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PRELIMINARY RESULTS ON THE HYDROLYSIS AND CARBONATE COMPLEXATION OF DIOXOPLUTONIUM(V)

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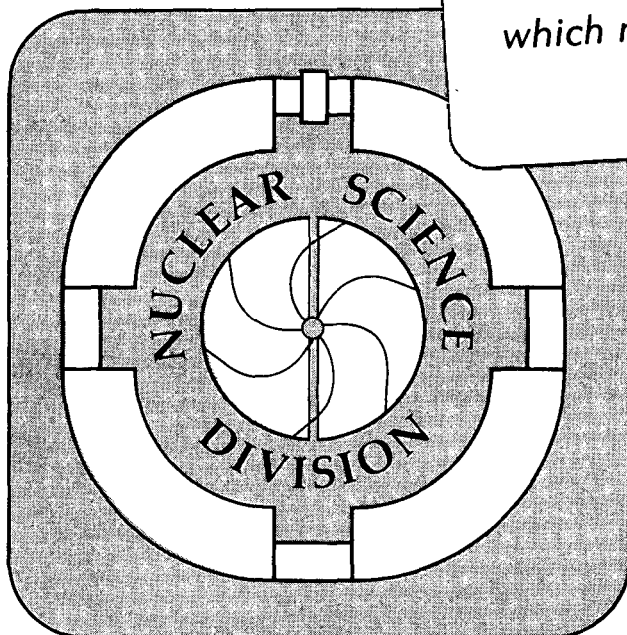
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## Preliminary Results on the Hydrolysis and Carbonate Complexation of Dioxoplutonium(V)

D.A. Bennett, D.C. Hoffman,  
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November 1987

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This work was supported by the Nevada Nuclear Waste Storage Investigations Project, managed by the Waste Management Project Office of the United States Department of Energy, Nevada Operations Office and the Director, Office of Energy Research, Division of Nuclear Physics of the Office of High Energy and Nuclear Physics of the U. S. Department of Energy under Contract DE-AC03-76SF00098.

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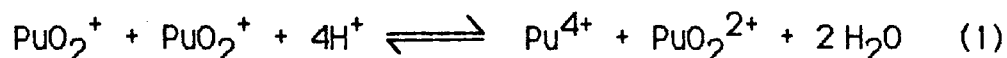
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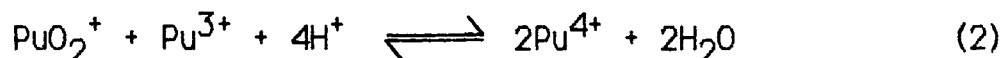
The hydrolysis and carbonate complexation reactions of dioxoplutonium(V) were studied in near neutral aqueous systems. These experiments involved the addition of hydroxide or carbonate to Pu(V) in a perchlorate medium. Changes in the electronic absorption spectra provided information about the chemical properties of Pu(V). The results indicate that Pu(V) does not hydrolyze below pH 7.15. In the carbonate complexation studies,  $\log \beta_{11}$  was measured to be  $4.4 \pm 0.7$ .

## I. INTRODUCTION

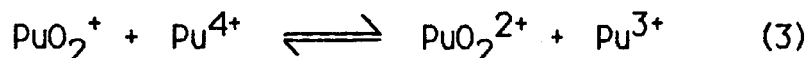
The pentavalent oxidation state of plutonium in aqueous solution was discovered in 1944<sup>1</sup>. This oxidation state is thermodynamically unstable with respect to disproportionation into the +4 and +6 oxidation states in acidic solutions. As can be seen from Eq 1, the equilibrium of the disproportionation reaction is pH dependent<sup>2</sup>.



Pu(V) can also react with Pu(III) at a rate 35 times faster than the disproportionation reaction<sup>3</sup> at the same pH, as shown in Eq 2.



The study of Pu(V) is further complicated by the rapid equilibrium reaction which occurs when plutonium exists in several oxidation states.



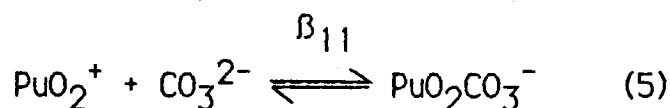
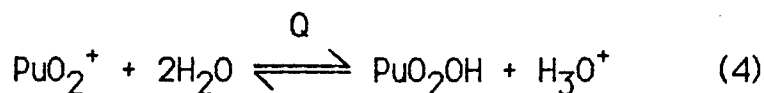
Until recently, essentially all plutonium chemistry was performed under acidic conditions. Consequently, the pentavalent oxidation state was considered unimportant and has not been extensively investigated.

However, recent solubility studies of plutonium in near neutral aqueous solutions have shown that Pu(V) is a dominant soluble species.<sup>4,5</sup> These solubility studies were conducted in groundwater from a well on the Nevada Test Site known as J-13 (see Table 1 for composition<sup>6</sup>) and from 0.1 M NaClO<sub>4</sub>. The results have shown that 40 to 82 per cent of the soluble plutonium exists in the +5 oxidation state at pH 7 and 25°C. The

overall solubility of plutonium depends on the initial oxidation state and was significantly enhanced in the groundwater compared to the perchlorate solution. For example, when the initial species is in the +5 oxidation state, the solubility increases from  $(2 \pm 1) \times 10^{-9} \text{M}$  in perchlorate solution to  $(8 \pm 3) \times 10^{-6} \text{M}$  in J-13 water. Nitsche also observed that regardless of the initial oxidation state (+4, +5, or +6), the soluble plutonium at steady state was converted nearly totally to  $\text{PuO}_2^+$  and  $\text{PuO}_2^{2+}$ . The  $\text{PuO}_2^+ : \text{PuO}_2^{2+}$  ratio was always 2:1 with the exception of the initially  $\text{Pu}^{4+}$  in J-13 water where equal amounts of the species were present at steady state. These results indicate that Pu(V) may play a major role in the possible migration of plutonium in groundwater.

