

Studies on Reaction between Solochrome Violet RS and Cetyltrimethyl Ammonium Bromide and its Subsequent Complexation Studies with Y(III) and $\text{UO}_2(\text{VI})$.

MRS. A. S. MAHAKALKAR and K.N. MUNSHI*

*Department of Chemistry
Nagpur University, Nagpur-440 010, India*

Spectrophotometric method was used to study the formation of dye (solochrome violet RS) and surfactant (cetyltrimethyl ammonium bromide) complex at proper set of conditions. This modified reagent was then used to form complexes with Y(III) and $\text{UO}_2(\text{VI})$. Composition, stability constant and analytical parameters of these complexes have been evaluated.

INTRODUCTION

The addition of the quaternary salts to the deeply coloured solution of dyes causes a marked colour change. The shift is caused by the short range electrostatic forces on the surface of the micelle double layer. The interesting property of the aggregates formed is their ability to form coloured complexes with various cations. The sensitivity primarily decides the usefulness and importance of the reagents developed for the spectrophotometric determination of metal ions. As is evident from the literature, a number of reagents have been reported for the lanthanides¹⁻⁴. Many of these, however, lack in sensitivity. In this context, micelle forming cationic surfactants can be used to increase the sensitivity of the colour reactions.

The addition of surfactants to the acid-base indicators showed that there was a considerable increase in the absorbance when surfactant solutions were added to the indicator solutions. However, in some reactions a decrease in colour intensity of organic dyes on addition of surfactant has been reported. In such cases the modified reagents become much more suitable for the sensitization of the colour reactions of metal ions. The addition of metal ions to these sensitised indicators results in the formation of intense, water-soluble, coloured complexes.

The beryllium-chrome azulol S complex was sensitized⁵ in the presence of zepinamine at pH 5.2. Svobda and Chromy have reported a detailed study on the reaction of xylenol orange on micelles and their complexing behaviour^{6,7} on lanthanum(III). West and coworkers⁸ have modified pyrocatechol violet by adding cetyltrimethyl ammonium bromide and used it for the determination of molybdenum, antimony and aluminium. A large amount of work has been reported from our laboratory on the spectrophotometric determination of metal ions⁹⁻¹² in the presence of cetyltrimethyl ammonium bromide (CTAB).

In this communication, the results of the experiments carried out on solochrome

violet RS (SVRS) in the presence of cetyltrimethyl ammonium bromide (CTAB) and their interactions with some of the metal ions are reported.

EXPERIMENTAL

For absorbance measurements, a UV Shimadzu spectrophotometer UV-240, a Japanese model, was employed. A 1-cm thickness of the solutions was employed by using matched glass cells supplied with the instrument; distilled water blanks were used. For pH measurements, Elico pH meter (Model LI-10) operated on 220 volts stabilized AC mains and expanded pH meter were used, with a glass and calomel electrode system. pH was adjusted with the help of hydrochloric acid and sodium hydroxide solutions of suitable concentrations.

All the chemicals used were of analytical grade. A 1.0×10^{-3} M SVRS solution was prepared in double distilled water by dissolving the purified sample. The surfactant cetyltrimethyl ammonium bromide (CTAB) (10^{-2} M) solution was prepared from BDH grade samples in 20% aqueous methanol and standardised by titrating these against silver nitrate solution for bromide ion content. Metal solutions of 1.0×10^{-2} M were prepared by dissolving lanthanide oxides (purity 99.9%) in minimum quantity of HCl and making up the volume with distilled water. 10^{-2} M solutions of uranyl acetate and thorium nitrate were prepared from AR grade samples. Solutions of required concentrations were prepared by appropriate dilution of these solutions.

The following general procedure was strictly followed in all the experiments. The surfactant solution was added to the dye solution which was then allowed for equilibration for 15–20 minutes. Metal ion solution was then added to the dye-surfactant solution and allowed to equilibrate for 20 minutes for the complete complex formation, after which the absorbance readings were recorded. All the experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Absorption spectra of SVRS in the absence and presence of CTAB

The addition of CTAB to SVRS solution brings about a change in colour. The absorption spectra was recorded at different pH values (1.0–12.0) in the absence and presence of CTAB. The wavelengths of maximum absorbance of SVRS in the absence and presence of surfactant are summarized in Table 1.

