

Research Article



Synthesis, Characterization and Spectrophotometric Study on Some New Chromotropic acid azo dyes: Analytical Application on Thorium Determination

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ABSTRACT

Mono and bis chromotropic acid (CTA) azo dyes (I-IV) were synthesized from coupling reaction between chromotropic acid and diazotized sulfa drugs (sulfadimidine or sulfaguanidine). The prepared CTA azo dyes were characterized by elemental analysis, IR, and ¹H-NMR spectroscopy. The dissociation constants of the prepared CTA azo dyes were determined spectrophotometrically. The interaction of azo dyes (I-IV) with thorium metal ions were studied spectrophotometrically. The reaction conditions were optimized. The results show that the complexes were formed in the ratio of 2:1, 1:1, 2:1, and 1:1 (dye: Th(IV)) with dye I, II, III and IV, respectively. The molar absorptivities (ϵ) were 1.34×10^4 , 3.35×10^3 , 7.23×10^3 , and 8.33×10^3 L mol⁻¹ cm⁻¹. The application of dye I, III and IV, the most sensitive dye (highest ϵ value), as a chromophoric reagent in the spectrophotometric determination of thorium metal ions and its use as a metallochromic indicator in spectrophotometric titration of thorium were investigated.

Keywords: chromotropic acid, sulfadimidine, sulfaguanidine, Azo dyes, spectrophotometry.

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INTRODUCTION

Chromotropic acid (IUPAC name is 2,7-naphthalenedisulphonic 4,5-dihydroxy, disodium salt, C₁₀H₆O₈S₂Na₂) is very famous analytical reagent. It is a bidentate ligand used for the spectrophotometric determination of many metal ions¹, nitrate², ozone³, and formaldehyde⁴. Many azo dyes were prepared from chromotropic acid (chromotrope 2B, chromotrope 2C, arsenazo III, ...). These azo dyes, in spite of having high molecular weight, are water soluble and exhibit very high stability in solution. CTA azo dyes can be prepared in three forms, mono-, bis- and di- azo dyes which impart diversity to this class of compounds⁵. CTA azo dyes used as a chromophoric reagent in the spectrophotometric determination of many metal ions especially Th(IV), U(VI), Zr(IV) and many rare earth metals⁶ and as metallochromic indicators using ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CDTA)⁷. Also, they used in analytical determination of different pharmaceutical drugs⁸ with a good sensitivity.

Sulfa drugs are the oldest chemically synthesized antimicrobial agents and are still widely used today for the treatment of various bacterial, protozoal and fungal infections⁹. The basic sulfonamides structure includes the

sulfonamide group and the amino group in the para position of the benzene ring¹⁰. They are strongly basic, hence they can be readily soluble in the acid medium¹¹.

In this work a new mono- and bis- azo dyes from coupling reaction between chromotropic acid and diazotized sulfa drugs^{12, 13} (sulfadimidine or sulfaguanidine) are prepared. The prepared azo dyes were investigated by different tools. The interaction of the prepared CTA azo dyes with thorium metal ion was studied. Analytical applications of the most sensitive dye in the spectrophotometric determination of Th(IV) were studied. Also, it has been studied as a metallochromic indicator in spectrophotometric titration of Th(IV) against EDTA or F⁻ ions.

MATERIALS AND METHODS

Materials

All materials and reagents were laboratory pure chemicals. The key organic chemicals used were chromotropic acid sodium salt 60% provided by ACROS organic, sulfadimidine and sulfaguanidine were from Aldrich. Other chemicals used were sodium nitrite (Qualikems, India), anhydrous sodium carbonate (ADWIC, Egypt), sodium hydroxide (Oxford India), ethylenediaminetetraacetic acid (EDTA) disodium salts (WINLAB, England), hydrochloric acid (35%-38%) (Research-lab fine chemicals industries, India). Organic solvents used were dimethyl formamide (ADWIC, Egypt), Acetone (ADVENT CHEMBIO, India), ethanol (SDS, France), isopropanol (SDS, France) were used after purification with recommended methods¹³. Bidistilled water was used in all preparation and dilutions. Both DMF and acetone were dried with anhydrous sodium sulfate.



Instrumentation

The characterization of azo dyes (I-IV) was carried out by the elemental analyses using a PerkinElmer 2400 CHN elemental analyzer at the microanalytical center, faculty of science, Cairo university. The IR measurements were recorded applying the KBr disc technique using test scan Shimadzu FTIR spectrometer. The $^1\text{H-NMR}$ spectra of azo dyes under investigation were recorded using Varian 300 MHz NMR Spectrometer using deuterated dimethyl sulfoxide ($\text{D}^6\text{-DMSO}$) and deuterium oxide (D_2O) as solvents and tetramethylsilane as internal standard. The pH of the solution was measured by Hach sense ion+ pH 31, effect of temperature was studied using memmert thermostatic water-bath. The absorption spectra were measured using Jenway 6715 spectrophotometer with software version 3.7 in a matched quartz cuvette with optical path length 1.00 cm. All data were manipulated with Microsoft Excel[®] 14.

