Spectrophotometric Microdetermination of Thorium(IV) and Uranium(VI) with Chrome Azurol-S in Presence of Cationic Surfactant

A. B. UPASE*, A. B. ZADE and P. P. KALBENDE

Department of Chemistry, Laxminarayan Institute of Technology
R.T.M. Nagpur University, Nagpur, M.S-440010, India

*Department of Chemistry, Shri Sitaramji Chaudhary Science College
Warud, Dist- Amravati, M.S-444906, India

ab_zade18@yahoo.com

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Abstract: Cationic surfactant, cetyldimethylethylammonium bromide (CDMEAB), sensitize the color reactions of Th(IV) and U(VI) with chrome azurol-S (CRAS). Formation of water soluble deeply colored ternary complexes of metal ions show large bathochromic shift. Same stoichiometric composition of ternary complexes with 1:2:4 molar ratio (M-CRAS-CDMEAB) have been observed for both the metal ions and are responsible for enhancement in molar absorptivities and sensitivities at shifted wavelength. The ternary complexes of thorium(IV) and uranium(VI) exhibit absorption maxima at 640 and 620 nm with molar absorptivities 85500 and 69600 L.mol⁻¹.cm⁻² respectively. Beer's law were obeyed in concentration range 0.12-0.185 ppm for Th(IV) and 0.13-0.162 ppm for U(VI) in presence of CDMEAB. Conditional formation constants and various analytical parameters have been evaluated and compared the results of binary and ternary complexes. Enhancement in the molar absorptivities in presence of CDMEAB clearly indicated the usefulness of these colored reactions for microdetermination.

Keywords: Spectrophotometry, Chrome azurol-S (CRAS), Cetyldimethylethylammonium bromide (CDMEAB), Thorium(Th), Uranium(U), Ternary complexes.

Introduction

Both thorium and uranium are of great interest as they are used in the production of energy in nuclear reactors. Thorium has not been used extensively as power reactor fuel because it has some inherent limitations in the fuel cycle which ultimately operates on U²³³. Since, monazite sand possesses thorium of 10-11% concentration of ThO₂ in the amount 2×10⁵ tones of thorium and can be extracted satisfactorily from monazite by NaOH leaching and

further purified with tertiary butyl phosphate. But the thermal breeding advantages of thorium could not be achieved in aqueous solution because of extreme corrosion problems and complicated decay scheme going from ${}_{90}\text{Th}^{232} \rightarrow {}_{92}\text{U}^{233}$ which gives rise to an excessive cost for processing technique and thus provides sufficient justification for abandoning most of thorium development in favor of uranium fuel cycles. Application of fluidized bed technique in gases conversion process for uranium is creating environmental problems. Uranium is more abundant in earth crust than mercury and is present in the same amount as that of tin and molybdenum and is widely distributed. Thorium exists with only one natural isotope Th^{232} and is not very rare. Most of it is obtained as a byproduct in a process of complex phosphate extraction method of rare earths during the processing of monazite.

Considerable interest has been developed in last few decades for the determination of trace amount of thorium and uranium in environmental sites of energy production in nuclear reactor. This initiated the present investigation for development of simple, convenient and reliable method for microdetermination. Most of the reported methods as discussed below, found to have some limitations for its determination at low concentration and are applicable only at high concentration of metal ions. Number of reagents has been reported for the determination of various metal ions as binary complexes by spectrophotometry however, most of them lack in sensitivity to the extent of their determination when present in very small concentration.

A very few ternary or mixed ligand complexes appear in the literature for their spectrophotometric microdeterminations. Mamedova and coworkers¹⁻³ studied the complexation of tungsten(VI), vanadium(V), molybdenum(VI), copper(II) and titanium(IV) with pyrogallol red(PGR) and bromopyrogallol red(BPGR) in presence of cationic surfactant like cetylpyridinium bromide and OP-7. Cationic surfactants, such as cetylpyridinium bromide (CPB), sensitized the color reaction of Nb(V) with 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid (I_a), 5-(benzothiazolylazo)2,5-naphthalenediol (I_b), 5-(2-benzothiazolylazo) 8-hydroxyquinoline(I_c) and 4-(2- benzothiazolylazo)2,2-biphenyldiol (I_d) reagents⁴.