The absorption spectrum at pH 1.0–2.0 shows no change in the absence as well as in the presence of CTAB. Between pH 3.0–5.0, there is very little change in λ_{\max} but absorbance decreases in the presence of CTAB. At pH 6.0 there is change of 60 nm, showing a bathochromic shift along with lowering in the absorbance. From pH 7.0 to 12.0, a bathochromic shift of 15 nm is observed in the presence of CTAB. This change in the absorbance maximum, in the presence of CTAB, in the acidic as well as in the alkaline region may be attributed to the possible formation of a dye-surfactant complex.

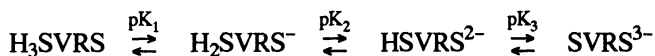
TABLE 1
 λ_{\max} OF SVRS AT DIFFERENT pH VALUES

In the absence of CTAB		In the presence of CTAB	
pH	λ_{\max} (nm)	pH	λ_{\max} (nm)
1.0–2.0	500	1.0–2.0	500
3.0–5.0	500	3.0–5.0	495
6.0	500	6.0	560
7.0–11.0	540	7.0–11.0	555
12.0	535	12.0	520(550)

Dissociation constants (pK values) of SVRS

The spectrophotometric method of determination of dissociation constants by Albert and Serjeant¹³ depends on the direct determination of the protonated and deprotonated species in a series of non-absorbing buffer solutions whose pH is so chosen that the compound to be measured is present wholly as that species. The wavelength chosen is an analytical wavelength at which the greatest difference between the absorbances of the two species is observed.

SVRS has three replaceable protons out of which one is due to the presence of $-\text{SO}_3\text{H}$ group while the other two are due to the presence of two $-\text{OH}$ groups. The dissociation equilibria of SVRS may therefore be represented as



The three pK values as expected are evaluated in the absence as well as in the presence of CTAB and are given in Table 2.

TABLE 2
 pK VALUES OF SVRS IN THE PRESENCE AS WELL AS IN THE
 ABSENCE OF CTAB

pK values	In the absence of CTAB	In the presence of CTAB
pK ₁	1.8	1.7
pK ₂	7.6	6.2
pK ₃	11.5	11.0

The pK values of SVRS (± 0.1) in the presence of CTAB show definite decrease. This decrease is, however, most prominent for pK₂ values where the lowering to the extent of 1.6 units is observed.

Composition of SVRS–CTAB complex

The stoichiometry of the SVRS–CTAB complex was studied at pH 6.0 and at 500 nm (Fig. 1). The same experiment was tried in the alkaline region but no definite ratio could be achieved, as the absorbance first showed a decrease and then an increase.

It may be concluded from the curves that there is successive decrease in the absorbance values of the reagent up to the point where the SVRS–CTAB ratio is