Therefore, the hydrolysis ( $Q$ ) and carbonate complexation ( $\beta_{11}$ ) constants of Pu(V) are important parameters to measure since Table 1 shows that these groundwaters are slightly basic (pH 7.1) and the major anionic species is bicarbonate/carbonate.

If you assume that only the first complex is formed, then  $Q$  and  $\beta_{11}$  can be calculated from Equations 6, 7, and 8 by measuring the changes in shape and position of a particular spectrophotometric absorption band as the hydroxide or carbonate concentration is altered,



$$A = \epsilon_1 c_1 + \epsilon_2 c_2 \quad (6)$$

$$C_T = c_1 + c_2 \quad (7)$$

$$\beta_{11} = c_2 / c_1 c_c \quad (8)$$

where  $A$  is the absorbance at a particular wavelength,  $\epsilon_1$  and  $\epsilon_2$  are the respective molar absorptivities of the non-complexed and complexed species at that wavelength,  $c_1$  is the concentration of non-complexed  $\text{PuO}_2^+$ ,  $c_2$  is the concentration of complexed  $\text{PuO}_2^+$ ,  $C_T$  is the total  $\text{PuO}_2^+$  concentration, and  $c_c$  is the concentration of the  $\text{OH}^-$  or  $\text{CO}_3^{2-}$ .

The spectrophotometric technique is advantageous because it is a direct method of measurement. The instrument used in these experiments has the additional advantage of fiber optic cables which allow measurements to be made inside the alpha box. This feature permits measurements to be made *in-situ* and eliminates the need to pass radioactive samples out of the alpha box.

The similarity observed among actinides with the same oxidation state can be used to predict the behavior of  $\text{Pu(V)}$ . The hydrolytic and carbonate complexation constants of  $\text{NpO}_2^+$  have been measured as follows: <sup>7,8</sup>

$$\log Q = -9.12 \pm 0.15$$

$$\log \beta_{11} = 4.49 \pm 0.06$$

$$\log K_{sp} = -10.14 \pm 0.04$$

Kraus' lower limit for the  $\text{p}K_a$  of the hydrolysis reaction for  $\text{Pu(V)}$

( $\text{p}K_a \geq 9.7$ )<sup>9</sup> is consistent with the results for  $\text{Np(V)}$  and provides a useful introduction to the behavior of  $\text{Pu(V)}$ .



**Stock Solutions.** A Pu stock solution,  $5.70 \times 10^{-3} \text{M}$ , was prepared from 99.8 per cent pure  $^{242}\text{Pu}$  supplied through the U.S. Department of Energy's Heavy Element Production Program at Oak Ridge National Laboratory. The original stock solution had been stored in  $\text{HClO}_4$  for several years in glass, so it was purified via anion exchange chromatography using Biorad AG-1X8 resin (200-400 mesh). The procedure has been previously described.<sup>10</sup> The purified Pu solution was converted to a  $\text{HClO}_4$  medium by evaporating the  $\text{HCl-HI}$  solution to dryness, adding concentrated  $\text{HNO}_3$  and fuming to dryness twice, and then fuming with concentrated  $\text{HClO}_4$ . The final Pu stock solution was approximately 2M  $\text{HClO}_4$ . The Pu concentration of this solution was determined by radiometric assay.

$\text{PuO}_2^+$  stock solutions were prepared fresh each day. The appropriate aliquot of Pu stock was boiled down and then fumed with 1ml concentrated  $\text{HClO}_4$  to near dryness. The precipitate was dissolved in an aliquot of concentrated  $\text{HClO}_4$  and further diluted with  $10^{-3} \text{M}$   $\text{HClO}_4$ . The oxidation state of the resulting  $\text{PuO}_2^{2+}$  solution was confirmed spectrophotometrically. The Pu(VI) solution was then added to the appropriate volume of NaOH stock solution so that the final pH was near 3. Final adjustments to the pH were made with either the NaOH stock solution or 1M  $\text{HClO}_4$  as necessary. The Pu(VI) solution was then electrochemically reduced to Pu(V) by applying 0.777 V versus NHE.<sup>11</sup> The purity of the  $\text{PuO}_2^+$  stock solution was verified spectrophotometrically by comparison with previously reported spectra.<sup>12</sup>

A sodium hydroxide solution, 0.0420 M, was prepared from reagent grade low-CO<sub>2</sub> NaOH. It was standardized using freshly dried recrystallized potassium hydrogen phthalate with phenolphthalein indicator. The NaOH solution was maintained CO<sub>2</sub>-free according to the procedure outlined in Skoog and West.<sup>13</sup> The ionic strength of this solution was adjusted to 0.1 M by addition of the appropriate amount of NaClO<sub>4</sub>.

The sodium bicarbonate and carbonate solutions were prepared from reagent grade NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, respectively. The total carbonate concentration for a desired pH was calculated from Henry's law<sup>14</sup> and the carbonate solution equilibria assuming 1 atmosphere CO<sub>2</sub>. The solutions were acidified immediately prior to the addition of Pu(V). CO<sub>2</sub> gas was blown over the surface of the solution to maintain 1 atm pressure. The pH was monitored with combination glass electrodes and allowed to stabilize.

The perchloric acid solutions were prepared from double distilled, concentrated HClO<sub>4</sub> and stored in Teflon bottles.

