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Effect of some Surface Active Substances on the Spectrophotometric Determination of Th(IV) Using Some Coumarin Azo Dyes

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The complexes of Th(IV) with some 8-(Arylazo)-6,7-dihydroxy-4-methylcoumarin are investigated spectrophotometrically. The optimum conditions for chelation, pH, sequence of addition, time, solvents and stoichiometry are critically evaluated. The studies reveal that 1 : 1 and 1:2 (M : L) complexes are formed. Beer's law is constructed for the spectrophotometric determination of Th(IV) in presence and absence of some surface active substances. The studies reveal that the use of surfactants increases the sensitivity of the methods of determination by raising the values of molar absorptivity (ε). The methods are precise as given by low standard deviations ranging from 0.0097 to 0.0448 and high correlation coefficient (r) ranging from 0.9884 to 0.9996. The values of molar absorpitivity ε (LM^{-1} cm^{-1}), specific absorpitivity a (mL g^{-1} cm^{-1}) and Sandell sensitivity S (μg cm^{-2}) indicate the method to be quite sensitive compared to standard method using Thoron. The tolerance of interference of foreign ions is investigated in the presence and absence of surfactants. The photometric titration methods using EDTA and F^- as titrant are given.

INTRODUCTION

The spectrophotometric determinations of trace Th(IV) with some azo dyes have been extensively studied[1–3]. Spectrophotometric studies on Ce(III), Th(IV), U(VI) and VO(IV) complexes with 6,7-dihydroxy-4-methylcoumarin were done by Shafik *et al.*[4] 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (Thoron) has been used as a chromogenic reagent for the spectrophotometric and microdeterminaton of Th(IV)[5].

Coumarin nuclei have proved to be of great importance since they exhibit distinct physiological, photodynamic and bacteriostatic activity[6–8]

EXPERIMENTAL

The chemicals used in the present work were pure grade BDH products; the water used was always twice distilled from all-glass equipment. The ligands were synthesized as previously recommended[9]. The resulting ligands were crystallized till constant m.p. before use from either ethanol or acetic acid. The resulting dyes are represented by the following structural formula (I).

Solutions (10^{-3} M) of coumarin derivatives (Ia–Id) were prepared by dissolving accurate amounts in the appropriate volume of redistilled ethanol. 0.01 M solution

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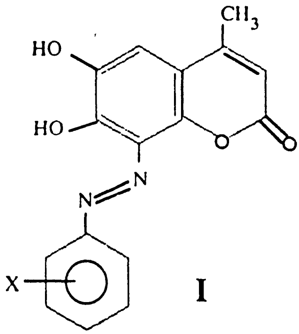

I

where X = H(a), Cl(b), *o*-COOH(c), *o*-OH(d)
m.p. (°C) 210 255 186 244

of Th(IV) nitrate was prepared and standardized spectrophotometrically[10]. 0.001 M solutions were prepared by accurate dilution. The tolerance of the different cations and anions was tested from 1-fold to 500-fold for metal ions and from 1 to 15-fold for lanthanide ions. Thiel buffer solutions were prepared from boric acid, succinic acid, sodium sulphate and borax according to recommended procedures[11]. The pH values of the resulting solutions were adjusted to 0.01 unit using HANNA 8519 pH-meter (Italy). SHIMADZU 160-A UV-visible recording double beam spectrophotometer was used in the spectrophotometric measurements. Solutions of 2×10^{-3} M of each of cetyldimethylethyl ammonium bromide, cetyltrimethylammonium bromide and cetylpyridinium chloride monohydrate were prepared by dissolving accurate amounts in the appropriate volume of bidistilled water. Transferred these solution to calibrated standard measuring flask and completed to the mark with bidistilled water.

1% Solutions of gelatin and gum arabic were prepared by dissolving 1 g of each in appropriate amounts of water, then heated on water bath and filtered. The filtrate was completed to 100 cm^3 in measuring flask with bidistilled water.

Procedure

Spectrophotometric determination of Th^{4+} ions

To solutions containing up to 23.20 $\mu g/cm^3$ of Th^{4+} ion add 2 cm^3 of the dyes (Ia–Id), respectivley. Add 1 and 2 cm^3 ethanol for Th-(Ic and Id) complexes to obtain 30 and 40% ethanolic medium. Complete up to 10 cm^3 with thiel buffer solutions of the recommended pH values. The absorbances of the resulting solutions were measured at λ_{max} 407, 401, 376 and 430 nm for Th-(Ia–Id) complexes respectively, against blank solutions containing the same ingredients except the metal ion; standard curves were thus constructed.

