

Notes

Spectrophotometric Determination of Uranium(VI) with Pyrocatechol Violet in Surfactant Media

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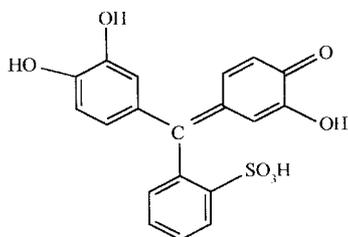
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The geographical distribution of uranium is of interest because the element is used in the production of energy in nuclear reactors. It is of interest of geochemists because it belongs to the rare earth elements and its geochemical pathways have not been studied as rigorously as those of the transition metals (*e.g.*, copper, lead, zinc, and cadmium). The stable oxidation state is uranium(VI) in oxygenated water, and its predominant form is the uranyl ion, which is complexed by carbonate in carbonate-bearing water.¹ Uranium(VI) occurs in sea water as anionic carbonate complexes, and has a very long residence time of $2-4 \times 10^6$ years.² Considerable interest has developed in the determination of trace uranium in environmental sites as well as in nuclear industry facilities.

Numerous methods for the spectrophotometric determination of uranium based on the use of balmic acid, morin, sodium fluoride, pyrogallol red, pyrogallol acid, etc. have been reported,³⁻¹⁰ but most of them require a solvent-extraction step and entail various disadvantages in terms of reproducibility, simplicity, rapidity and sensitivity.

Pyrocatechol Violet [PCV, I] or pyrocatechol sulfonaphthalein, a dye in the triphenylmethane series has been used for spectrophotometric determination of Aluminum(III) and others.^{11,12} The utility of Pyrocatechol Violet for spectrophotometric determination of uranium(VI) is reported rarely.



In this paper, the reaction of uranium(VI) with Pyrocatechol Violet and also the ternary complex involving cationic surfactant have been studied. The method developed was applied to the analysis of complex matrices for uranium(VI).

Experimental Section

Reagents. All chemicals in this experiment were analytical-reagent grade and double-distilled water was used. A stock standard solution of uranium(VI) of 1.0×10^{-3} M was prepared from U(VI) AAS 1000 ppm standard solution. The working standard solutions were prepared by diluting portions of the stock standard solution with distilled water. A stock standard solution of Pyrocatechol Violet (1.0×10^{-3} M) was prepared by dissolving 0.386 g of Pyrocatechol Violet in distilled water and diluting with water to 1 L.

The cetyltrimethylammonium bromide (CTMAB, 99%; obtained from the Sigma company) and sodium dodecyl sulfate (SDS; 99%; obtained from the Sigma company) were used without additional purification. The Triton X-100 (octylphenoxypolyethoxyethanol) used in this study was also obtained from Sigma Co. and used as received. The concentration of Triton X-100 was its calculated average molecular weight of 624 g mol^{-1} .

The solution pH 6.8 ± 0.2 was adjusted with hexamethylenetetramine (HTM)/hydrochloric acid buffer, showing no absorbance between 400 and 800 nm, including all surfactant ingredient.

The absorbances were measured with a Perkin Elmer 552S spectrophotometer. The pH was measured with a NOVA-310 pH-meter.

Procedures. An aliquot of a U(VI) standard solution was transferred to a 50 mL volumetric flask; 5.0 mL of the 1.0×10^{-3} M Pyrocatechol Violet solution and 2.5 mL of HTM solution (20%) were added. This was followed by the addition of 7.5 mL of 1.0×10^{-3} M surfactant solution. After adjusting the pH to 6.8 ± 0.2 with dilute hydrochloric acid or sodium hydroxide solutions, the solution was taken up to the mark with distilled water.

The absorbance of the solution at 400-800 nm was measured against a reagent blank as the reference.

Results and Discussion

Spectral characteristics. The absorption spectra of the U(VI)-PCV and U(VI)-PCV-CTMAB complexes and the

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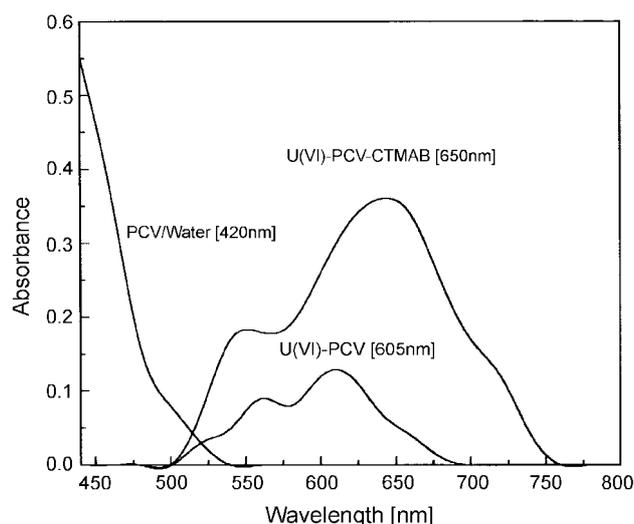


