ABSORPTION SPECTRA AND SPECIATION OF PLUTONIUM(VI) WITH PHOSPHATE

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ABSTRACT

Plutonium(VI)-phosphate species in aqueous solution, at pH < 2.4, formed two species: $PuO_2H_2PO_4^+$ (characterized by an 835 nm absorption band) and the solid phase $PuO_2(H_2PO_4)_2$. The stability constant (β) for the $PuO_2H_2PO_4^+$ species was determined to be log $\beta = 2.1 \pm 0.1$ (ionic strength = 0.6-0.9 M) and log $\beta^T = 2.6 \pm 0.15$ (zero ionic strength). Four Pu(VI)-phosphate species (absorption bands at 842, 846, 857, and 866 nm) formed at pH = 2.4 to 12.2 and are characterized by polynuclear behavior, the formation of precipitates, and colloidal properties. The 842 and 846 nm species are believed to be $[PuO_2(HPO_4)_m]_n$ and $[PuO_2(NaPO_4)_m]_n$. The 857 and 866 nm species area as yet unidentified.

INTRODUCTION

The speciation of plutonium with phosphate is of interest to radionuclide migration studies because phosphate is present in many groundwaters and may be used as an actinide getter in nuclear waste disposal. An actinide getter is a complexing agent that forms insoluble phases with actinides, thereby reducing their migration.

Plutonium(VI) is an important oxidation state in repository-relevant oxidizing systems and near-surface groundwaters. And yet, few papers have been published concerning Pu(VI) in phosphate solutions [1-5]. Most of the data reported pertain to solubility experiments [1-2] or the making and analyzing of Pu(VI)-phosphate solids [3-4]. Moskvin used solvent extraction to calculate stability constants but provided few details of his procedure [5].

Herein we report the results of experiments conducted to investigate Pu(VI) speciation in phosphate solutions. Absorption spectroscopy was used to investigate the speciation of Pu(VI) in phosphate solutions from pH = 0.3 to 12.2. Solubility experiments were performed in conjunction with the spectroscopic work and are reported elsewhere [6-8].

EXPERIMENTAL APPROACH

All water used was obtained from a Barnstead Nanopure ultrafilter, with water conductance greater than 18 MΩ-cm. The water was also boiled to remove carbon dioxide. Sodium perchlorate was prepared by adding sodium carbonate to concentrated perchloric acid. The sodium perchlorate solution was filtered and then crystallized by heating and evaporating the solution. The majority of the solutions tested had an ionic strength (I), as sodium perchlorate, between 0.5 M and 1.0 M. The chemicals used were analytical reagent grade from Mallinckrodt: sodium phosphate (dibasic and anhydrous), 85% phosphoric acid, 70% perchloric acid, sodium carbonate (anhydrous), and sodium hydroxide. Plutonium Pu-239 was originally obtained from Oak Ridge National Laboratory as an oxide. The Pu-239 had been stored in 4 M nitric acid. It was taken to dryness, redissolved in 8 M nitric acid, and run through a 1 cm by 10 cm column filled with Bio-Rad MP-1 resin that had been preconditioned with 8 M nitric acid solution. The eluent was taken to dryness and redissolved in 4 M nitric acid. A small amount of concentrated perchloric acid was added and slowly taken to near-dryness to oxidize the plutonium in the solution to the 6+ state. Absorption spectrometry was used to verify the oxidation state of the Pu(VI) solution.

Absorption spectroscopy of the Pu(VI)-containing solution was performed in the wavelength range of 400 to 900 nm, focusing on the range of 800 to 900 nm. The 831 nm band of PuO_2^{2+} was the focus of our study due to its large extinction coefficient, $\epsilon = 550\ \underline{M}^{-1}cm^{-1}$ [9], and large shift in wavelength when complexed. A slit width of 1 nm was used throughout, corresponding to the 831 nm band. A CARY 5E spectrometer was used to obtain the majority of the spectra. A Hitachi 340 was also used for the solutions at pH < 2.4.

Precipitates formed in many of the solutions and were analyzed using scanning electron microscopy (SEM) to obtain micrographs and elemental compositions. An Etec Autoscan microscope was used with a Kevex X-ray detector. Elements with an atomic number smaller than sodium could not be detected.

Photon correlation spectroscopy was used to determine the size of particles suspended in some of the solutions. A system 4700c photon correlation spectrometer by Malvern Instruments was used with the laser light at 514.5 nm.

RESULTS

The Pu(VI)-phosphate species observed can be divided into two regions, solution pH < 2.4 and pH > 2.4. Precipitates formed, even at low phosphate concentrations, at pH > 2.4. Plutonium(VI) hydrolysis was also investigated in order to distinguish the hydrolytic absorption from the absorption of the Pu(VI)-phosphate species.

Pu(VI) Hydrolysis

Absorption spectra were taken of Pu(VI) hydrolysis in solutions without phosphate and up to pH = 12.4. The spectra at pH = 5.6 and 10 are shown in Figures 1 and 2. These spectra are similar to the hydrolytic spectra reported by others [10-12]. Of importance to phosphate work presented later, Pu(VI) hydrolysis was not spectroscopically evident until pH > 4 for Pu(VI) concentrations below 1.3 x 10^{-3} M.

Pu(VI)-phosphate absorption spectroscopy at pH < 2.4

Phosphate was added to plutonium solutions at pH values from 0.3 to 2.3 and ionic strengths of 0.6 to 0.9 M. An absorption band at 835 nm appeared and increased as phosphate was added (see Figure 3). An isobestic point can be seen at 833 nm, signifying that only one Pu(VI)-phosphate species was being formed. The molar absorptivity for the 835 nm band was found to be $\epsilon_{835} = 372 \pm 17$ $M^{-1}cm^{-1}$.