Spectrophotometric determination of Th^{4+} in presence of SAS

The same procedure as mentioned above is applied using some SAS. The optimum amounts of SAS are 0.5 cm^3 of 1% gelatin for Th-(Ia–Id) respectively. For using cetyldimethylethylammonium bromide add 1.0 cm^3 for Th-Ia and Th-Id, 0.8 cm^3 for Th-Ib and 0.2 cm^3 for Th-Ic complexes. Using cetyltrimethylammonium bromide as SAS add 1.0 cm^3 for each of Th-Ia and Th-Id, 1.2 cm^3 for Th-Ib and 0.8 cm^3 for Th-Ic. Using cetylpyridinium chloride monohydrate as SAS add 0.8 cm^3 for Th-Ia, Th-Ic and Th-Id and 1.2 cm^3 for Th-Ib. Using gum arabic as SAS, add 1.2 cm^3 for Th-Ib and 0.6 cm^3 for Th-Ic complexes. The absorbances of the resulting solutions were measured at λ_{max}, *viz.* 407, 401, 376 and 430 nm for Th-(Ia-Id) complexes, respectively, against blank solutions containing the same ingredients except the metal ion. Standard curves were thus constructed.

Spectrophotometric titration of Th^{4+} with EDTA of F^- using (Ia–Id) as indicators

Successive volumes of 10^{-3} M EDTA or 4×10^{-3} M F^- ranging from 0.1 to 1.3 cm^3 were added to 0.4, 0.6, 0.8 and 1.0 cm^3 of 10^{-3} M Th^{4+} in presence of 2 cm^3 of 10^{-3} M of the dyes (Ia–Id) respectively. 1 and 2 cm^3 ethanol were added for Th-(Ic and Id) complexes to obtain 30 and 40% ethanolic medium. The resulting solutions were completed to 10 cm^3 with the recommended buffer solution in calibrated measuring flasks. The absorbances at λ_{max} were measured using the same volume of the dyes as blank. The measured absorbances were plotted against the added volume of EDTA of F^-. The plot consists of two intersecting lines. The end point was determined from the intersection.

RESULTS AND DISCUSSION

On mixing the dyes of 8-(arylazo)-6,7-dihydroxy-4-methylcoumarin derivatives and metal ion solutions, apparent colour change is observed as a result of complex formation. The absorption spectra of all complexes were investigated at different pH values in comparison to those of the free ligands. The optimum pH

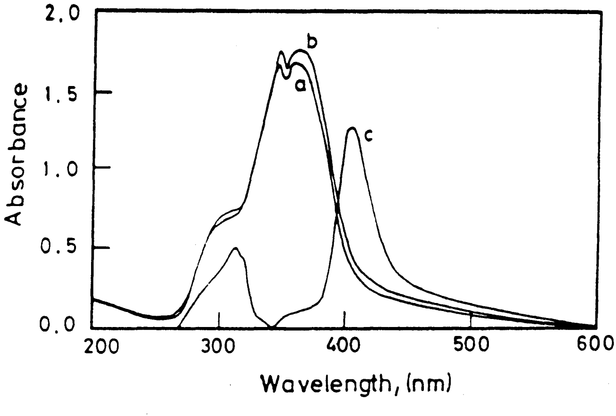

Fig. 1. Absorption spectra of Th(IV)-1a chelates at pH = 7.0
(a) Dye *vs.* $H_2O[L] = 5.0 \times 10^{-5}$ M
(b) Complex *vs.* $H_2O[ML] = 7.5 \times 10^{-5}$ M
(c) Complex *vs.* $Dye[ML] = 3.0 \times 10^{-4}$ M

values for complete formation of the above mentioned metal complexes are listed in Table-3. The absorption spectra of the ligand and complex against water and complex against ligand at the same pH are represented graphically in Fig. 1. The absorption spectra of complexes show that their maximum absorbances are shifted to longer wavelengths in comparison to the free ligands. λ_{max} of free ligands (Ia–Id) are 360, 361, 346 and 362 nm, respectively, while for the metal complexes, the corresponding values are 407, 407, 396 and 403 nm, respectively. The effects of time, sequence of addition of reagents and solvents on the formation of the above mentioned complexes were studied in detail. The colour of Th-(Ia–Id) complexes is formed instantaneously and remains stable for more than 24 h. The order (metal-ligand-buffer) was the best sequence of addition that gives high absorbance values. A trial to use organic solvents to increase or stabilize the absorbance of the complexes was made using methanol, ethanol, acetone and dioxane, up to 50%. The results show that all solvents have negative effect except ethanol. 20% ethanolic buffer is the best percentage for developing the colour of

