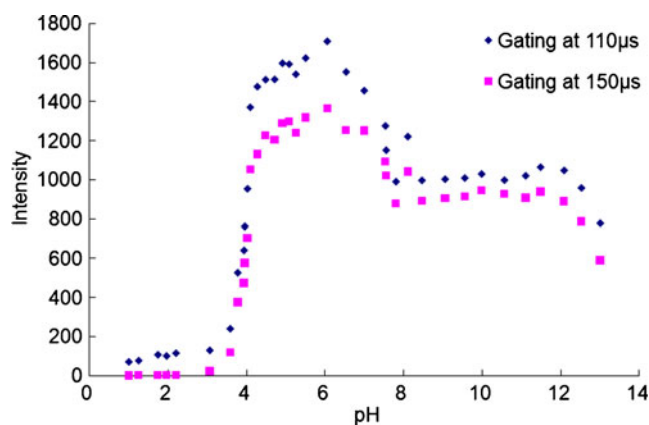
Sample code	Soil texture	Color	Sample collection location	Typical condition	Environmental area
1- UC	54% Sand 17% Silt 29% Clay <i>Sandy Clay Loam</i>	dark tan	Eastern Piedmont soil, Montpelier VA Upland area Est. soil penetration: 6 in	dry zone	wooded area
2- SF	48% Sand 31% Silt 21% Clay <i>Loam</i>	brown	Eastern Piedmont soil, Montpelier VA Semi-permanent flood zone Est. soil penetration: 6 in	wet zone	wooded area
3- JA	44% Sand 45% Silt 11% Clay <i>Loam</i>	dark brown	James River stream bed Hopewell VA Bottom of a shallow channel Est. soil penetration: 1 ft	submerged	nature preserve, downriver from industrial area
4- SC	<i>Sand</i>	light tan	Fisher Scientific (Sea Sand standard)	–	–

Fig. 1 Silica gel (500 mg) with uranyl (1.5 mg) at different pH. Excitation with UV 254 nm

gel is between 5 and 5.5 [16] and depends on the hydrolysis of uranyl ions [17], carbonate complexes and natural electrolytes [18–20]. Examples of typical surface speciation include SiO_2UO_2 , $\text{SiO}_2\text{UO}_2\text{OH}^-$ and $\text{SiO}_2\text{UO}_2\text{OHCO}_3^{3-}$. The first two species are fluorescent and are present at lower pH values (e.g. ≤ 7.5) while the carbonate species is non-fluorescent and is present at higher pH values (e.g. ~ 8.5). Therefore, while the uranyl fluorescence emission spectra and lifetime can be significantly enhanced inside of the porous silica gel due to geometrical sheltering from quenchers such as water and other quenching anions the surface speciation and corresponding emission spectrum are very sensitive to pH.

Silica gel has been employed as a component in a passive sensor for uranium detection in contaminated sand [21]. However, the feasibility of using silica gel for the extraction and detection of uranium from contaminated natural soil has not yet been reported. Here we report on an investigation of the influence of pH on the adsorption and fluorescence of uranyl within a solid silica gel matrix applied directly to the surface of uranyl contaminated soils.

It is shown that silica gel can be used to extract water containing dissolved uranyl from contaminated natural soils resulting in significantly enhanced fluorescence intensity and lifetime.

**Fig. 2** Fluorescence intensity of silica gel – uranyl mixture at different pH. Intensity calculated as the height of the actual peak in the emission spectra near 500 nm

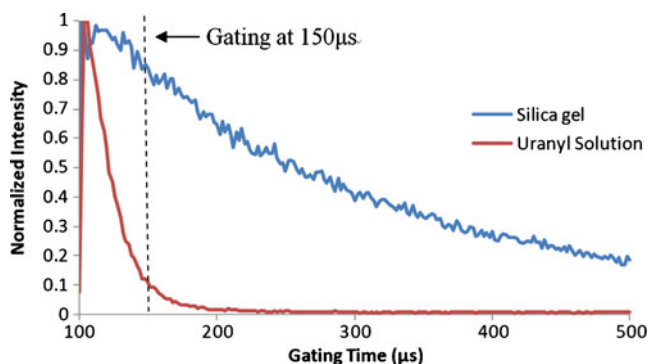


Fig. 3 The normalized decay curve of uranyl fluorescence from silica gel and uranyl solution at pH 5

Experimental

Materials

Uranyl nitrate hexahydrate was purchased from American Master Tech Scientific at A.C.S. Reagent grade and was used without further purification. Silica gel was obtained from Acros Organics with an average pore size of 4 nm, and a particle size in the range of 40–60 micrometers. Sulfuric acid solution was obtained from Fisher Scientific. Sodium hydroxide was obtained from Acros Orhanics in pellet form at 97 + % purity. Three natural soil samples were collected near Richmond VA. Dry sea sand was obtained from Fisher Scientific. Sand samples were prepared by wetting dry sand with 13% of DI water. Table 1 is a list of the soil and sand samples tested in this research.