Rare earths reported to form ternary complexes by Poluektov and coworkers⁵ as 1:2:4 metal- glycine-thymol blue- cetrimide with yttrium subgroup elements at an optimum of pH 7.8-8.5 and with cesium subgroup elements at pH 9-9.5. Kirrilov and coworkers⁶ have reported the formation of 1:2:4 complex of rare earth with glycine-cresol red and cetrimonium ion in an ammoniacal medium at pH 8-9 for reading at 616-620 nm to follow Beer's law for 0.04-1.7 $\mu\text{g/mL}$ of rare earth. A 1:2:2 complex of rare earths, eriochrome black T and diphenylguanidine in an acetate buffer solution for pH 6.35-6.8 have been introduced by Akhmedli⁷. Some of the rare earth elements with chrome azurol S in presence of cetyltrimethylammonium bromide and triton X-100 were determined spectrophotometrically⁸. Attempts have been made in the early 70's to improve the sensitivity of some reagents for the microdetermination of rare earths using cationic surfactants like cetyltrimethylammonium bromide and cetylpyridinium bromide⁹⁻¹¹ by increasing the absorbance of the binary complex resulted into heightened molar absorptivity and sensitivity, which has become a useful tool in microdetermination of metal ions. Rare earth elements by flow injection analysis based on their reaction with xylenol orange in presence of CPB were carried out by spectrophotometric method¹².

A 1:1:2 ternary complex of neodymium-gallein-cetrimide at 622 nm have been reported¹³. The surfactant (CPB) sensitized analytical reaction of cerium(IV) with some triphenylformazan derivatives was studied by Ahmed *et al.*¹⁴. In spectrophotometric determination of some lanthanides with triphenylmethane dyes such as chrome azurol- S, eriochrome cyanine R and pyrocatechol violet in presence of cetyltrimethylammonium

bromide, cetylpyridinium bromide and tetradecyldimethyl benzylammonium bromide (zephiramine) have been studied by Jarosz and observed the highest sensitivity of scandium complex with zephiramine and chrome azurol-S¹⁵. A spectrophotometric reagent 2-hydroxy-1-naphthaldehyde-*p*-hydroxybenzoic hydrozone was used for the determination of lanthanum(III) in presence of CTAB¹⁶. Neodymium in mixed rare earths with semi-xylenol orange and cetylpyridinium chloride was determined by spectrophotometric method¹⁷. Ciclopirox olamine was determined *via* ternary complex with Tb(III) and EDTA by spectrofluorimetric method¹⁸. Lanthanum, holmium and manganese in synthetic ceramics, (La_(0.8-x)Ho_xSr_{0.2}MnO₃), by using chromogenic agent 5-Br-PADAP [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol] and triton X-100 as a surfactant were determined by spectrophotometric method¹⁹.

Both Th(IV) and U(VI) were determined as ternary complexes with methylthymol blue and cetyldimethylethylammonium bromide earlier in our laboratory²⁰. A 1:2:4 thorium-methylthymol blue - diphenylguanidine complex was reported by Makoto Otomo²¹. Spectrophotometric determination of uranium(VI) with pyrocatechol violet in surfactant media²² and ternary complexes of thorium with 8-hydroxy-5,7-dinitroquinoline and rhodamine-B²³ 5,7-dibromo-8-hydroxyquinoline and rhodamine-B²⁴ have also been reported. Thorium, lanthanum and yttrium in some geological and environmental samples were determined spectrophotometrically by using eriochrome cyanine R (ECR) in presence of surfactant TX-100 and CTAB²⁵.

The present study hence was planned to suggest really simple and reasonably good method for determination of these metal ions at low concentration, using the reported reagent chrome azurol-S (CRAS) as a binary complex and sensitizing the reagent with cationic surfactant (CDMEAB) as ternary complexes using spectrophotometer which is still frequently used because of its low cost and simplicity.