**Equipment.** A Model 200 Guided Wave Spectrophotometer was used for all absorption spectrophotometric measurements. The spectrometer was equipped with a 1200 line / mm grating, Si detector, and 0.063mm exit slit. The absorption peak at 569 nm was used for calculations of PuO<sub>2</sub><sup>+</sup> complexation.

A Princeton Applied Research Model 264A Polarographic Analyzer/Stripping Voltammeter was used to reduce Pu(VI) to Pu(V). The electrochemical cells were comprised of three electrode systems. The working electrode was made from 40 mesh Pt screen. The counter electrode was separated from the working compartment by two Vycor

glass frit junctions and was made from coiled Pt wire. The reference electrode was Ag/AgCl in saturated NaCl/ AgCl and was separated from the working compartment by a single Vycor glass frit junction. The reference potential versus NHE was measured to be 207mV.

A Jenco Model 672 pH meter with a Beckman Model 39522 combination glass electrode with a Ag/AgCl reference was used for pH measurements. The saturated KCl solution was replaced with saturated NaCl/AgCl to prevent clogging of the junction by  $KClO_4$ . For pH measurements in the pH range 3 to 7, pH 4.00 buffer and pH 7.00 buffer solutions were used for calibration of the pH meter. In the pH range from 7 to 10, pH 7.00 and pH 10.00 buffer solutions were used for calibration.

### III. RESULTS AND DISCUSSION

The changes in peak shape and position between the free non-complexed  $PuO_2^+$  ion and the hydrolyzed or carbonate complexed species may be very small. Therefore, it is important to measure the absorption spectrum of the non-complexed  $PuO_2^+$  ion as accurately as possible. Figure 1 shows a typical absorption spectrum of  $PuO_2^+$  in pH 3 perchloric acid. The molar absorptivities of peak height and area are calculated from Beer's Law plots as shown in Figure 2 and summarized in Table 2.

During the first hydrolysis experiment, aliquots of the NaOH stock solution were added to a stock solution of  $PuO_2^+$  at pH 3.02. At approximately each 1/2 unit of pH, the pH was allowed to stabilize, the sample was centrifuged for 5 minutes, and then several absorption spectra were taken. The Pu(V) began precipitating at pH 5.71. Simultaneously, the peak height decreased without any measurable change in the width of the

absorption band at 569 nm. When the hydroxide ion replaces the coordinating water molecule, the symmetry of the complexes decreases and there is an increase in the number of normal modes of vibration. Consequently, hydrolysis usually results in a broadening of an absorption band. A portion of the measurements taken from pH 3.02 to pH 9.35, are shown in Figure 3. Because the predicted solubility product for  $\text{PuO}_2\text{OH}$  is relatively small, microprecipitation could have occurred. To test this hypothesis, a  $\text{PuO}_2^+$  solution was prepared at pH 7.15 by adding an equal volume of Pu(V) stock solution at pH 3 to a calculated concentration of NaOH so that the final pH was near 7. Once the pH had stabilized, the sample was centrifuged, assayed, and scanned. The molar absorptivity of the peak height and area remained consistent with the pH 3 sample. The results are shown in Table 2.

A similarly prepared solution of Pu(V) at pH 6.85 was monitored with time. Over a seven hour period, the absorption peak decreased, precipitate formed, and the pH dropped 1.0 unit. This delayed precipitation indicates possible carbonate contamination from the atmosphere. The dried precipitate was analyzed by Fourier Transform Infrared Spectroscopy. While the spectrum is not conclusive, there are absorption bands in the carboxyl stretching region between  $1500\text{--}1600\text{ cm}^{-1}$ . Future hydrolysis experiments will be conducted under inert atmosphere and the composition of the precipitate will be further investigated.

Efforts were then directed toward carbonate complexation.  $\text{PuO}_2^+$  was prepared in 1M  $\text{Na}_2\text{CO}_3$  (pH 12.0) and 0.5 M  $\text{NaHCO}_3$  (pH 8.0) and the resulting spectra are shown in Figure 4. The spectrum in 1M sodium carbonate agrees with the previously published results of Wester et al.<sup>15</sup> At pH 8, the peak at 569 nm has broadened and shifted so that it spans the region 551 to 565 nm. At pH 12, there is no significant peak between 551

and 565 nm and the prominent peak now occurs at 461 nm. The broadening at pH 8 may be partially caused by hydrolysis and future experiments will help quantify this effect. However, since the  $pK_a$  is  $\geq 9.7$ , this effect should be quite small. Spectra taken of  $\text{PuO}_2^+$  in carbonate solutions with pH values between 6.6 and 7.2 also exhibit this broadening and preliminary hydrolysis results have shown no change in peak shape over this region. Therefore, it seems highly probable that the observed changes in peak shape and position are a result of carbonate complexation.

The first carbonate complexation constant ( $\beta_{11}$ ) was calculated from four  $\text{PuO}_2^+$  solutions which were prepared under 1 atmosphere of  $\text{CO}_2$  with varying concentrations of  $\text{CO}_3^{2-}$ . As shown in Table 4 and Figure 5, a peak emerges at 551 nm as the  $\text{CO}_3^{2-}$  concentration increases. The peak at 569 nm decreases initially and then remains constant. From Equations 6,7 and 8,  $\log \beta_{11}$  is calculated to be  $4.4 \pm 0.7$ .