For the pH = 0.8 solution, a white solid became visible and precipitated instantly out of solution at a high phosphate concentration (concentrations given in caption of Figure 4). No new absorption band (see Figure 4) was observed and no shift in the baseline occurred. A baseline shift is indicative of light-scattering by particles.

Pu(VI)-phosphate absorption spectroscopy at pH > 2.4

At pH > 2.4, absorption bands formed at 842, 846, 857 and 866 nm, each corresponding to a different Pu(VI)-phosphate species. The pH regions where these bands formed are shown in Table 1 for I > 0.2 M and Pu(VI) > 5 x 10^{-4} M. At lower Pu(VI) concentration, either PuO_2^{2+} or hydrolytic species were formed instead of phosphate species. At lower ionic strengths but comparable Pu(VI) concentrations, the 842 nm species was present at pH > 5. Slow complexation kinetics was observed for the 842 nm species to convert to the 846 nm species and for the 846 nm species to convert to the 857 nm species if the pH of the solution was increased.

The Pu(VI)-phosphate species formed at pH > 2.4 are characterized by an elevated absorbance baseline and the formation of precipitates which were slow to settle out of solution. As the precipitates settled out of solution, the baseline and the absorption band decreased. Figure 5 gives the spectra over time at pH = 2.4 as precipitates settled out of solution. The 842 nm band and the baseline decreased, but the 831 nm band (PuO_2^{2+}) and the 835 nm band were not affected.

Figure 6 illustrates the effect of the precipitates settling out of solution for the 846 nm band. Furthermore, this figure indicates that the baseline increased as the wavelength decreased. This wavelength dependence is characteristic of the light scattering caused by a colloidal suspension [13].

When the solution was agitated, the precipitates disappeared and often the solution became misty. The solution with the 866 nm absorption band had green precipitates, and when it was agitated, the solution became the same color as the precipitates. (The precipitates were grey or white for the solutions with the 842, 846, and 857 nm bands.) Furthermore, the baseline and the absorption band increased to the original value. After agitation, the precipitates formed again and settled out of solution.

Denotkina and Shevchenko [3] noted similar behavior for the solid PuO_2HPO_4, which, when dissolved in water, remained suspended in solution at a concentration of 0.02 M after 24 hours.

842 nm absorption band

The formation of the 842 nm species was seen to be irreversible, to produce H^+, and to depend on the Pu(VI) concentration. The irreversibility was seen for a solution in which the pH was decreased from 2.6 (831 and 842 nm bands) to 2.0, where only the 831 and 835 nm bands should be present; moreover, 70 hours later none of the 842 nm species had converted to the 835 nm species. The production of H^+ was detected as a decrease in the pH when the 842 nm band was formed. The addition of a phosphate solution at pH = 3.33 to a Pu(VI) solution at pH = 3.33 resulted in the 842 nm band and a final pH of 3.0. Also, the addition of Pu(VI) solution at pH = 3.7 to phosphate solution at pH = 4.0 resulted in the 842 nm band and a final pH of 3.1.

Lowering the Pu(VI) concentration diminished the proportion of the Pu(VI) that formed the 842 nm species. This is illustrated by comparing two Pu(VI)-phosphate solutions, both at phosphate = 2.0×10^{-3} M. One solution [Pu(VI) = 4.05×10^{-4} M and pH = 2.8] had more than half of the Pu(VI) as the 842 nm species. The other solution [Pu(VI) = 4×10^{-5} M and pH = 3.0] had only the 831 nm species (PuO_2^{2+}).

The molar absorptivity for the 842 nm band was calculated by using Beer's law and assuming mononuclear species. Since the 842 nm band decreased as the precipitates settled out of solution, only spectra of solutions before any settling had occurred were used. Whether settling had occurred was determined by taking several spectra of the solution over time. The molar absorptivity was determined to be ϵ_{842} = 340 ± 20.

846 nm absorption band

The formation of the 846 nm band also depends on the Pu(VI) concentration. Lowering the Pu(VI) concentration resulted in an increase of hydrolytic Pu(VI) and a decrease of Pu(VI)-phosphate species. This dependence is illustrated by a comparison of two solutions, both at phosphate concentrations of 2.0×10^{-3} M and pH = 8.8. Based on the spectra, one solution at Pu(VI) = 1.05×10^{-3} M had only Pu(VI)-phosphate species, but the Pu(VI) in the other solution, at Pu(VI) = 4×10^{-5} M, was mostly hydrolytic.

The molar absorptivity of the 846 nm band was ϵ_{846} = 380 ± 20, determined in a manner similar as that used for the 842 nm band.

857 and 866 nm absorption bands

Only several solutions at pH > 9 were analyzed. The 857 nm absorption band, shown in Figure 7, was seen at pH from 9.5 to 10.6. However, in phosphate solutions at pH > 11.9, the Pu(VI) was usually hydrolyzed except for one solution at pH = 12.2, which had a Pu(VI)-phosphate absorption band at 866 nm (Figure 8). This solution had a higher phosphate concentration (phosphate = 5.3×10^{-3} M) than the other high pH solutions. The precipitates of the solution with the 866 nm band were removed, washed, and dissolved in water. Spectra of the dissolved precipitates had Pu(VI)-phosphate absorption bands at 846 and 857 nm.

Molar absorptivities, found in a manner similar as that used for the 842 nm band, were $\epsilon_{857} = 200 \pm 30$ and $\epsilon_{866} = 123 \pm 15$.