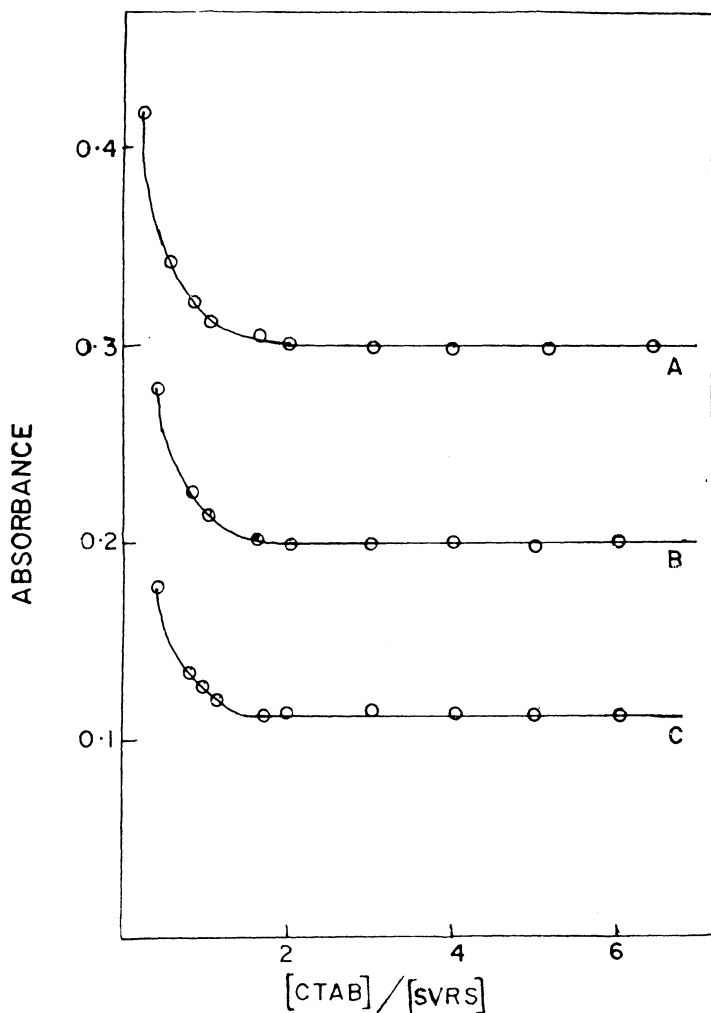


Fig. 1 Composition of SVRS-CTAB complex, pH = 6.0, $\lambda = 500$ nm, Final conc. of SVRS = 8.0×10^{-5} M (curve A); 6.0×10^{-5} M (curve B); 4.0×10^{-5} M (curve C)

reached to 1 : 2. The full formation of dye-detergent complex is thus observed at this minimal ratio. When this ratio has been exceeded, the absorbance of the SVRS remains unaltered even when an excess of ten times of CTAB has been added. This modified reagent species can be represented as $[\text{SVRS}(\text{CTAB})_2]$.

Effect of mineral salts

Figure 2 shows the effect of various mineral salts in the presence of CTAB in an acidic medium. Negligible effect is observed on the absorbance of SVRS-CTAB complex when chlorides of K^+ , Na^+ and NH_4^+ are added. The addition of sulphates of Na^+ and NH_4^+ shows an increase in the absorbance values. The nitrates have also affected the absorbance to a considerable extent.

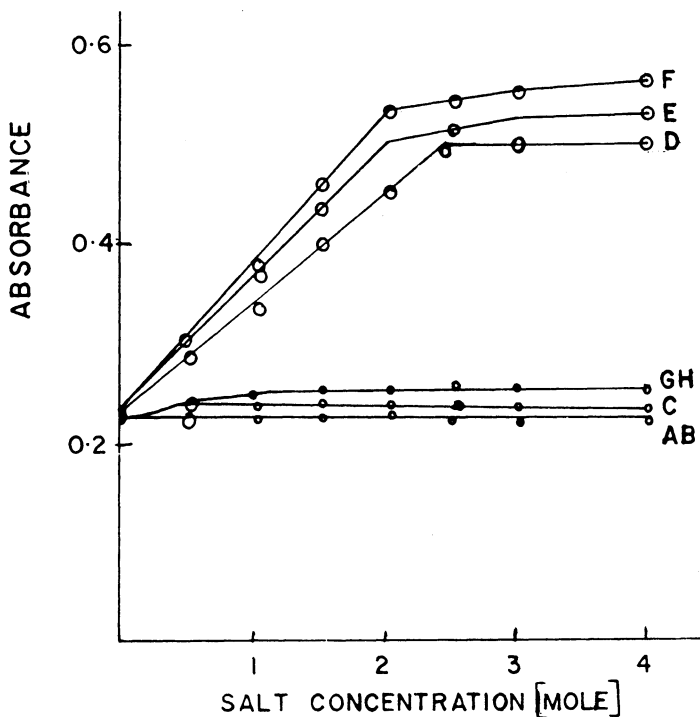


Fig. 2 Effect of mineral salts on SVRS-CTAB complex. pH = 6.0, $\lambda = 500$ nm, Final conc. of SVRS = 8.0×10^{-5} M, Curve A = KCl; B = NaCl; C = NH_4Cl ; D = KNO_3 ; E = NaNO_3 ; F = NH_4NO_3 ; G = Na_2SO_4 ; H = $(\text{NH}_4)_2\text{SO}_4$