#### IV. CONCLUSIONS

Because of the low molar absorptivity of  $\text{PuO}_2^+$  and the relative insolubility of the complexes, accurate measurement of the the hydrolysis and carbonate complexation constants is quite difficult. Dilute concentrations must be used so that the solubility products are not exceeded. This situation results in a very low signal to noise ratio which pushes the spectrometer to its detection limit. Future hydrolysis experiments will be conducted in an inert atmosphere box to help prevent precipitation. It will also be interesting to study the composition of the precipitate. The preliminary carbonate complexation results are quite encouraging. The lower limit established for  $\text{PuO}_2^+$ ,  $\log \beta_1 \geq 4.5$ , is in

agreement with other +5 actinides, primarily  $\text{NpO}_2^+$  which has a  $\log \beta_1 = 4.49$ . As predicted from the actinide contraction,  $\text{PuO}_2^+$  should form slightly stronger complexes than  $\text{NpO}_2^+$ . The carbonate complexation experiments can be improved by repeating the preliminary experiment and increasing the number of  $\text{CO}_3^{2-}$  concentrations studied. Future studies are also necessary to evaluate if the complex formed is actually a carbonate complex or a bicarbonate complex. Peak fitting programs will also be used to improve the accuracy and precision of the data analysis.

#### Acknowledgements:

This work was supported by the Nevada Nuclear Waste Storage Investigations Project, managed by the Waste Management Project Office of the United States Department of Energy, Nevada Operations Office and the Director, Office of Energy Research, Division of Nuclear Physics of the Office of High Energy and Nuclear Physics of the U. S. Department of Energy under Contract DE-AC03-76SF00098.

The authors are indebted to the Division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy, for making the  $^{242}\text{Pu}$  available through the Heavy Element Production Program at Oak Ridge National Laboratory.

Table 1. Reference Ground Water Composition for Water from Nevada Test Site Well J-13 (from Ref. 6)

| Species                       | Concentration<br>(mg/l) |
|-------------------------------|-------------------------|
| Ca                            | 14                      |
| Mg                            | 2.1                     |
| Na                            | 51                      |
| K                             | 4.9                     |
| Li                            | 0.05                    |
| Fe                            | 0.04                    |
| Ba                            | 0.003                   |
| Al                            | 0.03                    |
| SiO <sub>2</sub>              | 31                      |
| Sr                            | 0.05                    |
| F <sup>-</sup>                | 2.2                     |
| Cl <sup>-</sup>               | 7.5                     |
| SO <sub>4</sub> <sup>2-</sup> | 22.                     |
| NO <sub>3</sub> <sup>-</sup>  | 5.6                     |
| HCO <sub>3</sub> <sup>-</sup> | 120.                    |
| PO <sub>4</sub> <sup>3-</sup> | 0.12                    |

Additional Information: pH 7.1

Table 2. Molar absorptivities of  $\text{PuO}_2^+$  at different pH values

| pH   | wavelength<br>(nm) | molar absorptivity<br>( $\text{cm}^{-1}\text{M}^{-1}$ ) |
|------|--------------------|---|
| 3.02 | 569                | 14.6  |
| 3.02 | 551                | 3.9   |
| 7.15 | 569                | 15.2  |