Precipitates

Three precipitate-containing solutions (pH > 2.4) were analyzed by correlation photon spectroscopy (CPS). However, the CPS results for two of the solutions were not reliable because the particles suspended in solution were too large (> 2000 nm). Absorption spectra were taken before and after analyzing the remaining solution (pH = 4.1) with CPS. The 842 nm band and an elevated baseline were present. The particle size distribution is shown in Figure 9. The precipitates, when suspended in solution, were between 200 nm and 1200 nm in size.

An important observation concerning the precipitates was obtained from filtering performed in the solubility experiments [6-8]. The 400 nm and 50 nm filtrate of a settled solution (i.e., precipitates had settled out of solution) had a similar aqueous Pu(VI) concentration (determined by alpha scintillation counting) as the filtrate of a solution that was agitated before filtering (i.e., precipitates are suspended in the solution passed through the filter). Therefore, when the precipitates are suspended in the solution by agitation, they remain at a size greater than 50 nm.

The precipitates of solutions which had either the 842, 846, 857, or 866 nm bands as the only absorption band in the spectrum were removed from solution, washed three times with water at the appropriate pH, and prepared for SEM analysis. Table 2 shows the elemental composition of the precipitates, and Table 3 the composition of the solutions from which the precipitates were taken. The precipitates were amorphous except for the 842 nm species, which was poorly crystalline. The silicon is probably from glass leaching, and the calcium may be from impurities in the chemicals.

DISCUSSION

835 nm band at pH < 2.4

Only two species formed at pH < 2.4, one of which is a solid phase. We believe that the 835 nm species is $PuO_2H_2PO_4^+$ and that the solid phase, which is neutral, is $PuO_2(H_2PO_4)_2$. It is important to note that no hydrolysis should occur at this pH. Therefore, these species are Pu(VI)-phosphate species. The values for the stability constant (β) were calculated for the 835 nm species as $PuO_2H_2PO_4^+$, $PuO_2H_3PO_4^{2+}$, or PuO_2HPO_4 to show that the species is $PuO_2H_2PO_4^+$. The results are shown in Table 4. The concentration of PuO_2^{2+} was determined by its absorption at 831 nm and the concentration of the 835 nm species was found by subtracting the PuO_2^{2+} concentration from the total Pu(VI) concentration. The equation used is $\beta_{835} = [PuO_2H_nPO_4^{n-1}]/[PuO_2^{2+}][H_nPO_4^{n-3}]$. Pitzer's equations were used to calculate the values for pK and the activity coefficient of H^+ γ_{H+}). These values were used to find the $H_nPO_4^{n-3}$ concentration by the equations $K_n = [H_nPO_4^{n-3}][H^+]^n/[H_3PO_4]$ and $[H^+] = 10^{-pH}/\gamma_{H+}$.[7].

The species $PuO_2H_3PO_4^{2+}$ and PuO_2HPO_4 can not be the speciation since the values are dependent on the pH of the solution. Only $PuO_2H_2PO_4^+$ had a stability constant ($\log \beta_{835} = 2.1 \pm 0.1$, 0.6-0.9 M ionic strength) independent of the pH which indicates that $PuO_2H_2PO^+$ is the species formed. The thermodynamic value ($\log \beta^T_{835} = 2.6 \pm 0.15$, zero ionic strength) of the stability constant was calculated by using the Pitzer's equations to determine the activity coefficients for $[H_2PO_4^-]$ and $[PuO_2^{2+}]$

(UO_2^{2+} used as an analog of PuO_2^{2+} since no plutonium data was available). The activity coefficient of $PuO_2H_2PO_4^+$ was assumed to be unity [7].

Our results are in agreement with the Pu(VI) and U(VI) literature [2, 14-16]. The 835 nm absorption band was seen in Pu(VI) solutions of 1 M $HClO_4$, as well as 0.2 and 1.0 M H_3PO_4 [2]. Electrophoresis identified the 835 nm species to be a cation, and also identified, at phosphate concentrations at or above 0.206 M, a neutral species [2]. This neutral species is related to the solid we observed since solid phases are formed by neutral species. In the uranium(VI)-phosphate system at pH < 1 and phosphoric acid concentration up to 3.7 M [14-16], no polynuclear complexes were found, and $UO_2H_2PO_4^+$ and $UO_2(H_2PO_4)_2$ were proposed as aqueous species.

Polynuclear characteristics at pH > 2.4

The Pu(VI)-phosphate species formed at pH > 2.4 have many of the characteristics of polynuclear species: slow kinetics, irreversibility, and species formation that depends on the Pu(VI) concentration. Moreover, polynuclear species are likely since phosphate has a tendency to form bridges when bonded to a metal cation [17]. This bridging property disappears at low pH since H^+ effectively competes for the bridging sites on the phosphate molecule. This effect would explain why only mononuclear Pu(VI)-phosphate species exist at pH below 2.4.

Colloidal formation at pH > 2.4

The absorption bands at 842, 846, 857, and 866 nm were caused by colloidal-size precipitates suspended in solution. The elevated baseline of the spectra is characteristic of light scattering by a colloidal suspension. The filtration results show that agitating the solution forces the precipitates into solution and increases the baseline and the absorption band, but does not increase the concentration of plutonium species which have a particle size below the size of 50 nm. Therefore, the absorption band is increased by an increase of colloidal-size Pu(VI). Furthermore, the CPS analysis showed that the absorption band at 842 nm was present when the particles suspended in solution were at colloidal size. The precipitates may have been formed by colloidal aggregation.

<u>Pu(VI) species at pH > 2.4</u>

The proposed species are $[PuO_2(HPO_4)_m]_n$ for the 842 nm band and $[PuO_2(NaPO_4)_m]_n$ for the 846 nm band . The m and n subscripts are used because the number of phosphate atoms per plutonium and the number of plutonium atoms per species are not known. The species characterized by bands at 857 and 866 nm have not yet been determined.