Absorption spectra of the chelates in the absence and in the presence of CTAB

A series of solutions were prepared keeping the ratio of metal: SVRS as 1 : 4, 1 : 1 and 4 : 1. The pH of the mixtures were adjusted to different pH values in all the cases. The absorption spectrum was then recorded in the visible region from 350 nm to 650 nm.

Absorbance maxima of SVRS and its complexes in the absence and presence of CTAB have been summarized at pH values from 4.0 to 6.0 in Table 3. SVRS shows λ_{max} at 500 nm in the pH range 4.0 to 6.0. In the presence of CTAB, SVRS shows a peak at 495 nm at pH 4.0 and 5.0 and at 555 nm at pH 6.0.

The λ_{max} of SVRS is not much altered in the presence of metal ions under study. SVRS forms only one stable complex with uranyl, thorium, yttrium and europium ions in the absence and presence of CTAB: Considering all aspects of study, the pH range and the wavelength where the maximum difference between complex and free ligand was observed, the wavelength of study was selected accordingly: pH 4.0 for $\text{UO}_2(\text{VI})$ -SVRS complex at 590 nm, pH 4.0 for $\text{UO}_2(\text{VI})$ -SVRS-CTAB complex at 580 nm and pH 6.0 for $\text{Y}(\text{III})$ -SVRS-CTAB complex at 500 nm (Figs. 3 and 4).

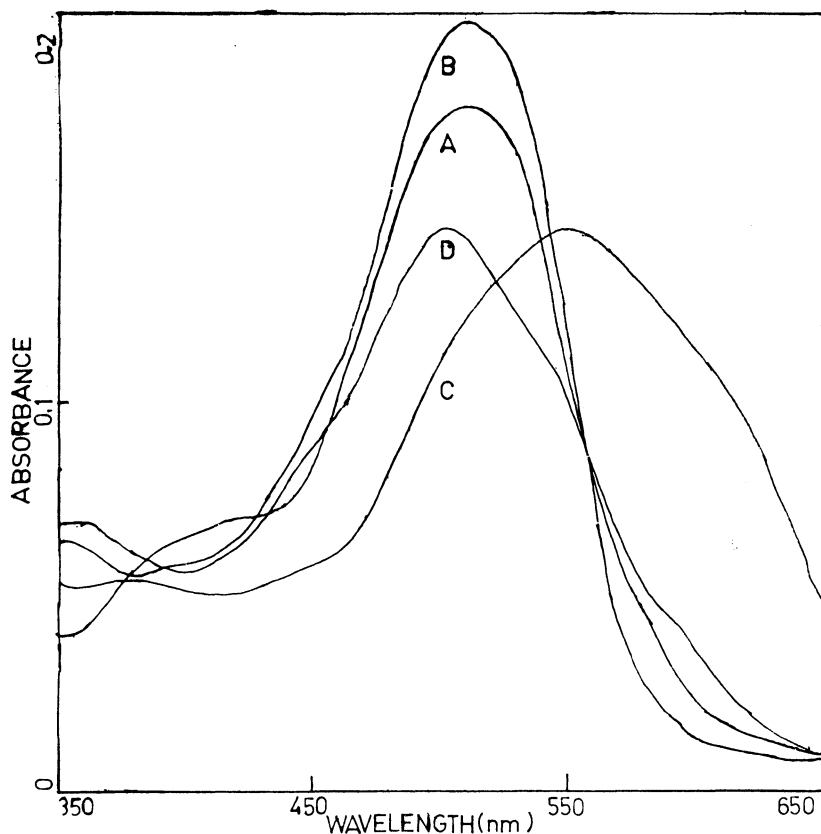


Fig. 3. Absorption spectra of Y(III) complex of SVRS: pH = 6.0, Conc of SVRS = 2.0×10^{-5} M, Conc. of CTAB = 2.0×10^{-4} M, Conc. of Y(III) = 8.0×10^{-5} , Curve A = SVRS, Curve B = Y(II)-SVRS, Curve C = SVRS-CTAB, Curve D = Y(III)-SVRS-CTAB