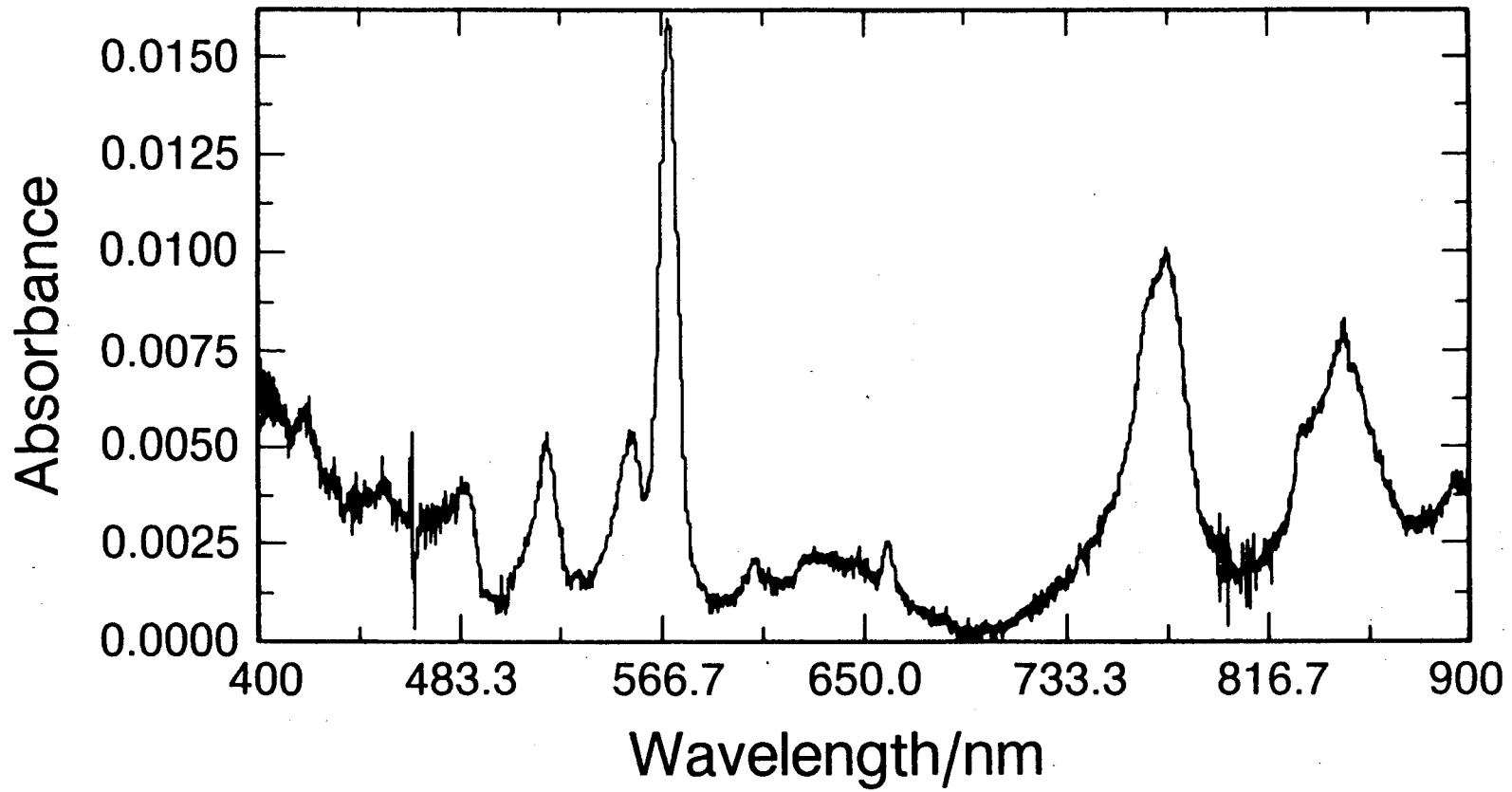


Table 3. Change in absorbance spectrum of  $\text{PuO}_2^+$  as a function of  $[\text{CO}_3^{2-}]$ 

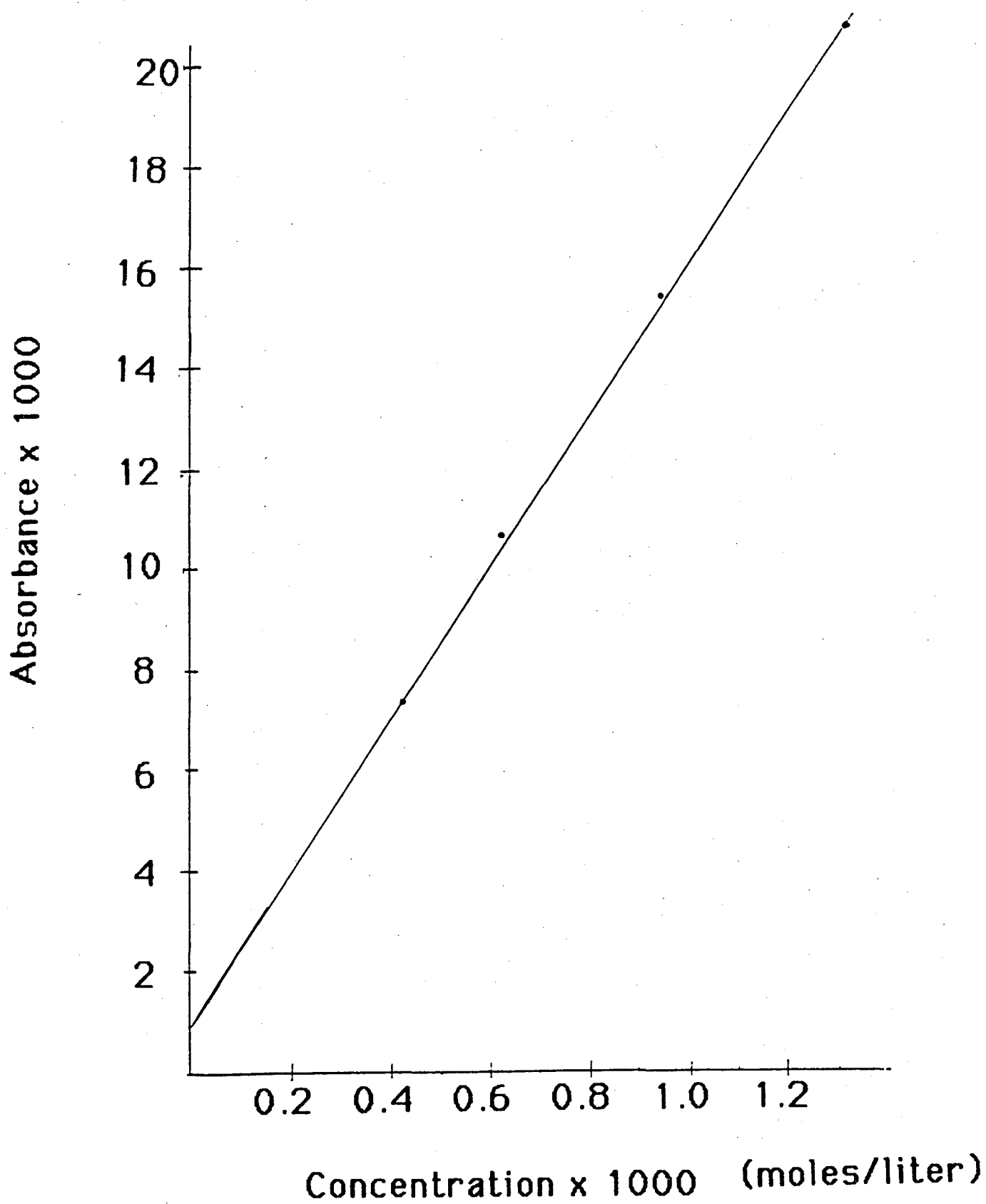
| pH   | $[\text{CO}_3^{2-}]$<br>(M) | $[\text{PuO}_2^+]$<br>(M) | Absorbance at<br>569 nm | Absorbance at<br>551 nm |
|------|-----------------------------|---------------------------|-------------------------|-------------------------|
| 4.50 | -----                       | $7.1 \times 10^{-4}$      | 0.0109                  | 0.0027                  |
| 6.62 | $4.4 \times 10^{-5}$        | $3.5 \times 10^{-4}$      | 0.0062                  | 0.0018                  |
| 6.80 | $1.0 \times 10^{-4}$        | $3.4 \times 10^{-4}$      | 0.0054                  | 0.0019                  |
| 7.13 | $5.0 \times 10^{-4}$        | $3.2 \times 10^{-4}$      | 0.0034                  | 0.0024                  |
| 7.23 | $8.0 \times 10^{-4}$        | $3.4 \times 10^{-4}$      | 0.0027                  | 0.0027                  |