The Pu(VI) [1-5] and U(VI) [13-23] phosphate literature does not discuss speciation other than in acidic solutions. One exception is Sandino and Bruno [23], who claimed that UO_2HPO_4 and UO_2PO_4 form in uranium-phosphate containing solutions for pH = 4 to 9.

The dominant aqueous phosphate species is $H_2PO_4^-$ in the pH region at which the 842 nm species forms. This explains the production of H^+, which is formed by the reaction $PuO_2^{2+} + H_2PO_4^- \rightleftharpoons PuO_2HPO_4 + H^+$. Furthermore, metal-phosphate precipitates and solids are known to act as cation exchangers. The cations (such as Na^+, K^+, NH_4^+, or Mg^{2+}) in solution will exchange places with the hydrogen cation in the phosphate molecule. Therefore, for solutions with a sufficiently high Na^+ concentration and low H^+ activity, $PuO_2(HPO_4)_m$ would be expected to convert to

$PuO_2(NaPO_4)_m$. The 846 nm band was rarely seen at low pH or low ionic strength because the H^+ activity was high enough to compete successfully with Na^+.

The elemental composition of the precipitates also supports this speciation scheme since the 842 nm precipitates had phosphorus and plutonium only but the 846 nm precipitates had phosphorus, plutonium, and sodium.

CONCLUSION

Plutonium(VI)-phosphate species formed mononuclear species at pH < 2.4 and species with polynuclear and colloidal characteristics at pH from 2.4 to 12.2. The species formed are summarized in Table 1. The speciation and absorption spectra reported were used to explain solubility experiments whose purpose was to determine the ability of phosphate to act as a Pu(VI)-getter.

ACKNOWLEDGMENT

This research was funded, in part, by the Civilian Radioactive Waste Management Fellowship program administered by Oak Ridge Associated Universities for the U.S. Department of Energy. Aspects of the work related to near-neutral speciation and Pu(VI) hydrolysis were supported by the Subsurface Science Program, DOE Office of Health and Environmental Research. We would also like to thank Carol Mertz for the photon correlation spectroscopy, John Sanecki for the scanning electron microscopy work, and Sheldon Landsberger for the interaction with the University of Illinois at Champaign-Urbana.

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Table 1 Summary of Pu(VI) speciation and absorption bands in phosphate solutions from pH = 0.3 to 12.2

Absorption Band	pH range at I > 0.2 M Pu(VI) > 5 x 10^{-4} M	ϵ if mononuclear	Speciation
831 nm	< 7.0	550 [9]	PuO_2^{2+}
835 nm	≤ 2.4	372 ± 17	$PuO_2H_2PO_4^+$
solid	≤ 2.4, high phosphate	n/a	$PuO_2(H_2PO_4)_2$
842 nm	2.4 to 5.0	340 ± 20	$[PuO_2(HPO_4)_m]_n$
846 nm	4.0 to 10.6	380 ± 20	$[PuO_2(NaPO_4)_m]_n$
857 nm	9.5 to 10.9	200 ± 30	n/a
866 nm	12.2	123 ± 15	n/a

Table 2 Elemental Composition (Molar Number) of the Precipitates Determined by Scanning Electron Microscopy

Precipitate	Na	Si	P	Cl	Ca	Pu
842 nm	0	0	1.0 ± 0.02	0	0	0.55 ± 0.01
846 nm	0.9 ± 0.2	0.2 ± 0.1	1.0 ± 0.2	0.03 ± 0.03	0	0.59 ± 0.05
857 nm	0	0.20 ± 0.01	1.0 ± 0.02	0.22 ± 0.01	0.85 ± 0.01	0.15 ± 0.002
866 nm	0.6 ± 0.4	1.5 ± 0.3	1.0 ± 0.2	0.15 ± 0.04	0	0.58 ± 0.04

Table 3 Composition of the Solutions(M) from Which Precipitates Were Taken

Precipitate	Pu	Phosphate	Na^+	ClO_4^-	pH
842 nm	3.3×10^{-4}	7.5×10^{-3}	0.88	0.88	2.72
842 nm	1.2×10^{-4}	9.2×10^{-3}	0.032	0	4.2
846 nm	3.3×10^{-4}	7.6×10^{-4}	0.87	0.86	7.13
846 nm	1.2×10^{-4}	2.8×10^{-2}	0.028	0	9.05
846 nm	3.4×10^{-4}	7.1×10^{-3}	0.89	0.87	6.95
857 nm	2.5×10^{-4}	0.275	1.3	0.64	10.9
866 nm	7.0×10^{-4}	5.3×10^{-3}	0.63	0.54	12.2

Table 4 Stability constants for the 835 nm species (assuming a complex with H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-})

pH of Solution	log β		
	$PuO_2H_3PO_4^{2+}$	$PuO_2H_2PO_4^+$	PuO_2HPO_4
0.8	1.1 ± 0.03	2.1 ± 0.03	7.9 ± 0.03
1.0	1.4 ± 0.03	2.1 ± 0.03	7.6 ± 0.03
1.4	1.9 ± 0.03	2.2 ± 0.03	7.4 ± 0.03
2.3	2.4 ± 0.03	2.1 ± 0.03	6.4 ± 0.03

Figure 1 Absorption Spectrum of a Pu(VI) Hydrolysis in a Phosphate-Free Solution for Pu(VI) = 1.2×10^{-3} $\underline{M}$ at pH = 5.6