Experimental

All absorbance measurements were carried out by using Hitachi U 2001 spectrophotometer with matched quartz cell with 1.0 cm thickness. For all spectral studies deionised distilled water was used as a reference solution. The pH values of these solutions were adjusted using Elico Li-10 pH meter, operated on 220 volts stabilizer with AC mains with glass and calomel electrodes assembly. The pH scale was standardized and frequently checked with potassium hydrogen phthalate solution of pH 4.02 and borax solution of pH 9.20. Analytical grade hydrochloric acid and sodium hydroxide solutions of suitable concentration were used for pH adjustment. Chrome azurol-S (CRAS) and cetyldimethylethylammonium bromide (CDMEAB), were supplied by sigma and Aldrich chemical company, USA respectively. Purity of CDMEAB was estimated by using argentometric titration for the determination of bromide ion content²⁶. Thorium nitrate and uranyl acetate of analytical grade purity were supplied by British drug house company, England. Stock solutions of CRAS, CDMEAB and metal ions were prepared of strength 1.0×10^{-2} M and subsequently diluted to desired concentrations using double distilled water.

General procedure

All the experiments were carried out at room temperature of 30 ± 2 °C. The CDMEAB solution was first added to CRAS solution and kept for equilibration for half an hour. Metal ion solution was then added to dye surfactant solution and again kept for half an hour to reach complete equilibrium. This order of mixing the solutions was maintained throughout the investigation.

Results and Discussion

Absorption spectra

Study of absorption spectra of CRAS in absence and presence of CDMEAB

Absorption spectra of CRAS shows wavelength of maximum absorption ($\lambda_{\max}$) at 480 nm in pH range 1.0-2.0, at 510 nm in pH 3.0-4.5, at 430 nm in pH range 5.5-11.0 and; 630 nm at pH 11.0 and above. The variations in absorbance maximum could be interpreted in terms of increasing dissociation of protons from CRAS. However, absorption spectra of CRAS in presence of CDMEAB showed the absorption maxima at 420 nm in pH 5.0-10.0, at 530 nm in pH range 1.0-4.0. No notable shifts in $\lambda_{\max}$ of CRAS have been observed in pH range 5.5-12.0 in presence of CDMEAB. These spectral changes indicate an early dissociation of proton in presence of CDMEAB takes place as expected theoretically and shows the ionic interaction between anionic CRAS and cationic CDMEAB. This ionic interaction results into decrease in pKa values with decrease in absorbance values as reported in the literature.

Effect of surfactant concentration on absorbance of CRAS at various wavelength in acidic range shows maximum decolorizing effect at the minimal ratio of 1:2 (CRAS:CDMEAB). When this ratio has been reached, the absorbance of CRAS remains unchanged even if fivefold excess of CDMEAB have been added. Thus, the CRAS in presence of CDMEAB can be represented as $[\text{CRAS}(\text{CDMEAB})_2]$ as a modified reagent as reported earlier²⁶.

Study of absorption spectra of binary and ternary complexes

Spectral study of binary and ternary complexes show $\lambda_{\max}$ at 590 and 640 nm for Th(IV) and at 620 and 630 nm for U(VI) respectively in acidic range. Plots of comparative absorption spectra at pH 6.5 for Th(IV) and at pH 5.0 for U(VI) where the maximum difference in absorbance have been observed between binary and ternary complexes as shown in Figures 1 and 2 respectively.