Figure 1

Absorption Spectrum of  $\text{PuO}_2^+$  in pH 3 Perchlorate



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Figure 2. Beer's Law Plot of  $\text{PuO}_2^+$  at pH 3

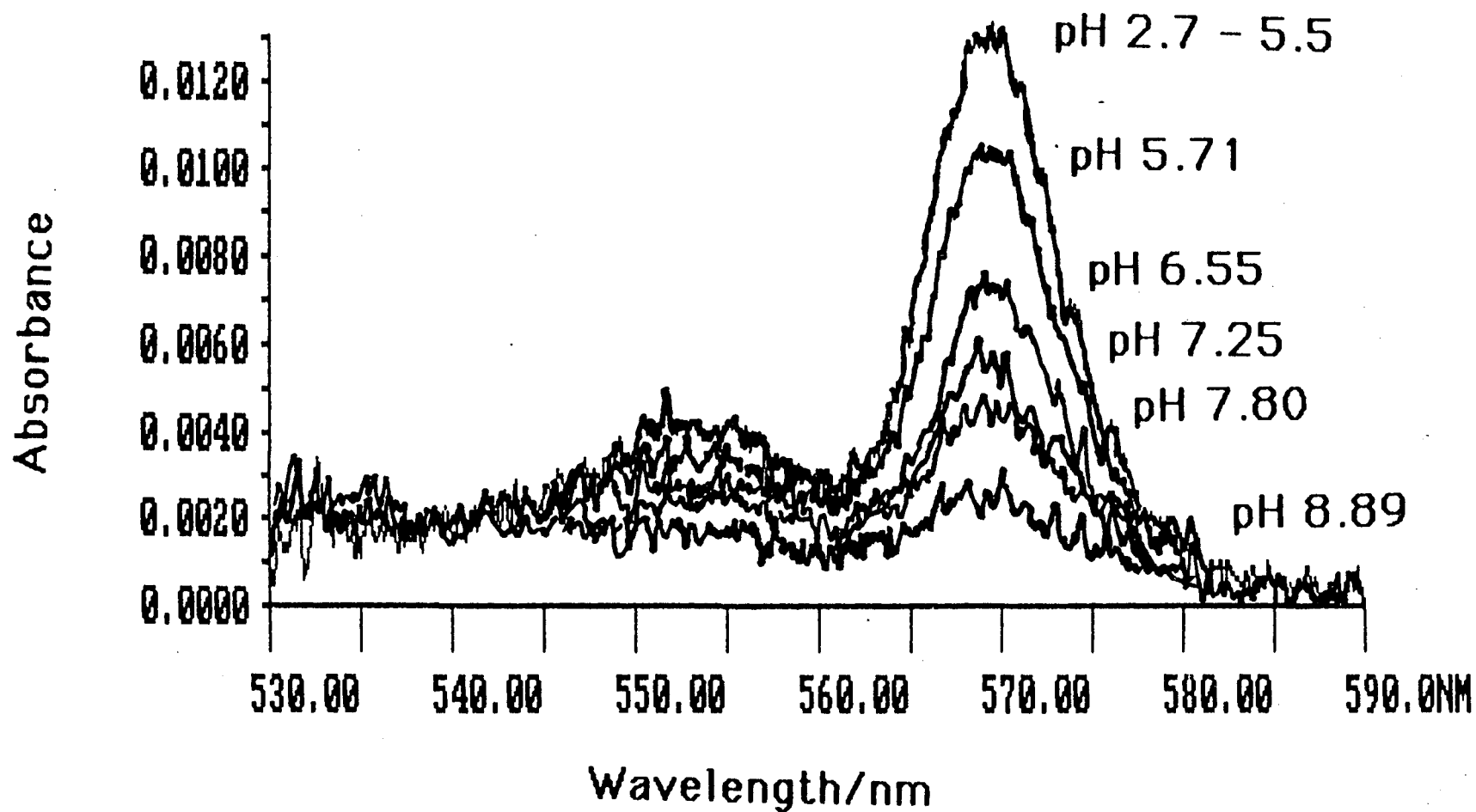
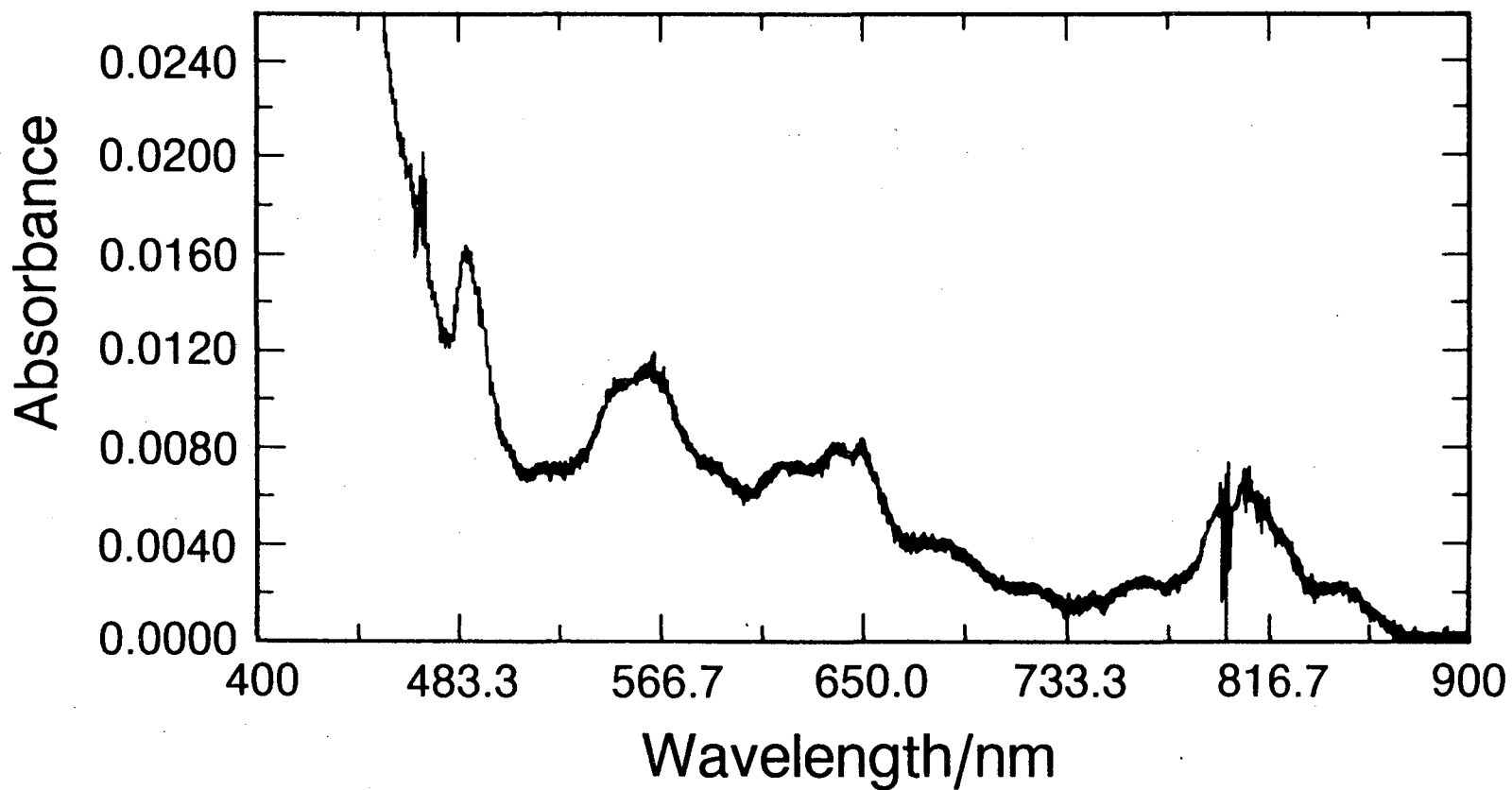