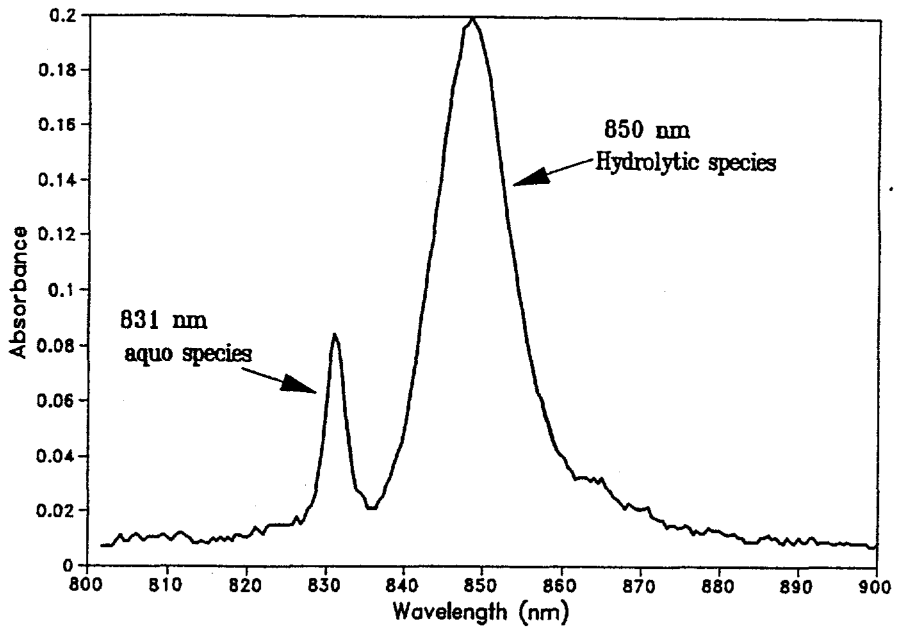


Figure 2 Absorption Spectrum of a Pu(VI) Hydrolysis in a Phosphate-Free Solution for Pu(VI) = 1.2×10^{-3} $\underline{M}$ at pH = 10.0

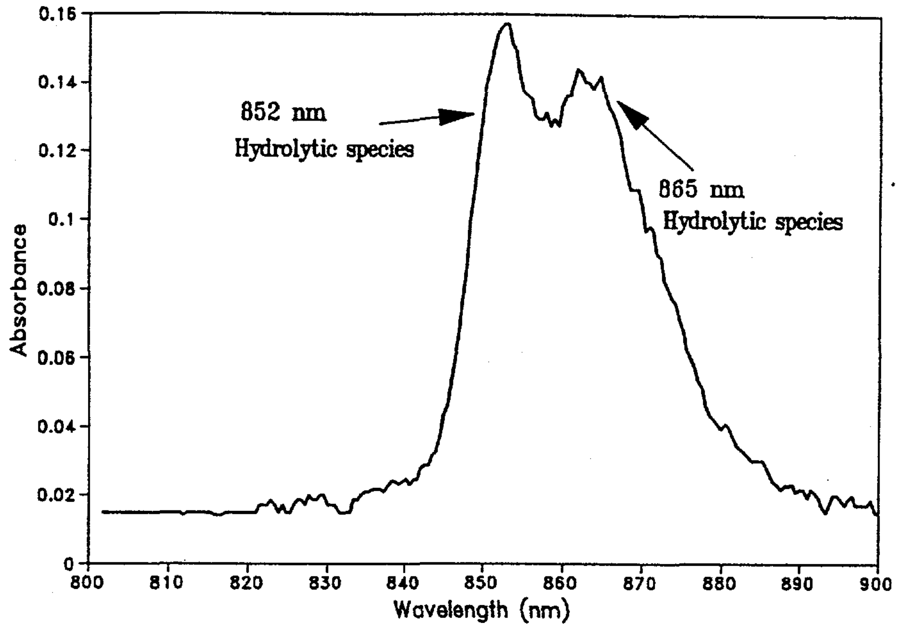


Figure 3 Absorption Spectrum of a Pu(VI)-Phosphate Solution at pH = 1.0, Pu(VI) = 1.0 x 10^{-3} M, and Phosphate = (a) 0 M, (b) 0.023 M, and (c) 0.062 M.