TABLE 3
 λ_{\max} OF SVRS AND ITS CHELATES IN THE ABSENCE AS WELL
 AS IN THE PRESENCE OF CTAB AT DIFFERENT pH VALUES

Systems	λ_{\max} (nm) at pH		
	4.0	5.0	6.0
SVRS	500	500	500
SVRS-CTAB	495	495	555
SVRS-UO ₂ (VI)	505	505	505
SVRS-CTAB-UO ₂ (VI)	510	510	510
SVRS-Th (IV)	500	500	500
SVRS-CTAB-Th(IV)	500	500	510
SVRS-Y (III)	500	500	500
SVRS-CTAB-Y(III)	500	510	510
SVRS-Eu (III)	500	500	500
SVRS-CTAB-Eu(III)	495	500	500

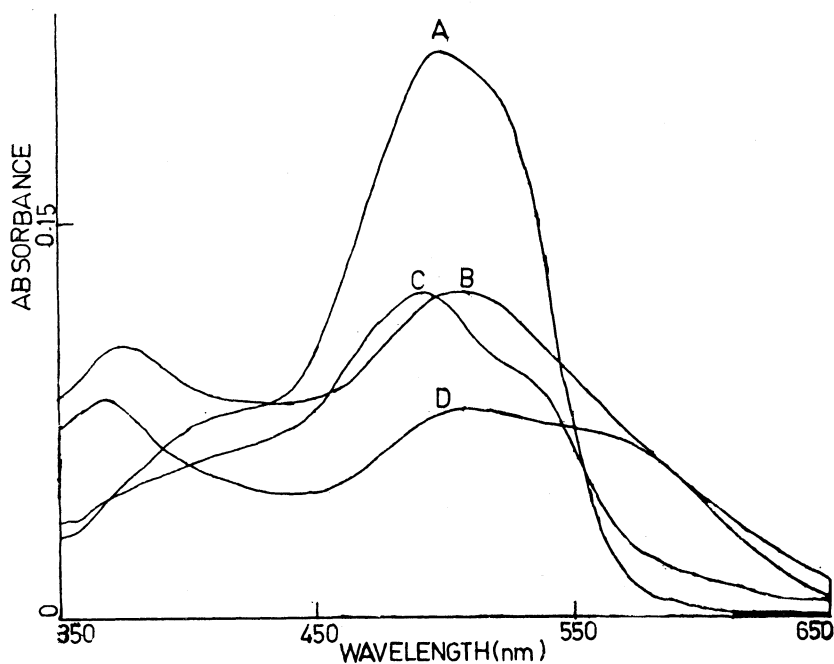


Fig. 4 Absorption spectra of $\text{UO}_2(\text{VI})$ complexes of SVRS. pH = 4.0, Conc. of SVRS = 2.0×10^{-5} M, Conc. of CTAB = 2.0×10^{-4} M, Conc. of $\text{UO}_2(\text{VI})$ = 8.0×10^{-3} , Curve A = SVRS, Curve B = $\text{UO}_2(\text{VI})$ -SVRS, Curve C = SVRS-STAB, Curve D = $\text{UO}_2(\text{VI})$ -SVRS-CTAB.

Composition of the chelates

Quantitative information on complex formation is obtained by determining the composition and the stability constants of the chelates formed. From the spectral studies, it was found that the reagent, SVRS, forms only one complex with metal ions under study. The composition of the chelates was studied by the Job's method of continuous variation and further confirmed by Mole ratio method. The stoichiometric composition between the $\text{UO}_2(\text{VI})$ and Y(III) and SVRS has been found to be 1 : 2 in the absence of CTAB and no change in composition have been further observed in the presence of CTAB.