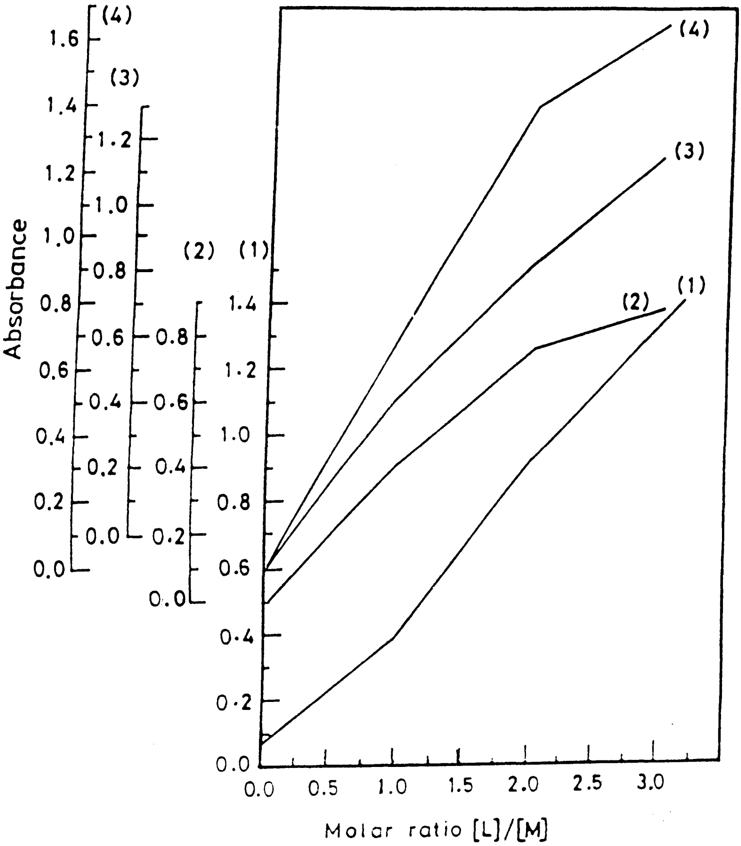

Fig. 2a. (1) Th(IV)-Ia at λ_{max} = 407 nm
(2) Th(IV)-Ib at λ_{max} = 401 nm
(3) Th(IV)-Ic at λ_{max} = 396 nm
(4) Th(IV)-Id at λ_{max} = 403 nm

Th-Ia and Ib complexes, 30 and 40% for Th-Ic and Id complexes, respectively. At these percentages of solvents the complexes formed are more stable and have higher absorbances than the other percentages of solvents. The results obtained from the molar ratio and continuous variation methods indicate that in all cases 1 : 1 and 1 : 2 (M : L) complexes were formed Figs. 2a and 2b.

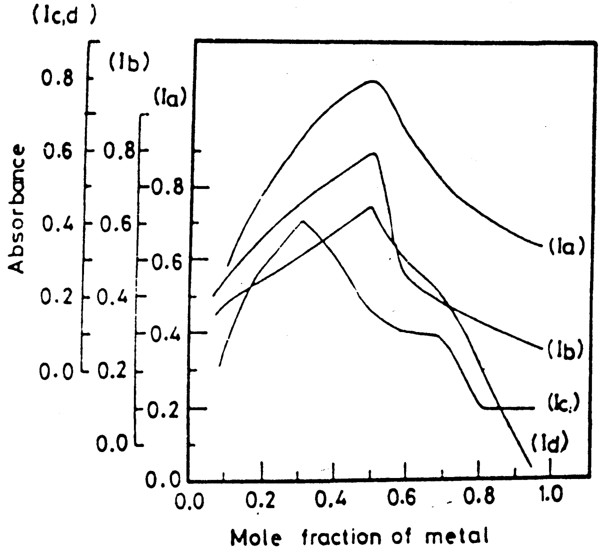

Fig. 2b. Continuous variation method far:
(a) Th(IV)-1a at $\lambda_{max} = 407$ nm
(b) Th(IV)-1b at $\lambda_{max} = 401$ nm
(c) Th(IV)-1c at $\lambda_{max} = 396$ nm
(d) Th(IV)-1d at $\lambda_{max} = 403$ nm