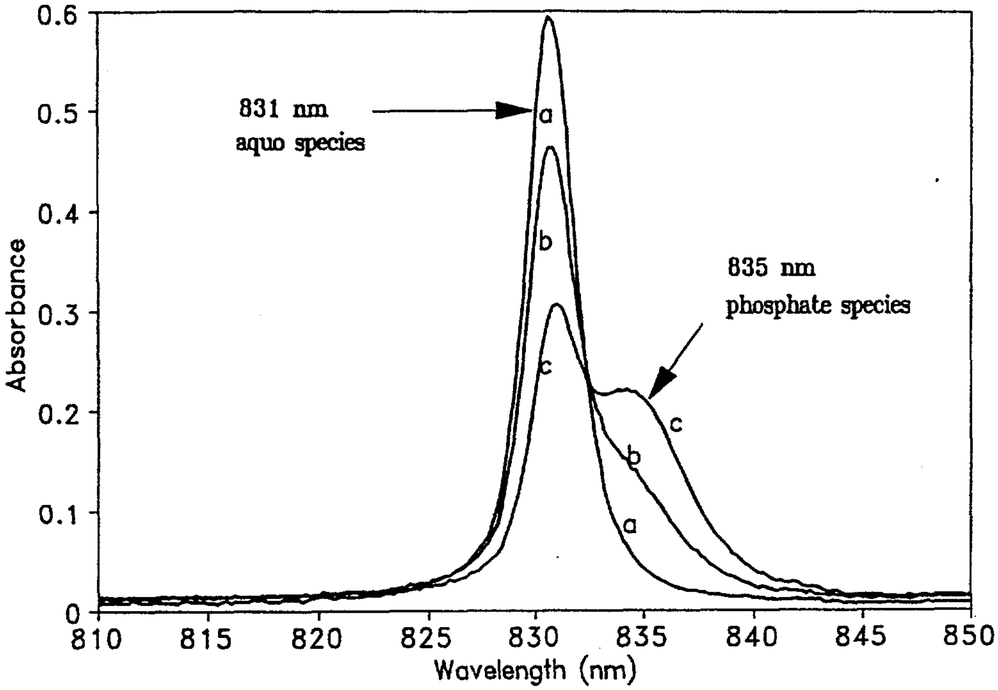


Figure 4 Absorption Spectrum of a Pu(VI)-Phosphate Solution at pH = 0.83, and Pu(VI) = 8.1×10^{-4} M and Phosphate = 0.10 M, (b) Pu(VI) = 6.8×10^{-4} M and Phosphate = 0.15 M, and (c) Pu(VI) = 5.9×10^{-4} M and Phosphate = 0.64 M

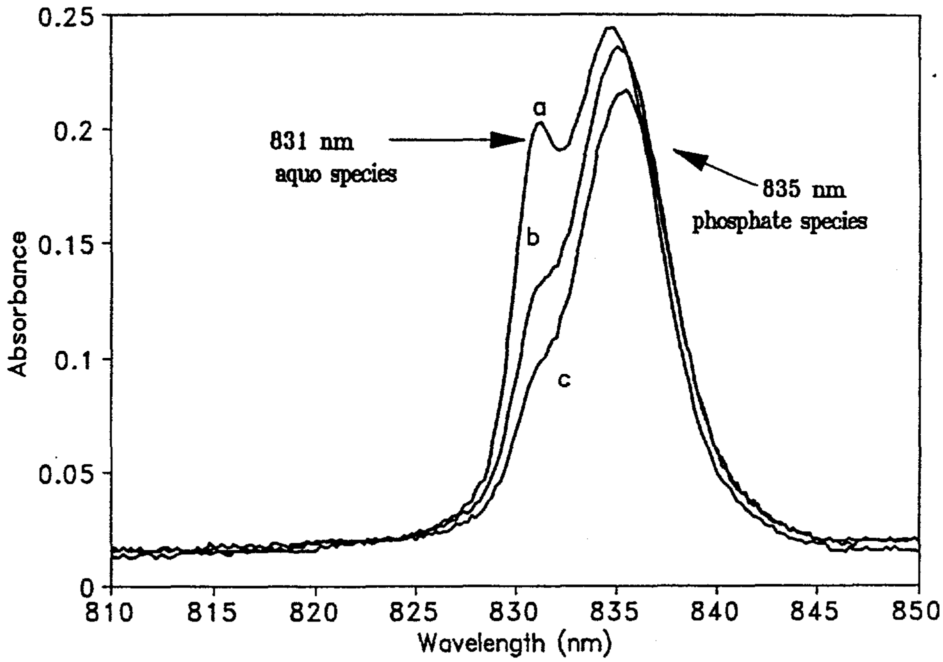


Figure 5 Absorption Spectrum of a Pu(VI)-Phosphate Solution over Time as the Precipitates Settled out of Solution: pH = 2.4, Pu(VI) = 8.2×10^{-4} $\underline{M}$, and Phosphate = 6.2×10^{-3} $\underline{M}$

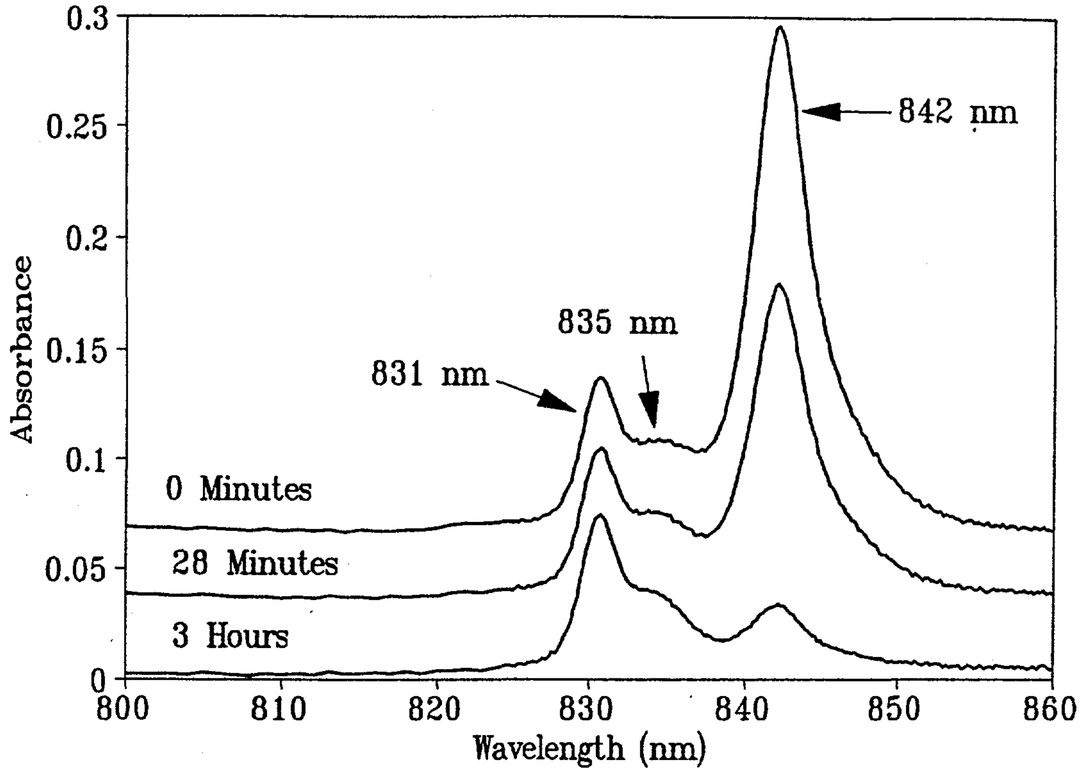


Figure 6 Absorption Spectrum of a Pu(VI)-Phosphate Solution over Time as the Precipitates Settled out of Solution: pH = 5.1, Pu(VI) = 8.2×10^{-4} $\underline{M}$ and Phosphate = 6.2×10^{-3} $\underline{M}$