Figure 1. Absorption spectra of Th(IV) at pH 6.5, A) CRAS-(Reagent); B) CRAS-CDMEAB-(Modified reagent); C) CRAS-Th(IV) at(pH 4.5)-(Binary complex) and D) CRAS-CDMEAB-Th(IV)-(Ternary complex)

Figure 2. Absorption spectra of U(VI) at pH 5, A) CRAS-(Reagent); B) CRAS-CDMEAB-(Modified reagent); C) CRAS-U(VI)-(Binary complex) and D) CRAS-CDMEAB-U(VI)-(Ternary complex)

Absorption spectra of CRAS alone as indicated by curve A in Figure 1 and 2 shows $\lambda_{\max}$ 430 nm at pH 6.5 and 470 nm at 5.0 respectively. Absorption spectra of CRAS in presence of fivefold excess of CDMEAB as represented by curve B indicates considerable decrease in absorbance values. Curve C in Figure 1 shows absorption spectra of Th(IV) complex of CRAS indicates the binary complexation with a shift in $\lambda_{\max}$ of CRAS from 420 to 590 nm. Precipitation of Th(IV) has been observed above pH 5.0, however there was no precipitation up to pH 7.0 in presence of CDMEAB. Curve-D in Figure 1 represents ternary complexation of Th(IV) with CRAS in presence of CDMEAB, which shows maximum absorption at 640 nm with a considerable increase in absorbance and thus a bathochromic shift of 50 nm have been observed.

In Figure 2 curve C represents absorption spectra of U(VI) complex with CRAS in absence of CDMEAB which shows $\lambda_{\max}$ at 620 nm indicating binary complex formation. However, absorption spectra of U(VI) complex with CRAS in presence of fivefold excess of CDMEAB as indicated by curve-A shows maximum absorption at 630 nm with increase in absorbance and thus a bathochromic shift of 10 nm has been observed.

Thus, the use of CDMEAB as a cationic surfactant has been found to most effective in improving absorbance with heightened molar absorptivity resulting into formation of intense colored ternary complexes with a bathochromic shift of 50 and 10 nm for ternary complexes of Th(IV) and U(VI) respectively.

Effect of pH

In Figures 3 and 4, curve-C is a plot of variations of $\lambda_{\max}$ with the change in pH of CRAS. Initially the $\lambda_{\max}$ of CRAS remains constant at 510 nm in pH range 2.5-4.0, it gradually decreases to 430 nm in pH range 4.0-5.0 and remains constant at 430 nm in pH range 5.0-7.0. In Figure 3 and 4, curve-D is a plot of variations of $\lambda_{\max}$ with change in pH of CRAS in presence of CDMEAB. The $\lambda_{\max}$ Shifts from 510 to 530 nm in pH range 2.5-3.5, it gradually decreases from 530 to 420 nm in pH range 3.5-5.0 and remains constant at 420 nm in pH range 5.0-7.0.

In pH range 2.5-3.5, $\lambda_{\max}$ of Th(VI) complex in presence of CDMEAB gradually decreases from 650-640 nm and remains constant at 640 nm up to pH 7.0 is represented by curve B in Figure 3. However binary complex of Th(IV) shows $\lambda_{\max}$ at 590 nm up to pH 4.5 above which precipitation of the complex has been observed. Thus a bathochromic Shift of 50 nm in the formation of ternary complex in wider pH range in presence of CDMEAB has been observed.

Figure 3. Variations in $\lambda_{\max}$ with changes in the pH of: A) [CRAS+Th(IV)]-(Binary complex); B) [CRAS+CDMEAB+Th(IV)]-(Ternary complex); C) [CRAS]-(Reagent) and D) [CRAS+CDMEAB]-(Modified reagent)

Figure 4. Variations in $\lambda_{\max}$ with changes in the pH of: A) [CRAS+U(VI)]-(Binary complex); B) [CRAS+CDMEAB+ U(VI)]-(Ternary complex); C) [CRAS]-(Reagent) and D) [CRAS+CDMEAB]-(Modified reagent)

In pH range 2.5-7.0, $\lambda_{\max}$ of U(IV) complex in presence of CDMEAB remains constant at 640 nm and is represented by curve B in Figure 4. Binary complex of U(VI) shows $\lambda_{\max}$ at 620 nm in the pH range 3.5-5.0. It gradually increases from 520-620 nm in the pH range 2.5-3.5 and decreases from 620 nm to 430 nm in the pH range 5.0-6.0. Thus a bathochromic shift of 20 nm in the formation of ternary complex has been observed in presence of CDMEAB. The pH range of stability of constant wavelength have been found to be 2.5-4.5 for binary complex and 3.5-6.5 for ternary complex of Th(IV) in absence and presence of CDMEAB respectively. The pH range of stability of constant wavelength have been found to be 3.5-5.0 for binary complex and 2.5-7.0 for ternary complex of U(VI) in absence and presence of CDMEAB respectively.