Preparation of azo dyes

The accurate weight of sulfa drug (Sulfadimidine or sulfaguanidine) corresponding to 0.01 mol was dissolved in 3 mL concentrated HCl and 5 mL distilled water. The mixture was stirred in ice bath for 5 minutes. Then, a cold solution of sodium nitrite (0.011 mol) was added slowly to form the diazonium salt⁴. After that, coupling reaction⁷ was then happened by adding slowly a chromotropic acid solution (0.01 mol) in sodium carbonate medium. But when bis azo dyes were the goal, the concentration of the sulfa drug and sodium nitrite were doubled, and the sodium carbonate was replaced by sodium hydroxide medium. After that the resulting dye solutions were acidified with concentrated HCl and were left to dry in air and collected. Then, the crude dye was dissolved in 1 mL dry DMF and filtered. The filtrate was collected in a large volume of dry acetone (500 mL), then filter out the recrystallized⁸ azo dyes.

Solutions

A 10^{-3} mol/L solution of each dye and thorium metal ions were prepared by dissolving the accurately weighed amount in distilled water. Solutions of interfering cations or anions were prepared from their respective salts. Then, the effect of increasing concentration of each ion on the Th complexes was studied. A 0.1 mol/L HCl and 2.0 mol/L NaOH solution were prepared.

Spectrophotometric studies

Determination of the acid dissociation constant

The acid dissociation constants of azo dyes (I-IV) were determined spectrophotometrically. A 5 mL of 10^{-3} mol/L of each dye were transferred to 100 mL volumetric flask then completed to the mark with 0.1 mol/L HCl and poured in a 250 mL beaker. The pH of the solution was measured and the spectrum of that solution was recorded from 250 nm to 700 nm at room temperature. The solutions were then partially neutralized with freshly prepared concentrated sodium hydroxide solution. The pH of the

solution was measured, and the spectrum of the solution at such pH values was recorded using distilled water as a blank. Since the total volume of the base added did not exceed 1% of the total volume of the test solution, dilution correction was unnecessary. The absorbance-pH diagrams were constructed which used for determination of pKa values by the half height method¹³.

Spectrophotometric studies on thorium complexes with azo dyes(I-IV)

The interaction between Th(IV) and the dyes(I-IV) was studied. The following conditions were studied to determine the optimum conditions for complexes formation: effect of pH, selection of the suitable wavelength, effect of reagent concentration, effect of temperature, effect of time and effect of solvents

Determination of the stoichiometric ratio of the complexes

The molecular stoichiometry of the formed complexes was determined with the continuous variation⁽¹⁵⁾ and molar ratio methods¹⁶.

Analytical Applications

Procedure for calibration curve

A series of solutions containing up to 18.6 $\mu\text{g/mL}$ of Th(IV) in 10 mL volumetric flask were prepared, add 1 mL of 10^{-3} mol/L of dye I and dilute the volume to the mark with water. In case of dye II, III and IV the Th(IV) concentration were up to 23.2 $\mu\text{g/mL}$ and the volume of azo dye was 2 mL of 10^{-3} mol/L of dye solution. Then record the absorbance at 580, 615, 600, and 605 nm for Th-dye I, Th-dye II, Th-dye III, and Th-dye IV, respectively, against the dye solution containing the same ingredients except the Th(IV) metal ions.

Spectrophotometric titration of Th(IV) with EDTA or fluoride ions using dye I as indicator

Spectrophotometric titrations of Th(IV) using EDTA or F^- ions as a titrant were performed using azo dye I, III and IV as indicators⁽¹⁷⁾. Successive volumes of 10^{-3} mol/L of EDTA or 4×10^{-3} mol/L sodium fluoride solution ranging from 0.1 to 1.0 mL were added to a definite volume of 10^{-3} mol/L of thorium (not exceeds 1 mL) followed by the addition of 1 mL of 10^{-3} mol/L of dye solution, then the volume diluted to 10 mL in a volumetric flask. The end point can be either determine by spectrophotometrically by measuring the absorbance at λ_{max} and plotting absorbance against the volume of EDTA or fluoride. Two straight lines obtained intersect at the end point.