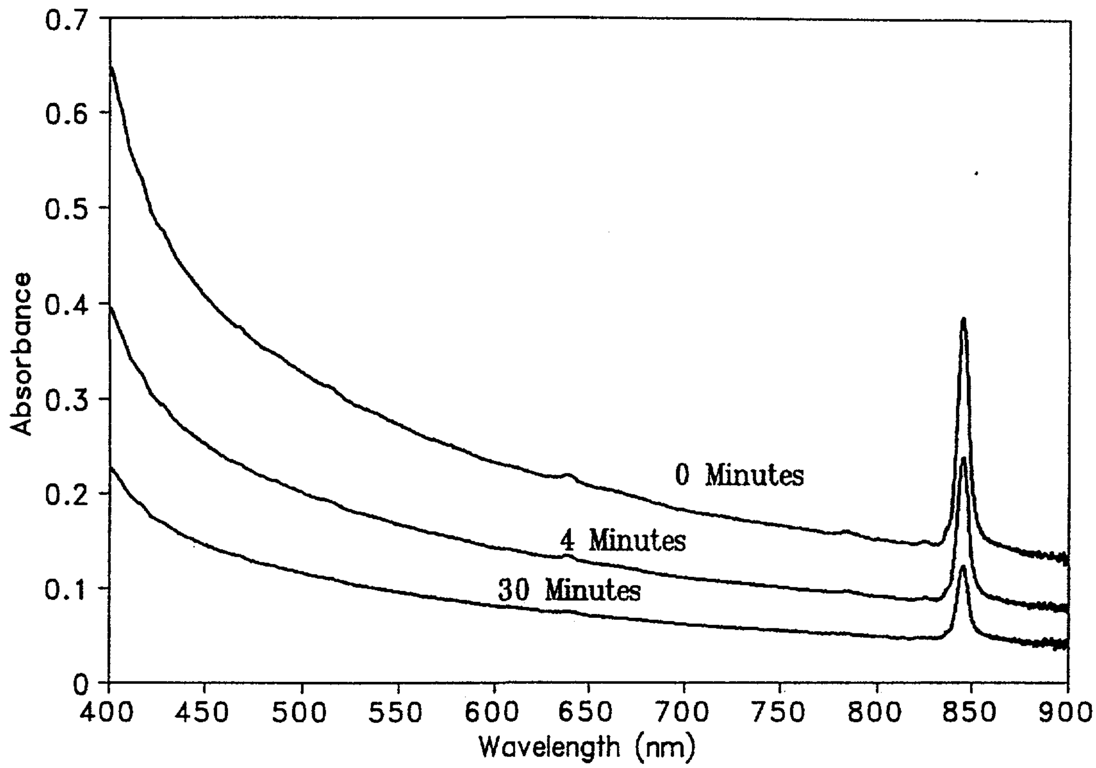


Figure 7 Absorption Spectrum of a Pu(VI)-Phosphate Solution over Time as the Precipitates Settled out of Solution: pH = 10.6, Pu(VI) = 3.3×10^{-4} M and Phosphate = 6.6×10^{-3} M