Effect of SAS: The studies revealed that the addition of different volumes of some SAS ranging from 0.1–1.3 cm^3 to the optimum conditions of Beer's law increases the concentration range obeyed. The optimum volumes of surfactants added are: 0.5 cm^3 of 1% gelatin for Th-(Ia–Id) complexes; 1.0 cm^3 of 2×10^{-3} M cethyldimethylethylammonium bromide for Th-Ia and Th-Id complexes; 0.8 cm^3 for Th-Ib complex and 0.2 cm^3 for Th-Ic complex; 1.0 cm^3 of 2×10^{-3} M cetyldimethylethylammonium bromide for Th-Ia and Th-Id complexes; 1.2 cm^3 for Th-Ib and 0.8 cm^3 for Th-Ic complex; 0.8 cm^3 of 2×10^{-3} M cetylpyridinium chloride for Th-Ia, Ic and Id complexes and 1.2 cm^3 for Th-Ib complex; 1.2 cm^3 of gum arabic for Th-Ib and 0.6 cm^3 for Th-Ic complex. The addition of these surfactants also increases the sensitivity of determination by increasing the values of ε by a factor ranging from 1.20 to 2.36. Using SAS also enhances the tolerance of interference of different cations and anions and some lanthanides than in absence of surfactants.

Apparent stability constants of the complexes: The stoichiometry of the formed complexes were studied using standard spectrophotometric method as the molar ratio[12] and continuous variation[13, 14] methods, applying the relation:

$$K_n = \frac{A/Am}{(1 - A/Am)^{n+1}[L]^2 n^2}$$

where, A = Absorbance at a given ligand conc. [L],

Am = Limiting absorbance,

n = Stoichiometric ratio (number of ligand molecules in the chelate molecule)

The results are reported in Table 1.

TABLE-1

STABILITY CONSTANTS OF Th^{4+} COMPLEXES OF LIGANDS (Ia-Id)

Complex	MR		CV	
	log β_1	log β_2	log β_1	log β_2
Th-Ia	6.60	12.37	6.53	12.35
Th-Ib	6.76	12.37	—	12.35
Th-Ic	6.80	12.46	6.88	12.51
Th-Id	6.65	11.38	6.61	11.22

MR = molar ratio method.
CV = continuous variation method.

The order of stability constants for log β_1 is Th-Ic > Th-Ib > Th-Id > Th-Ia which show that the electron donating group —COO^- has higher stability constant than the electron withdrawing groups Cl^- and OH^- than unsubstituted. But there is a little bit change for log β_2 values as log β_2 for OH group is less than unsubstituted which may be attributed to sterric hindrance of OH group.

Effect of foreign ions: The interference effect on the determination of Th(IV) by the selected ligands Ia–Id was tested for some cations and anions both in the presence or absence of surfactants.

As shown in Table-2, for Th-Ia complex the tolerance values are 50-fold for NH_4^+, K^+, NO_3^- and ClO_4^- ions. Some lanthanide ions do not interfere up to 10-fold like La^{3+}, Nd^{3+} and Dy^{3+} ions. The presence of 1% gelatin enhances the tolerance ≥ 100-fold for $K^+ > Co^{2+} \approx Ni^{2+} \approx Cl^- \approx Br^-$ ions. Using cetyldimethylethylammonium bromide as surfactant enhances the tolerance of NH_4^+ up to 100 folds, Y^{3+} shows no interferance up to 10 folds. The tolerance > 50 folds was not observed in any of the other interfering ions. The use of cetyltrimethylammonium bromide as surfactant enhances the tolerance ≥ 100-fold for $NH_4^+ > Cl^- \approx Br^- \approx Ca^{2+} \approx I \approx NO_3^-$ ion. The use of cetylpyridinium cholride as surfactant shows tolerance values ≥ 100-fold for $NO_3^- > Br^- > Cl^- > I^-$ ions.