Variation of absorbance with change in pH of complexes in presence of CDMEAB at $\lambda_{\max}$ 640 nm for Th(IV) and 630 nm for U(IV) is represented in Figure 5. Absorbance of Th(VI) complex in presence of CDMEAB at 640 nm increases in pH range 3.0-3.5 and remains constant at 0.420 in pH range 3.5-6.5 and it decreases in pH range 6.5-7.0. Similarly absorbance of U(VI) complex of CRAS in presence of CDMEAB at 640 nm increases in pH range 3.0-4.0 and remains constant at 0.60 in pH range 4.0-6.0 and it again decreases in pH range 6.0-7.0.

Figure 5. Variations in absorbance at the $\lambda_{\max}$ with changes in the pH of: A) $\lambda_{\max}$, 640 nm of CRAS-CDMEAB-Th(IV); B) $\lambda_{\max}$, 640 nm of CRAS-CDMEAB-U(VI)

Thus optimum pH range of stability of complex formation of constant absorbance have been found to be 3.5-6.5 at the $\lambda_{\max}$ 640 for Th(IV) and 4.0-6.0 at the $\lambda_{\max}$ 640 nm for U(VI). Thus the complexation in presence of CDMEAB takes place in wider pH range with increase in absorbance values as compared to binary complexes indicating sensitization of the reagent in presence of cationic surfactant which can be explored for the microdetermination of metal ions under study when present in small concentration and undetectable by binary complexation.

Composition of complexes

The composition of binary and ternary complexes were studied by Job's method of continuous variation²⁷ and further confirmed by mole ratio method and found to be 1:2 for Th(IV) to CRAS and 1:1 for U(VI) to CRAS. However, the molar ratio of ternary complexes of Th(IV) and U(VI) with CRAS was found to 1:2 in presence of CDMEAB. Stoichiometric composition of ternary complexes as Th(IV)-CRASCDMEAB and U(VI)-CRAS-CDMEAB may be expressed as 1:2:4.

Stability constant of complexes

The values of log K {where, $K=[ML_2]/[ML][L]$ } *i.e.* stability constants have been calculated from the curves of Job's method of continuous variations and mole ratio method and are given in Table 1. The values for particular metal in presence of CDMEAB are higher in presence than in absence which shows that the complexes are stabilized in presence of cationic surfactant CDMEAB.

Table 1. Composition and log K values of thorium and uranyl chelates of CRAS in absence and presence of CDMEAB

Metal ions	Study in A-absence B-presence of CDMEAB	pH	Wavelength, nm	Composition M:R or M:(R:S)	log K values by	
					Job's method	Mole ratio method
Th(IV)	A	4.5	590	1:2	8.90	8.90
Th(IV)	B	6.5	640	1:2:4	10.02	10.01
U(VI)	A	5.0	620	1:1	5.46	5.45
U(VI)	B	5.0	640	1:2:4	9.90	9.92

Analytical applications of complexes of Th(IV) and U(VI) in presence of CDMEAB

Formation of intense colored ternary complexes in presence of CDMEAB with high absorbance values at shifted wavelength in wider pH range have been observed in the present investigation resulting into higher molar absorptivity which has been used as a useful property for microdetermination of metal ions understudy. Various analytical parameters have been studied and compared with the binary complexes to prove the sensitization and importance of the cationic CDMEAB.

Rate of color formation and stability of color at room temperature

Highly soluble colored complexes in presence of CDMEAB were formed instantaneously at ambient temperature (25 ± 1 °C). On increasing temperature up to 60 °C, no change in the absorbance values has been observed. The absorbance of complexes remains constant for at least 48 hrs then decreases gradually.