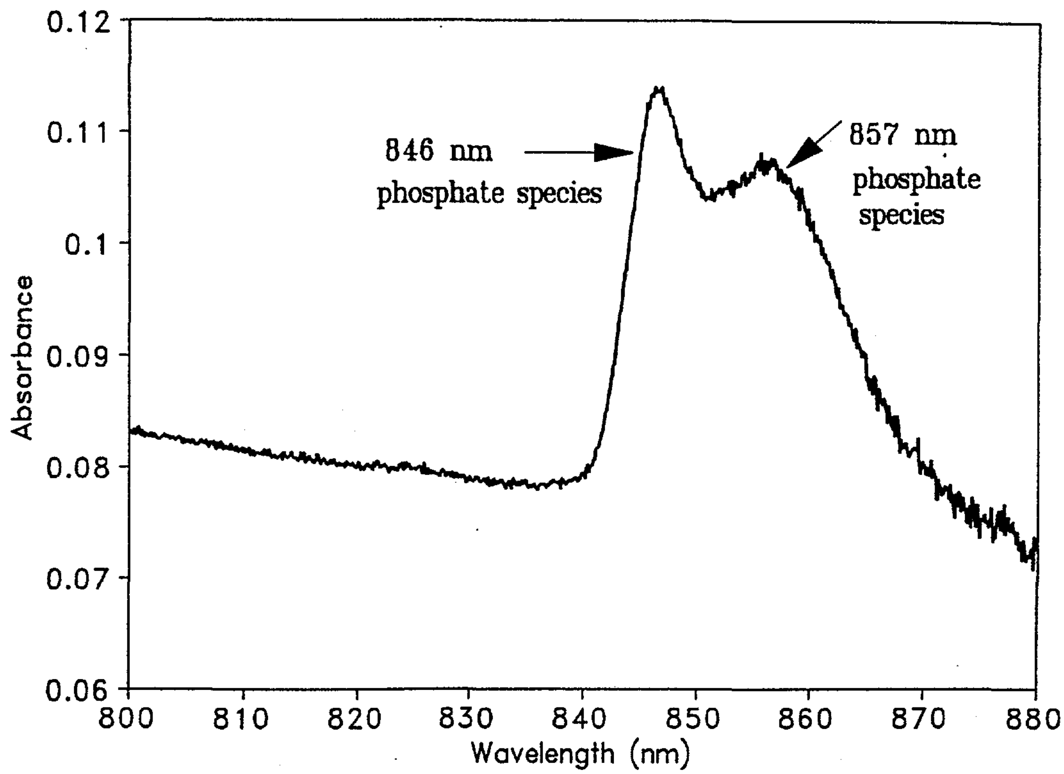


Figure 8 Absorption Spectrum of a Pu(VI)-Phosphate Solution over Time as the Precipitates Settled out of Solution: pH = 12.2, Pu(VI) = 7.0×10^{-4} $\underline{M}$, and phosphate = 5.3×10^{-3} $\underline{M}$

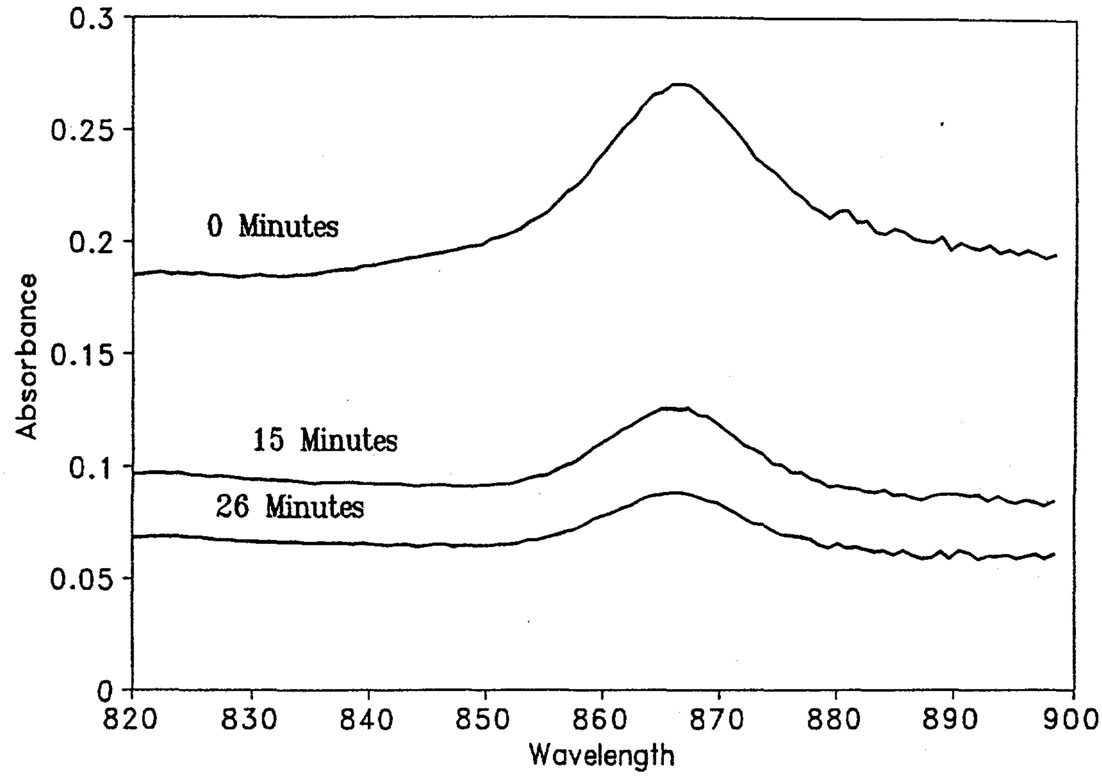
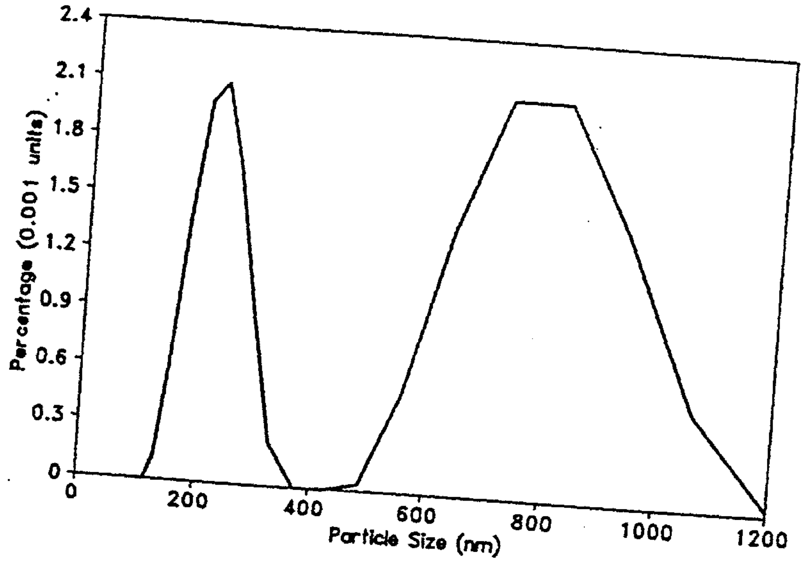


Figure 9 Size Distribution of the Particles Suspended in a Pu(VI)-Phosphate Solution at I = 0.002 M and pH = 4.1. The 842 nm band was present in the spectrum of this solution



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