pH measurements of aqueous samples

Titration samples were prepared by mixing 10 mL of deionized water, 500 mg of silica gel, and 0.55 mL 0.01 M (1.5 mg UO_2^{2+}) uranyl nitrate. After careful mixing, the samples were sealed and aged for 1 day to allow uranyl to interact with the silica gel. pH was adjusted by titrating

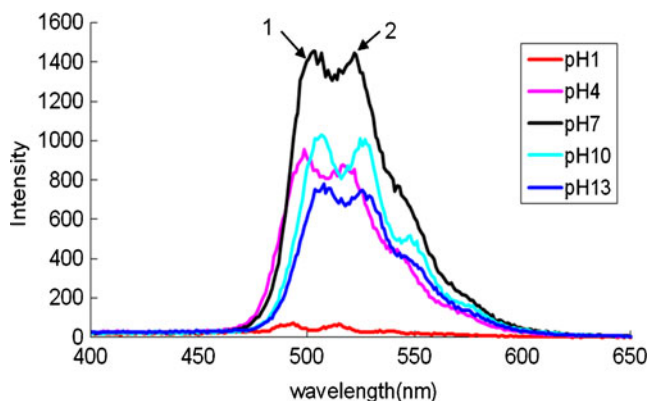


Fig. 4 Emission spectra of uranyl solution with silica gel at different pH. Arrow shows the two peaks used for intensity calculations

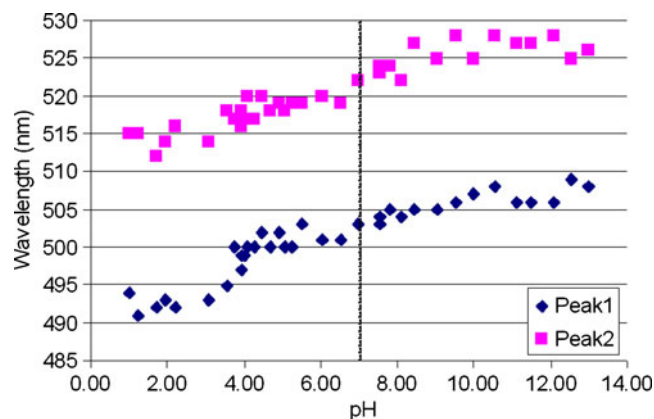


Fig. 5 Position of the uranyl peaks near 500 nm (peak 1) and 520 nm (peak 2) at different pH

sulfuric acid or sodium hydroxide. pH values were measured using an Orion 3-Star pH-meter equipped with Orion 8103BN ROSS Combination pH Electrode. The samples were mixed carefully and held for 1 min to settle the silica gel before measuring the pH value.

Uranyl extraction from soil by silica gel

Original soil samples were placed in plastic Petri dishes and 42 μ L 0.01 M 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. 5 mg of silica gel powder 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.

Fluorescence measurement

Fluorescence spectra were recorded with a Quanta Master spectrofluorometer by Photon Technology International

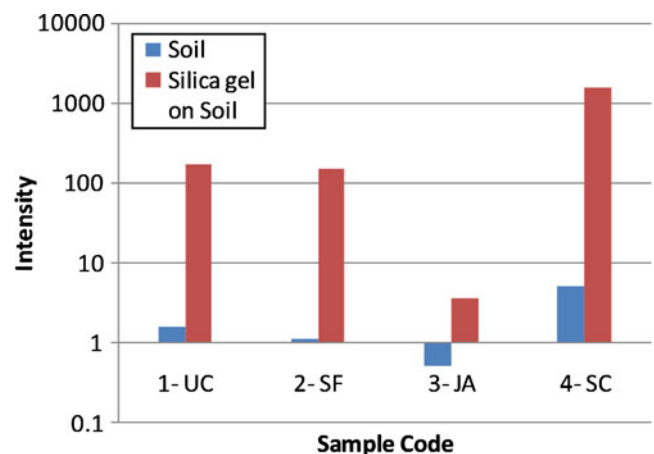


Fig. 6 Comparison of fluorescence intensity for different soils. Excitation at 280 nm, emission at 498 nm with gating time 150 μ s

Table 2 pH of soil samples

Sample code	Direct measurement of the original soil	Protocol with DI water dilution 1:5	Adding uranyl 100ppm
1- UC	4.32	4.46	4.3
2- SF	4.01	3.90	3.98
3- JA	7.19	7.24	7.22
4- SC	4.96	5.85	4.28

(PTI) equipped with a xenon pulse lamp for sample excitation. The pulse lamp allows the recording of gated fluorescence spectra. Gating-times of 110 μ s and 150 μ s were employed to test for background fluorescence rejection. All tests were performed with an excitation wavelength of 285 nm. Fluorescence emission was recorded in the area of uranyl fluorescence at 400–650 nm. The delay times are counted from the beginning of the excitation impulse of the instrument and the pulse duration is approximately 104 μ s. For instance, this means that with a delay time of 110 μ s, the actual delay time is about 6 μ s if it is counted from moment when the excitation impulse falls.