For Th-Ib complex in absence of surfactants a tolerance of ≥ 100-folds in case of $NO_3^- > Br^- \approx I^-$ ions is observed. The use of 1% gelatin as surfactant enhances the tolerance values to ≥ 100-fold for $NH_4^+ \approx K^+ \approx Cl^- \approx Br^- \approx NO_3^- > Ca^{2+} \approx I^-$ ions. Nd^{3+} and Tm^{3+} have no interfering effect up to 10-fold. The use of cetyldimethylethylammonium bromide as surfactant enhances the tolerance to ≥ 100-fold for

$Br^- > Cl^- \approx Ca^{2+} \approx NO_3^-$ $NH_4^+ \approx I^-$ ions. Dy^{3+}, Tm^{3+} and Lu^{3+} have no interfering effect up to 10-fold. The use of cetyltrimethylammonium bromide as surfactant enhances the tolerance to 500-fold for NH_4^+, 300-fold for Br^- ions. The tolerance is enhanced to 100-fold for Ca^{2+} and NO_3^- ions. Dy^{3+}, Tm^{3+} and Y^{3+} do not interfere up to 10-fold. The use of cetylpyridinium chloride as surfactant enhances the tolerance up to ≥ 100-fold for $Br^- > Mg^{2+} \approx Ca^{2+}$ ions. The presence of gum arabic enhances the tolerance ≥ 200-fold for $Br^- > NH_4^+ \approx Mg^{2+} \approx Mn^{2+}$ and NO_3^- ions. Nd^{3+} and Tm^{3+} have no interfering effect up to 10-folds.

For Th-Ic chelate in absence of surfactants the tolerance ≥ 100-fold in case of $NH_4^+ \approx K^+ \approx Br^- > Ca^{2+} \approx Mn^{2+} \approx Cr^{3+} \approx I^-$ and NO_3^- ion. The presence of gelatin as surfactant increases the tolerance to 100-fold for Mg^{2+} and Cl^- ions only but for most ions has either decreasing or no appreciable effect on the tolerance value. The use of cetyldimethylethylammonium bromide enhances the tolerance to 10-fold for Dy^{3+}, Tm^{3+} and Lu^{3+} ions but for most ions has either decreasing or no appreciable effect. The use of cetyltrimethylammonium bromide or cetylpyridiniumchloride or gum arabic shows no appreciable increase for the tolerance values of some ions; however, the tolerance values of the remainder ions has been decreased (Table-2).

TABLE-2

TOLERANCE VALUES FOR THE INFLUENCE OF FOREIGN IONS ON THE DETERMINATION OF Th^{4+} WITH THE DYES Ia-Id IN ABSENCE AND PRESENCE OF SOME SURFACTANTS

Foreign ion Th^{4+}	Tolerance (Folds)										
	Ia					Ib					
	I	II	III	IV	V	I	II	III	IV	V	VI
NH_4^+	50	50	50	300	50	50	200	100	500	50	200
Na^+	>500	>500	>500	>500	>500	>500	>500	>500	>500	>500	>500
K^+	30	300	20	20	20	20	200	100	20	50	200
Mg^{2+}	10	10	20	10	10	20	200	20	10	100	200
Ca^{2+}	10	500	20	100	10	20	100	200	100	100	30
Sr^{2+}	20	50	10	turbid	10	10	10	10	50	10	10
Ba^{2+}	10	10	10	40	10	10	10	20	50	10	10
La^{3+}	10	5	5	ppt	5	5	5	5	5	5	5
Nd^{3+}	10	5	5	10	10	5	10	5	5	5	10
Sm^{3+}	5	5	5	5	5	5	5	5	5	5	5
Eu^{3+}	5	5	5	5	5	5	5	5	5	5	5
Gd^{3+}	5	5	5	5	5	5	5	5	5	5	5
Dy^{3+}	10	5	5	5	5	5	5	10	10	5	5

Foreign ion Th^{4+}	Tolerance (Folds)										
	Ia					Ib					
	I	II	III	IV	V	I	II	III	IV	V	VI
Er^{3+}	5	5	5	5	5	5	5	5	5	5	5
Tm^{3+}	5	5	5	5	10	5	10	10	10	5	10
Y^{3+}	5	10	5	5	10	5	5	5	10	5	5
Lu^{3+}	5	5	5	10	5	5	5	10	5	5	5
Co^{2+}	20	100	10	50	10	10	10	10	10	10	10
Cr^{3+}	10	10	10	turbid	10	20	10	10	10	10	50
Cl^{-}	30	100	20	200	100	50	200	200	50	50	100
Br^{-}	30	100	20	200	200	100	200	300	300	300	300
I^{-}	30	50	20	100	100	100	100	100	50	50	100
NO$_3^-$	50	50	20	100	300	200	200	200	100	100	200
ClO$_4^-$	50	50	50	50	40	40	30	50	50	50	30
Acetate	20	20	20	50	50	20	50	30	50	50	20