TABLE 4
COMPOSITION OF THE COMPLEXES OF SVRS

Systems	Condition of study		Composition M : SVRS : CTAB	
	pH	Wavelength (nm)	Job's method	Mole ratio method
$\text{UO}_2(\text{IV})$ -SVRS	4.0	590	1 : 2	1 : 2
$\text{UO}_2(\text{VI})$ -SVRS-CTAB	4.0	580	1 : 2 : 4	1 : 2 : 4
Y(III)-SVRS-CTAB	6.0	500	1 : 2 : 4	1 : 2 : 4

It is necessary to mention that, as the absorbance of SVRS was fairly dominating at the wavelength of study in Y(III)-SVRS-CTAB system, the graph of Job's method of continuous variation was plotted against the Δ -absorbance (difference in absorbance between complex and free ligand).

Stability constants

Log K values of the chelates of $UO_2(VI)$ and Y(III) metal ions with SVRS in the absence and presence of CTAB have been recorded in Table-5. The values of stability constants have been calculated by Job's method of continuous variations and Mole ratio method. The log K values, in presence of CTAB, are found to be more than in the absence of CTAB.

TABLE 5
LOG K VALUES OF THE CHELATES OF SVRS IN THE ABSENCE AND IN PRESENCE OF CTAB

Chelates	pH	Wavelength (nm)	Log K values	
			Job's method	Mole ratio method
$UO_2(VI)$	4.0	590	9.78	9.81
$UO_2(IV)$ -CTAB	4.0	580	10.02	9.95
Y(III)-CTAB	6.0	500	8.90	9.72

Analytical applications of chelates of SVRS in presence of CTAB

Various analytical parameters are evaluated critically and the results are discussed below.

As described earlier, the order of addition of the reactants should be followed very strictly. In all the cases CTAB solution was added to SVRS solution. This solution was kept for 30 minutes for equilibration to which metal ions solution was then added. The colour intensity of the mixture of reactants, in presence of excess of reagent solution and tenfold excess of CTAB solution, remains constant from 20° to 60°C.

The colour formation does not depend upon the reaction time and is almost instantaneous. The maximum absorbance was achieved after 20 minutes of the addition of the reactants and no change was then observed even after 24 hrs. All the measurements were made 30 minutes after the preparation of the solution in all the experiments.

Effect of reagent concentration

To the modified reagent solution, metal ion solution was added. CTAB solution was kept ten times in excess. The total volume was made upto 25 ml. The pH of the solution was adjusted accordingly and the absorbance was recorded at the wavelength of study. The effect of excess of reagent was determined in $UO_2(VI)$ system in the absence as well as in the presence of CTAB, and for Y(III) only in the presence of CTAB. It was found that a threefold concentration of the reagent is essential for maximum colour development in the absence and in the presence of CTAB.

pH-range of stability of the absorbance of the systems

The absorbance values of the complex remaining constant within a certain pH-range is considered as a stable pH-range. The absorbance of the system was noted at the wavelength of study selected. The CTAB solution was taken ten times in excess the reagent solution. The values are given in Table 6.

Beer's law and photometric range

The linearity between the absorbance of the chelates in the presence of CTAB and concentration of metal ions was tested by taking the different volumes of metal ion solution, at the pH and wavelength of study.

The effective range for the photometric determination was calculated by plotting the Ringbom plot of log of metal ion concentration versus % transmittance. The results are given in Table 6.

Sensitivity and molar absorptivity

Molar absorptivities of the complexes were determined by taking a constant amount of SVRS and different amount of excess metal ions with ten times excess of CTAB. The values of molar absorptivities and sensitivities of metal complexes in the absence and presence of CTAB at the wavelength of study are given in Table 6.