Results and discussion

pH measurements of aqueous samples

Beakers containing silica gel in uranyl nitrate solution at different pH levels are shown in Fig. 1 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 [16]. Uranyl hydroxylation initiates near a pH of 3 and

Fig. 7 Fluorescence enhancement with silica gel after 5 days of aging. Sample numbers corresponded to the samples in Table 1. Left – under ambient light, right – under 254 nm UV irradiation

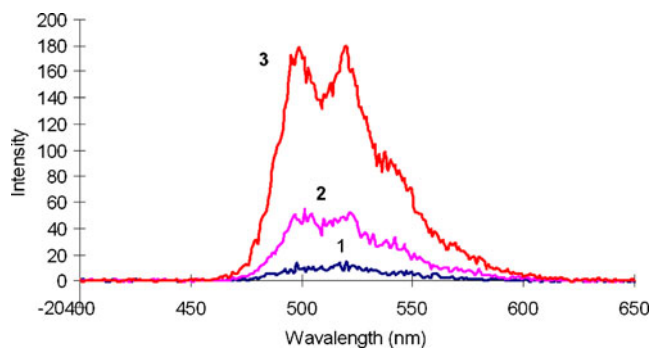
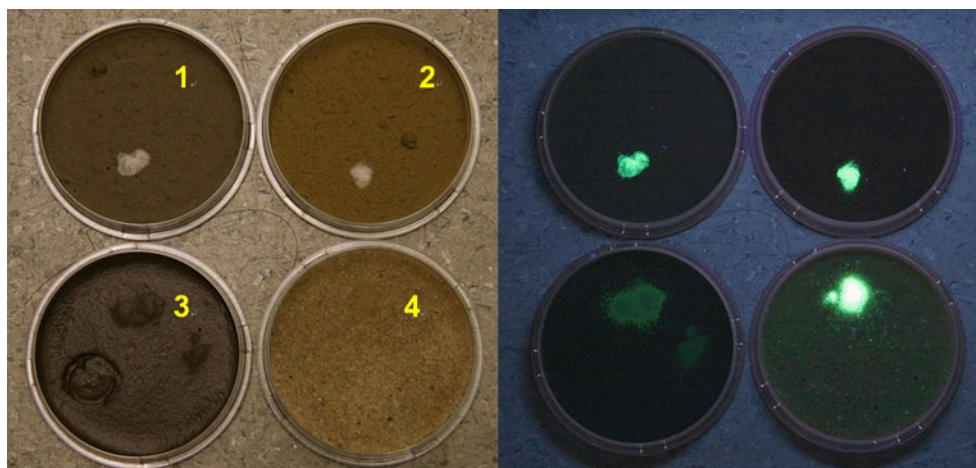


Fig. 8 Fluorescence spectra of the sample #2 recorded at three different times: 1 – immediately after silica gel deposition, 2–4 h later, 3–5 days later

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 2 shows the intensity of the characteristic fluorescence peak near 500 nm as a function of pH at two different gating times (110 μ s and 150 μ s). Figure 3 shows the fluorescence intensity of the 500 nm 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 150 μ s gating time is very low because the uranyl fluorescence lifetime in solution is short as shown in Fig. 3. 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 150 μ s 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 Fig. 3 which was obtained at pH 5.

Figure 4 shows the uranyl fluorescence emission spectra at different pH values. The emission spectrum at each pH value shows two strong characteristic peaks near 500 nm and 520 nm. The characteristic peak wavelength increases monotonically (red shifts) with pH as shown in Fig. 5.

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 22 nm. From pH 4–7 the characteristic peak separation is 18 nm and for pH values higher than 10 the characteristic peak separation is 20 nm. 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 [22]. 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.

Uranyl extraction by Silica gel from contaminated natural soil

Figure 6 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. Uranyl ions are transported by water from the moist soil into the silica gel and the kinetics of the process depends strongly on the soil porosity. 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 h 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 7 shows optical images of the fluorescence enhancement for silica gel applied to the surface of the four soil samples shown in Fig. 6. 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.

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 8 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 4 h later and then 5 days later. A detailed investigation of the kinetics of uranyl migration in the various soil types is beyond the scope of this paper, but our results confirm that the kinetics will vary significantly depending on various soil features.

Our measurements show that the addition of 100 ppm of uranyl does not significantly change the pH of the natural loam soil samples, but it does reduce the pH of the sea sand sample due to its low buffer capacity. Table 2 gives the original pH values of the four soil samples in comparison to the pH after the addition of DI water and after the addition of 100 ppm uranyl nitrate.

Conclusions

The effect of pH on uranyl fluorescence in silica gel was investigated. The pH was shown to affect the fluorescence intensity and lifetime as well as the peak position and peak separation. The characteristic emission peak position exhibits a Bathochromic shift with increasing pH and the narrowest peak separation, associated with the lowest ground state vibrational energy, occurred in the neutral pH region where the silica gel exhibited the best fluorescence enhancement (i.e. pH 4–7). The feasibility of uranyl detection from environmental soil samples was demonstrated, but the kinetics for uranyl extraction from clay can be slow. 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.

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