Figure 3. Absorbance spectrum of  $\text{PuO}_2^+$  as a function of pH

Figure 4a

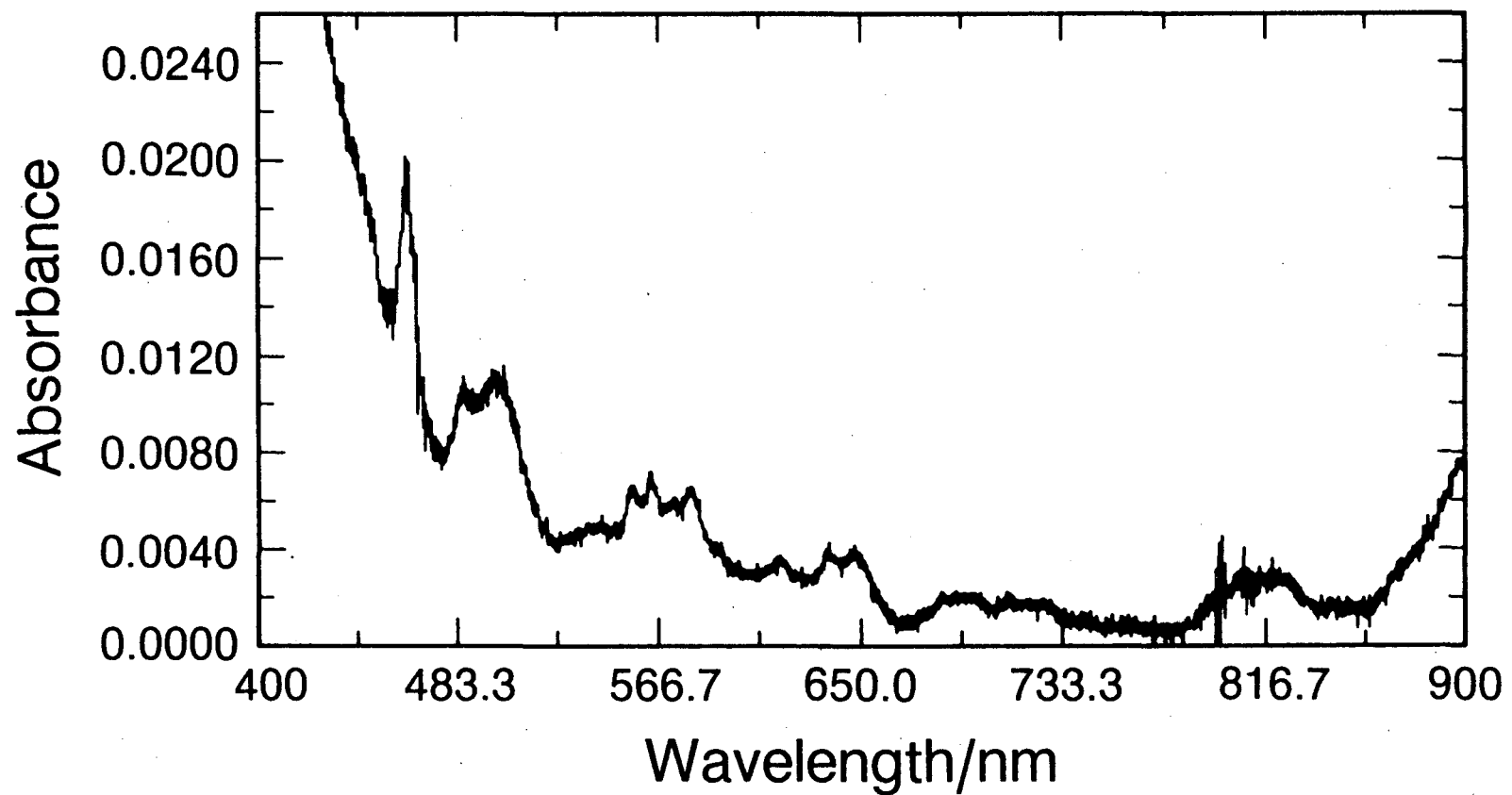
Absorption Spectrum of  $\text{PuO}_2^+$  in 0.5 M  $\text{NaHCO}_3$  (pH 8.0)