Figure 1. Absorption spectra of PCV, U(VI)-PCV and U(VI)-PCV-CTMAB complex at pH 6.8. U(VI): $1.0 \mu\text{g mL}^{-1}$, PCV: 1.0×10^{-4} M, CTMAB: 1.5×10^{-4} M.

reagent blanks are shown in Figure 1. The green U(VI)-PCV complex had an absorption maximum at 605 nm in neutral or slightly acidic media. The U(VI)-PCV-CTMAB complex showed a red-shift of the absorption maximum to 650 nm, with an increase in absorbance.

The effect of pH on the absorbance of the U(VI)-PCV-CTMAB system at 650 nm was studied against the reagent blank. Maximum absorbance was obtained at pH 6.5-7.2. In more acidic or more alkaline solutions, absorbances decreased because of incomplete complex formation and hydrolysis of the complex. From this we concluded that the optimum pH to carry out all experiments ranged from 6.6 to 7.0.

The effects of cationic surfactants [cetyltrimethylammonium bromide (CTMAB), dodecyltrimethylammonium bromide (DTMAB)], nonionic surfactants [Brij 58, Triton X-100] and anionic surfactant [sodium dodecyl sulfate (SDS)] on the U(VI)-PCV complexes were studied. As shown in Table 1, the cationic surfactants increased the absorbance of the U(VI)-PCV complex, but the anionic and nonionic surfactants showed no positive effect or diminished it. As shown in Table 1, the use of CTMAB as a cationic surfactant was most effective in improving absorbance, and the color development was stable and reproducible. This suggests that

Table 1. Absorption characteristics of U(VI)-PCV complex in the different surfactants

| Surfactant | λ_{max} (nm) | Abs | E.F.* |
|--------------|-----------------------------|-------|-------|
| None | 605 | 0.112 | — |
| CTMAB | 650 | 0.374 | 3.34 |
| DTMAB | 612 | 0.302 | 2.70 |
| SDS | 603 | 0.143 | 1.28 |
| Triton X-100 | 605 | 0.107 | 0.96 |
| Brij 58 | 605 | 0.173 | 1.54 |

E.F*: Enhancer Factor. U(VI): 1.0 ppm, PCV: 1.0×10^{-4} M, Surfactants: 1.0×10^{-4} M, pH: 6.8

the U(VI)-PCV complex interacts with the cationic surfactant and forms the ternary complex through hydrophobic solvation of the chelate. The absorbance increased with an increase in CTMAB concentration up to 1.5×10^{-4} M, but the absorbance decreased with further increases in CTMAB. Therefore, 1.5×10^{-4} M of CTMAB was selected for further investigation.

Composition of complex. To study the composition of U(VI)-PCV-CTMAB ternary complex, measured the mole ratio of U(VI) and PCV in U(VI)-PCV complex with and without CTMAB. The mole ratio of U(VI) and PCV in the U(VI)-PCV complex was determined by the continuous variation method¹³ with measurement of the absorbance of each solution containing a different volume fraction of U(VI) and PCV of the same concentration. The molar composition of U(VI) to PCV was 1 : 1 in the absence of CTMAB and 1 : 2 in the presence of CTMAB. The stoichiometric mole ratio of U(VI) to PCV of the U(VI)-PCV complex changed from 1 : 1 to 1 : 2 in the presence of CTMAB. The molar ratio of U(VI) to, CTMAB in the U(VI)-PCV-CTMAB complex was determined by the method mentioned above. It appeared that the molar ratio of U(VI) and CTMAB in the ternary complex of U(VI)-PCV-CTMAB was 1 : 1. The positive charge of the cationic surfactant would attract the negatively charged complex or mixed-ligand complex, forming a 1 : 1 (mole ratio) complex of CTMAB and U(VI)-PCV.