Effect of reagent concentration

Maximum color formation have been observed when the solution contained three fold for Th(IV) and two fold for U(VI), molar excess of modified reagent with respect to metal ion solution. However, in absence of CDMEAB the amounts of CRAS required for complete color formation were found to be five and four times than those of Th(IV) and U(VI) metal ions concentration respectively.

Beer's law and effective photometric ranges

By varying metal ion concentration CRAS (2 mL of 5.0×10^{-4} M) and measuring the absorbance at the pH and wavelength of study chosen for respective metal ion, the linearity between the absorbance of chelates and metal ions in presence of CDMEAB has been carried out. The Beer's law range as well as effective photometric range for both Th(IV) and U(VI) metal ions has been calculated from these data and the Ringbom plot²⁸ in absence and presence of CDMEAB. The values are recorded in Table 2.

Table 2. Photometric determination of Th(IV) and U(VI) metal ions with CRAS in absence and presence of CDMEAB

Metal ions	Study with CDMEAB	Beer's law range, ppm	Effective photometric range, ppm	Sandell's sensitivity, $\mu\text{g}/\text{cm}^2$	Molar absorptivity
Th(IV)	A	0.23-2.08	0.92-1.62	0.0073	31300
Th(IV)	B	0.12-1.85	0.46-1.39	0.0029	85500
U(VI)	A	0.27-2.16	0.81-1.90	0.0089	35200
U(VI)	B	0.13-1.62	0.27-1.62	0.0034	69600

A- Absence and B- Presence of CDMEAB

The average values of molar absorptivities and Sandell's sensitivities²⁹ (against 0.01 absorbance) calculated in absence and presence of fivefold excess of CDMEAB for each complex have been shown in Table 2 which shows considerable increase in sensitivity of these ternary complex forming reactions in presence of CDMEAB as compared to binary complexes indicating the usefulness and the importance in microdetermination.

Procedure for microdetermination of individual Th(IV) and U(VI)

Solution containing 30 to 70 μg of metal ion was adjusted to 6.5 for Th(IV) and 5.0 for U(IV) ions. The modified CRAS was prepared by adding about five fold excess of CDMEAB solution to CRAS solution and keeping it for half an hour for equilibration 2 mL of this modified CRAS solution of the same pH was added to above metal ion solution. The volume was made to 50 mL with distilled water of same pH. The absorbances were recorded at 640 nm for Th(IV) and U(VI) metal ions against reagent blank. The absorbances of these unknown solutions were then compared with calibration curves obtained under similar condition. Results of seven determinations by taking 69.60 $\mu\text{g}/50$ mL Th(IV) ions and 67.50 $\mu\text{g}/50$ mL U(VI) ions showed standard average deviation of 0.025 and 0.027 respectively (Table 3).

Table 3. Microdetermination of individual metal ions

Metal ions	Amount taken, $\mu\text{g}/50$ mL	Amount found $\mu\text{g}/50$ mL	Standard average deviation
Th(IV)	69.60	69.77	0.025
U(VI)	67.50	67.65	0.027

Effect of foreign ions

It was observed that Cu^{2+} and In^{3+} interfere at all concentrations for both the metal ions under study. Polycarboxylate anion such as oxalate and EDTA (Ethylenediamine tetraacetic acid) give negative errors.

Conclusion

The sensitization of CRAS has taken place in presence of cationic CDMEAB ensuing into the formation of intense colored ternary complexes with bathochromic shift and increase in absorbance values at shifted wavelength resulted into the formation of heighten sensitivity and absorptivity in wider pH range. The complexes between CRAS and both the metals under study in the presence of CDMEAB are very stable and more sensitive in presence than in absence of surfactant. This developed method for the microdetermination of Th(IV) and U(VI) is inexpensive involves the use of readily available reagents, allows rapid determination at low operating costs and can be used in a simple laboratory pH meter and spectrophotometer. The procedure showed simplicity, adequate sensitivity and having low limit of detection with comparatively very few interferences and more accurate than the other methods reported earlier.

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