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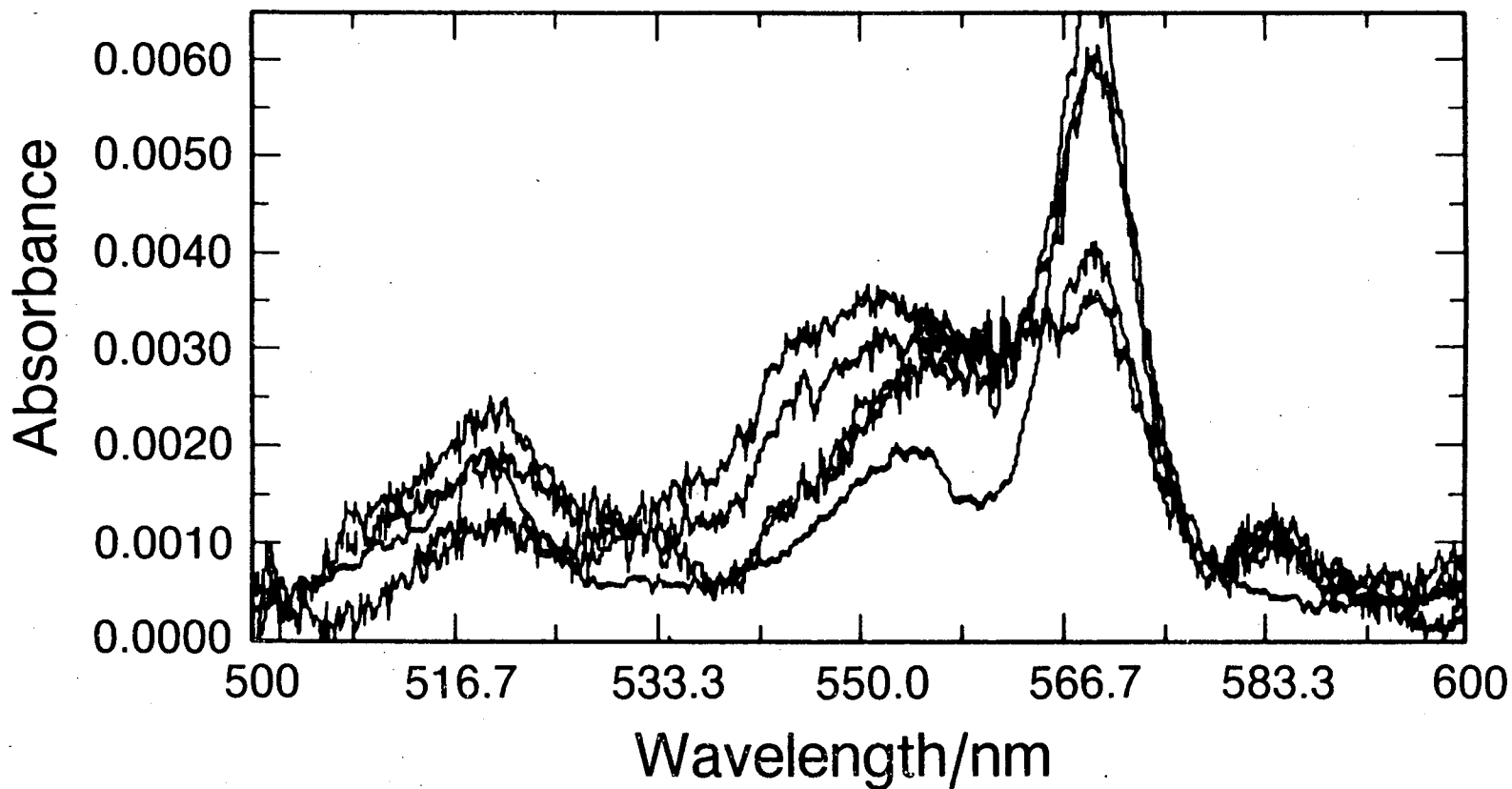
Figure 4b

Absorbance Spectrum of  $\text{PuO}_2^+$  in 1M  $\text{Na}_2\text{CO}_3$  (pH = 12.0)



XBL 878-10318

Figure 5 Pu (V) Peak Shift as a Function of Carbonate



XBL 878-10319

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