Calibration, molar absorptivities and precision. In determination of U(VI) as the binary and ternary complexes was obeyed up to 1.0 g mL^{-1} uranium in the final solution measured. The molar absorptivities of the binary and ternary complexes, found by least-squares analysis of 10 results, were $2.4 \times 10^4 \text{ mole}^{-1}\text{cm}^{-1}\text{L}$ and $9.5 \times 10^4 \text{ mole}^{-1}\text{cm}^{-1}\text{L}$ at 650nm, respectively.

Beer's law was obeyed over the concentration range 0-2.2 $\mu\text{g mL}^{-1}$. The detection limit (S/N=3) was $0.15 \mu\text{g mL}^{-1}$ and the relative standard deviation at the $0.5 \mu\text{g mL}^{-1}$ U(VI) level was 3.4% (n=7).

Effect of diverse ions. Numerous cations and anions were examined by applying the method to a fixed amounts of U(VI) in the presence of increasing amounts of the ion being studied. The tolerance limit was taken as the amount that caused an error of $\pm 5\%$ in the absorbance. For the determination of $1.0 \mu\text{g/mL}$ U(VI) by this method, the foreign ions can be tolerated at the levels given in Table 2.

PCV forms stable complexes with various metal ions, including transition metal ions. The results indicate that the

Table 2. Tolerance limit for diverse ions on the recovery of 1.0 ppm U(VI)

| Tolerance limit (ppm) | Foreign ions |
|-----------------------|---|
| 25 | Mg(II), Ca(II), Cl^- , NO_3^- |
| 10 | Au(III), Pt(IV) |
| 5 | Cd(II), Co(II), Mn(II), Sn(II) |
| 2.5 | Cu(II), Cr(III), Ni(II) |
| 1.0 | Sn(II), Y(III), Zr(IV) |
| 0.5 | Fe(III), Al(III), EDTA |

Table 3. Sensitivities of reagents for the spectrophotometric determination of U(VI)

| Method | Molar absorptivity [mole ⁻¹ cm ⁻¹ L] | λ_{\max} [nm] | Reference |
|--|---|--------------------------|----------------|
| 2-(3,5-Dibromo-2-Pyridyl azo)-5-Diethylaminophenol | 9.1×10^4 | 576 | 5 |
| 2-(5-bromo-2-Pyridyl azo)-5-diethylaminophenol | 7.4×10^4 | 565 | 14 |
| Chlorophosphonazo III | 1.0×10^5 | 669 | 16 |
| Pyrocatechol Violet | 9.5×10^4 | 650 | present method |

Table 4. Analytical data of uranium in monazite sand

| | Present method | | ICP method | |
|---------------|-----------------------|------------|-----------------------|------------|
| | Found (%) | RSD (%) | Found (%) | RSD (%) |
| Monazite sand | 2.88×10^{-4} | 3.5 | 3.03×10^{-4} | 1.2 |

concentration range of 0.5-1.0 ppm for Al(III), Fe(III), Sn(II), Zr(IV) and Y(III) are upper limits for interference. Polycarboxylate anion, such as oxalate and EDTA (ethylene diamine-tetraacetic acid) gave negative errors.

Comparison with some other reagents: Pyrocatechol Violet compares well with the most sensitive and widely used reagents for the spectrophotometric determination of U(VI). The sensitivities of the various reagents are compared in Table 3.

Applications.

Determination of uranium in Monazite sand: The proposed method was applied for the determination of uranium in Monazite sand. The matrix elements, such as Al(III), Fe(III) and other rare earths coexist in Monazite sand. A 0.5 g sample was dissolved with 1 : 3 HCl + HNO₃ and the residue was dissolved in 10 mL of 1 M HCl, diluted with 10 mL of distilled water and filtered if needed. Finally, the solution was taken up to 50 mL with distilled water in volumetric flask. An aliquot of solution (10 mL) was taken individually and analyzed by the proposed procedure after masking Al(III) with 1×10^{-5} M urea solution.¹⁵ Generally urea is used as a precipitant of Al(III), Ga(III), Th(IV), Bi(III), Fe(III), Sn(IV). Table 4 shows that the analytical values obtained by this method are in good agreement with the data by ICP-AES.

The precision of the method is satisfactory with a RSD of 3.5%. A correlation coefficient of 0.992 was obtained for ten replicate analyses.

Conclusion

The present study provides a sensitive method for the determination of uranium and is excellent in terms of simplicity. No extraction step is required and hence the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed method should be useful for assay of trace amounts of uranium ion in Monazite sand sample.

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