TABLE 6
ANALYTICAL PARAMETERS OF THE SYSTEMS OF SVRS IN THE
PRESENCE OF CTAB

Systems	Wavelength of study (nm)	pH-range of stability	Beer's law range (ppm)	Photometric range (ppm)	Molar absorptivity $E_m \times 10^3$	Sandell's sensitivity $S \times 10^{-2}$
UO ₂ (VI)-SVRS	590	3.7-5.0	2.4-30.5	2.6-10.0	1.7	6.5
UO ₂ (VI)-SVRS-CTAB	580	3.8-5.0	1.0-16.7	1.6-10.0	1.1	4.4
Y(III)-SVRS-CTAB	500	5.6-7.0	0.9-4.4	1.6-4.0	1.0	8.0

Effect of foreign ions

The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of a large number of foreign ions. It was observed that Cu²⁺ and Ti³⁺ interfere largely in all the three systems. VO²⁺, Ni²⁺, La³⁺ and Co²⁺ also interfere in the systems, while determination is possible in the presence of Pb²⁺, Zn²⁺, Cd²⁺, Fe³⁺, Mg²⁺, Ca²⁺ and Ba²⁺.

Anions like Cl⁻, Br⁻ and I⁻ do not interfere in all the systems while anions like tartarate, oxalate, fluoride and citrate interfere at all concentrations.

Procedure for microdetermination

The pH of the solution containing 25 µg to 50 µg of metal ions was adjusted accordingly. The modified reagent solution of same pH was added to it (the modified SVRS reagent is prepared by adding tenfold excess of CTAB solution

and keeping it for at least 0.5 hr for complete reaction). The volume was made upto 25 ml with distilled water and absorbance of this solution is measured at wavelength of study. The absorbance of this unknown solution was compared with the calibration curve obtained under similar conditions. Table 7 records the accuracy of the spectrophotometric determination of metal ions under study with SVRS giving the values of deviations.

TABLE 7
SPECTROPHOTOMETRIC DATA FOR SVRS SYSTEM IN THE ABSENCE AND PRESENCE OF CTAB

Systems	Mean absorbance	Mean deviation	Relative mean deviation %
UO ₂ (VI)-SVRS	0.274	0.0021	0.76
UO ₂ (VI)-SVRS-CTAB	0.511	0.0017	0.33
Y(III)-SVRS-CTAB	0.295	0.0015	0.51

Statistical evaluation of proposed analytical methods

In order to decrease the effect of random errors in the result of analysis, usually more than one determinations are performed. But none of these determinations give the true value, as they contain errors. Therefore, the aim in analysis is to find the most probable value of the result and to assess its degree of precision.

Precision and accuracy of the methods proposed

Conclusions can be drawn on the basis of data given in Table 8 regarding (i) the root mean square deviation (σ), (ii) the most probable analytical error (E), the difference (Δ) between arithmetic mean (\bar{X}) and true or most expected (X_t) value of absorbance for the systems studied.

TABLE 8
PRECISION DATA FOR ABSORBANCE MEASUREMENTS

Systems	\bar{X}	σ	E	$\bar{X} - E$	$\bar{X} + E$
UO ₂ (VI)-SVRS	0.274	0.0025	0.0029	0.271	0.277
UO ₂ (VI)-SVRS-CTAB	0.511	0.0018	0.0021	0.509	0.513
Y(III)-SVRS-CTAB	0.295	0.0016	0.0019	0.293	0.297

TABLE 9
ACCURACY OF DETERMINATION EXPRESSED IN TERMS OF ($\Delta < E$)

Systems	\bar{X}	X_t	$\Delta = X_t - \bar{X}$	ϵ
UO ₂ (VI)-SVRS	0.274	0.273	-0.001	0.0029
UO ₂ (VI)-SVRS-CTAB	0.511	0.511	0.000	0.0021
Y(III)-SVRS-CTAB	0.295	0.295	0.001	0.0019

The precision and accuracy data recorded in Tables reveal that the methods proposed are precise as well as accurate.

The value of most probable analytical error, determined with root mean square deviation, σ for ten replicate determinations ranges between 0.0016 to 0.0025 at the confidence limit of $t = 0.995$ or 99.5%. If the number of determinations are further increased that would subsequently decrease the value of t_{α} , the expected decrease in the probable errors would also decrease the level of confidence limit. Therefore, it may not be worthwhile to perform more than ten replicate determinations as has been done in the present course of studies.

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