	Ic						Id				
	I	II	III	IV	V	VI	I	II	III	IV	V
NH$_4^+$	300	300	50	20	30	300	50	50	50	30	30
Na^{+}	>500	>500	>500	>500	>500	>500	>500	>500	>500	>500	>500
K^{+}	200	200	50	20	50	200	20	10	20	10	10
Mg^{2+}	20	100	20	10	10	50	20	10	20	10	10
Ca^{+}	100	100	10	10	10	30	20	10	20	10	10
Sr^{2+}	10	10	10	10	10	10	10	10	10	10	10
Ba^{2+}	5	10	5	10	10	10	10	10	10	10	10
La^{3+}	5	5	5	5	5	5	5	5	5	5	5
Nd^{3+}	5	5	5	5	5	5	5	5	5	5	5
Sm^{3+}	5	5	5	5	5	5	5	5	5	5	5
Eu^{3+}	5	5	5	5	5	5	5	5	5	5	5
Gd^{3+}	5	5	10	5	5	5	5	5	5	5	5
Dy^{3+}	5	5	5	5	5	5	5	5	5	5	5
Er^{3+}	5	5	10	5	5	5	5	5	5	5	5
Tm^{3+}	5	5	5	5	5	5	5	5	5	5	5
Y^{3+}	5	5	10	5	5	5	5	5	5	5	5
Lu^{3+}	5	5	10	5	5	5	5	5	5	5	5

Foreign ion Th^{4+}	Tolerance (Folds)										
	Ic						Id				
	I	II	II	IV	V	VI	I	II	III	IV	V
Co^{2+}	10	10	10	10	10	10	10	10	10	10	10
Cr^{3+}	100	200	30	20	10	10	10	10	10	10	10
Cl^{-}	ppt	100	20	20	20	10	20	20	20	20	20
Br^{-}	200	100	20	20	20	ppt	20	20	20	20	20
I^{-}	100	100	50	50	50	200	20	20	20	20	20
NO$_3^-$	100	100	50	50	30	200	30	20	20	20	20
ClO$_4^-$	30	100	10	10	10	200	10	10	10	10	10
Acetate	10	10	10	10	10	10	30	10	30	10	10

I : In absence of surfactant.
II : In presence of gelatin.
III : In presence of cetyldimethylethylammonium bromide.
IV : In presence of cetyltrimethylammonium bromide.
V : In presence of cetylpyridiniumchloride monohydrate.
VI : In presence of gum arabic.

For Th-Id chelate the use of all surfactants mentioned above does not increase the tolerance for all interfering ions; on the contrary they have a decreasing effect for most of them. It all cases Na$^+$ show tolerance value > 500-fold. It was found that Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, molybdate, phosphate, oxalate, Fe(CN)$_6^{4-}$, Fe(CN)$_6^{3-}$, tartrate, EDTA and CDTA seriously interfere in presence and absence of surfactants.

Validity of Beer's law: Beer's law was verified and found to be satisfactorily obeyed for the concentration ranges 4.64–23.20 μg/cm^3 for Th(IV) with (Ia-Id), 2.32–23.20, 0–23.20, 2.32–23.20 and 2.32–23.20 μg/cm^3 in presence of gelatin, 0–23.2 μg/cm^3 in presence of cetyldimethylethylammonium bromide. 0–23.20, 2.32–23.20, 0–23.20 and 0–23.20 μg/cm^3 in presence of cetyldimethylethylammonium bromide, 0–23.20 μg/cm^3 in presence of cetylpyridinium chloride, 0–23.20 μg/cm^3 using Ib and Ic, respectively in presence of gum arabic. The molar absorptivity (ε), specific absorptivity (a)[15] and Sandell sensitivity (S)[16] were calculated and their values are listed in Table-3, from which we can see that the values of ε, a and S are comparable to standard method[10] using Thoron. The addition of some surface active substances also increases the sensitivity of determination by increasing the values of ε by a factor ranging from 1.20–2.36 times.

F-test: Comparing the obtained F^{-17} values with the tabulated values at 95% confidence level, the value obtained was always less than the tabulated value at three degrees of freedom in the numerator and denominator, n = 4. Hence, it can be concluded that there is no systematic difference in precision between the standard and proposed methods.

t-test: The accuracy with respect to the standard method[10] was assessed by calculation of Student's t-values[17]. Comparing the obtained t-values with tabulated values at three degrees of freedom, n = 4. The results show that the confidence level was always between 95–99%. Therefore, it can be concluded that there is no significant difference between the proposed method and the standard one. Statisical analysis of data shows that the slope calculated does not significantly differ from the ideal value of unity.

Ringbom optimum range: For accurate colorimetric analysis Ringbom plot has been drawn from which the Ringbom[18, 19] optimum range for analysis was determined and their values are listed in Table-3.

TABLE-3
CUMULATIVE DATA OF THE OPTIMUM CONDITIONS FOR SPECTROPHOTOMETRIC DETERMINATION OF Th^{4+} USING (Ia–Id)

Complex	Th-Ia	Th-Ib	Th-Ic	Th-Id
Colour	Yellow	Pale yellow	Yellow	Pale yellow
pH	7.0	6.0	7.0	7.0
λ_{max} nm of ligand	360	361	346	362
λ_{max} nm *vs.* H_2O	364	362	348	362
vs. ligand	407	407	396	403
Beer's law linear[a] range μg/cm³	4.64–23.20	4.64–23.20	4.64–23.20	4.64–23.20
Ringbom linear range μg/cm³	6.31–15.85	4.68–19.95	6.16–19.93	5.37–15.85
F-value	1.59	5.59	3.71	2.40
t-value	0.10	2.18	1.92	3.02
ε	6.33×10^3	4.36×10^3	3.48×10^3	6.22×10^3
a	0.0270	0.0200	0.0140	0.0260
S	0.0360	0.0470	0.0670	0.0370
s	0.0120	0.0060	0.0060	0.0090
r	0.9990	0.9994	0.9994	0.9994
Beer's law linear[b] range μg/cm³	2.32–23.20	0–23.20	2.32–23.20	2.32–23.20
Ringbom linear range μg/cm³	3.98–18.62	4.07–21.38	4.17–21.38	3.71–21.38
F-value	1.45	1.25	1.45	3.63
t-value	1.75	1.49	4.49	2.09
ε	8.88×10^3	7.31×10^3	6.06×10^3	7.49×10^3

Complex	Th-Ia	Th-Ib	Th-Ic	Th-Id
a	0.0380	0.0310	0.0260	0.0320
S	0.0260	0.0320	0.0380	0.0310
s	0.0360	0.0150	0.0300	0.0210
r	0.9909	0.9976	0.9969	0.9959
Beer's law linear[c] range μg/cm^3	0–23.20	0–23.20	0–23.20	0–23.20
Ringbom linear range μg/cm^3	3.98–20.42	3.80–20.42	4.68–20.89	3.80–20.89
F-value	2.07	2.72	1.42	3.62
t-value	1.41	2.27	2.58	3.46
ε	8.38×10^3	7.74×10^3	571×10^3	1.47×10^4
a	0.0360	0.0330	0.0240	0.0630
S	0.0270	0.0290	0.0400	0.0150
s	0.0540	0.0330	0.0290	0.0530
r	0.9804	0.9913	0.9878	0.9938
Beer's law linear[d] range μg/cm^3	0–23.20	2.32–23.20	0–23.20	0–23.20
Ringbom linear range μg/cm^3	4.57–19.05	4.16–20.42	5.89–20.89	3.23–19.95
F-value	1.39	1.65	1.12	1.94
t-value	3.32	2.76	4.74	3.93
ε	8.85×10^3	5.40×10^3	5.17×10^3	1.22×10^4
a	0.0370	0.0230	0.0220	0.0520
S	0.0270	0.0430	0.0440	0.0190
s	0.0250	0.0130	0.0240	0.0270
r	0.9960	0.9972	0.9893	0.9959
Beer's law linear[e] range μg/cm^3	0–23.20	0–23.20	0–23.20	0–23.20
Ringbom linear range μg/cm^3	3.02–19.95	3.47–22.39	6.76–20.89	3.09–15.85
F-value	2.38	3.20	1.92	2.97
t-value	2.18	3.40	3.94	2.65

Complex	Th-Ia	Th-Ib	Th-Ic	Th-Id
ε	1.03×10^4	6.89×10^3	5.64×10^3	1.40×10^4
a	0.0440	0.0290	0.0240	0.0600
S	0.0220	0.0330	0.0410	0.0160
s	0.0460	0.0210	0.0280	0.0440
r	0.9996	0.9952	0.9884	0.9952
Beer's law linear[f] range μg/cm^3		2.32–23.20	0–23.20	
Ringbom linear range μg/cm^3		4.37–21.38	5.62–21.88	
F-value		4.06	2.20	
t-value		1.56	3.40	
ε		6.51×10^3	7.38×10^3	
a		0.0280	0.0320	
S		0.0350	0.0310	
s		0.0090	0.0180	
r		0.9989	0.9969	

(a) In absence of surfactants.

(b) In presence of 0.5 mL of 1% gelatin as surfactant.

(c) In presence of 2×10^{-3} M cetyldimethylethylammonium bromide, 1.0 mL for Ia and Id, 0.8 mL for Ib and 0.2 mL for Ic.

(d) In presence of 2×10^{-3} M cetyltrimethylammonium bromide, 1.0 mL for Ia and Id, 1.2 mL for Ib and 0.8 mL for Ic.

(e) In presence of cetylpyridinium chloride, 0.8 mL for Ia, Ic and Id, 1.2 mL for Ib.

(f) In presence of gum arabic, 1.2 mL for Ib and 0.6 mL for Ic.

ε : Molar absorptivity (L mol^{-1}. cm^{-1}). s : Standard Deviation.

a : Specific absorpitivity (mg^{-1}. cm^{-1}). r : Correlation Coefficient.

S : Sandel sensitivity (μg cm^{-2}).

* : The colour of the dyes (Ia-Id) are red, red, orange red and reddish brown, respectively.

† : Tabulated F-value = 9.28 at 95% confidence level, at three degrees of freedom in the numerator and denominator.

‡ : Tabulated t-values at 95 and 99% confidence level are 3.18 and 5.84, respectively.

Spectrophotometric Titration of Th(IV)

The application of the dyes (Ia–Id) as indicators for the spectrophotometric titration of Th^{4+} with EDTA and F$^-$ has been ascertained. With the aid of this method up to 232.0 μg/cm^3 of Th^{4+} can be determined with good accuracy and precision using EDTA and F$^-$ as titrants.

TABLE-4

SPECTROPHOTOMETRIC TITRATION OF Th^{4+} WITH EDTA AND F^- USING THE DYES (Ia–Id) AS INDICATORS

Dye	Metal ion amount (μg) Taken	Found (x)* i	Found (x)* ii	Recovery % i	Recovery % ii	Rel. Error pph i	Rel. Error pph ii	Rel. St. Dev. % i	Rel. St. Dev. % ii
Ia	92.82	92.67	92.085	99.84	100.03	–0.0016	0.0003	0.18	0.05
	139.22	139.17	139.20	99.97	99.99	–0.0003	–0.0001	0.15	0.01
	185.63	185.63	185.64	100.00	100.01	0.0000	0.0001	0.04	0.02
	232.04	232.12	232.02	100.03	99.99	0.0003	–0.0001	0.04	0.01
Ib	92.82	92.66	92.84	92.82	100.02	–0.0018	0.0002	0.20	0.07
	139.22	139.27	139.23	100.04	100.01	0.0004	0.0001	0.15	0.02
	185.63	185.83	185.65	100.11	100.01	0.0001	0.0001	0.04	0.02
	232.04	232.27	232.07	100.10	100.01	0.0010	0.0001	0.06	0.03
Ic	92.82	92.85	92.86	100.03	100.03	0.0003	0.0004	0.07	0.06
	139.22	139.21	139.14	99.99	99.94	–0.0001	–0.0006	0.015	0.04
	185.63	185.84	185.65	100.12	100.01	0.0012	0.0001	0.10	0.01
	232.04	232.16	232.09	100.05	100.02	0.0005	0.0002	0.07	0.01
Id	92.82	92.88	92.77	100.06	99.95	0.0006	–0.0005	0.16	0.09
	139.22	139.28	139.26	100.04	99.94	0.0004	–0.0006	0.22	0.03
	185.63	185.63	185.65	100.00	100.01	0.0000	0.0001	0.12	0.03
	232.04	232.04	232.09	100.00	100.02	0.0000	0.0002	0.05	0.02

X : Mean value of three determinations.

(i) : Using 10^{-3} M EDTA as titrant; (ii) : Using 4×10^{-3} MF^- as titrant.

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