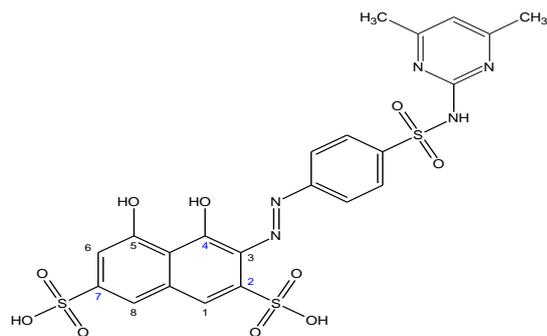
RESULTS AND DISCUSSION

Characterization of the synthesized CTA azo dyes (I-IV)

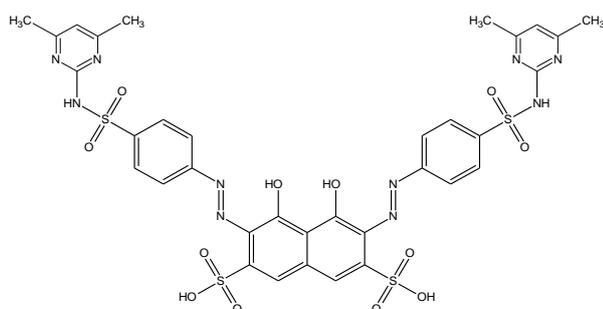
The synthesized CTA azo dyes (I-IV) are solids colored stable in air and highly soluble in water. The analytical data from the elemental analysis are shown in Table 1. The results were in good agreement with those calculated for suggested formulae.



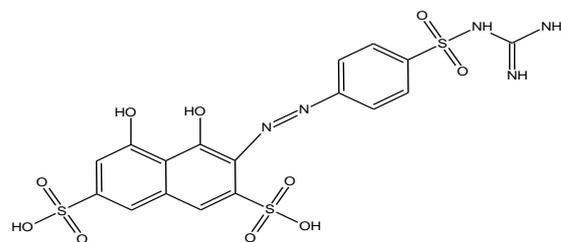
The structures of the prepared azo dyes are represented in Schemes (1-4).



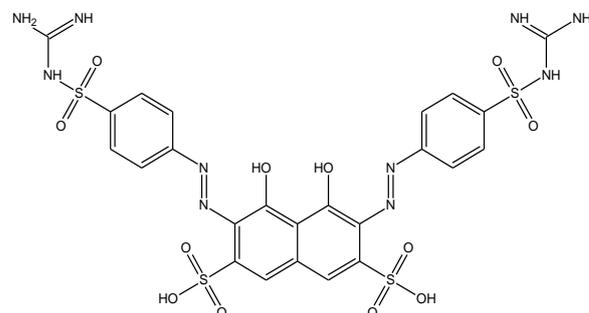
Scheme 1. structure of Dye I (3 sulfadimidine azo chromotropic acid)



Scheme 2. structure of Dye II (3,6 sulfadimidine bis azo chromotropic acid)



Scheme 3. structure of Dye III (3 sulfaguanidine azo chromotropic acid)



Scheme 4. structure of Dye IV (3,6 sulfaguanidine bis azo chromotropic acid)

Table 1: Elemental analysis of the prepared chromotropic acid azo dyes

| Dye | Formula (Molecular weight) (g/mol) | color | Calc. (found) | | |
|-----|---|-------------|---------------|-------------|---------------|
| | | | % C | % H | % N |
| I | C ₂₂ H ₁₉ N ₅ O ₁₀ S ₃ (609.60) | dark red | 43.35 (43.30) | 3.14 (2.91) | 11.49 (11.47) |
| II | C ₃₄ H ₃₀ N ₁₀ O ₁₂ S ₄ (898.91) | black | 45.43 (45.74) | 3.36 (3.24) | 15.58 (13.16) |
| III | C ₁₇ H ₁₅ N ₅ O ₁₀ S ₃ (545.51) | dark red | 37.43 (36.94) | 2.77 (2.38) | 12.84 (10.30) |
| IV | C ₂₄ H ₂₂ N ₁₀ O ₁₂ S ₄ (770.74) | dark violet | 37.40 (36.44) | 2.88 (2.66) | 18.17 (16.53) |

Infrared Spectra

The IR-spectra, Figure (1), of the chromotropic acid azo dyes under investigation show a broad band at 3436, 3441, 3434, and 3435 cm^{-1} for dye I, II, III, and IV, respectively, which corresponds to the stretching vibration frequency of the hydroxyl groups¹⁸. The broadening of this band may be due to that hydroxyl groups were involved in hydrogen bonding. There are two bands near 1630 and 1500 cm^{-1} corresponding to C=C stretching vibration⁸. The N=N stretching vibration¹⁸ appears at 1416, 1410 cm^{-1} and 1402 cm^{-1} for dye I, II, and IV, respectively, while for dye III this band overlapped with C=C skeletal vibration. SO₂ shows asymmetric and symmetric stretching vibrations at ranges 1190-1215 and 1041-1045 cm^{-1} , respectively¹⁹. The out of plane deformation of hydroxyl groups arises around 840 cm^{-1} . There are several peaks in the 1000–650 cm^{-1} region. These could be associated with various C–C stretching modes and out of plane deformation of the naphthalene C–H bonds. The bands appear at 607-641 cm^{-1} may be due to ν (C–S)¹⁸.

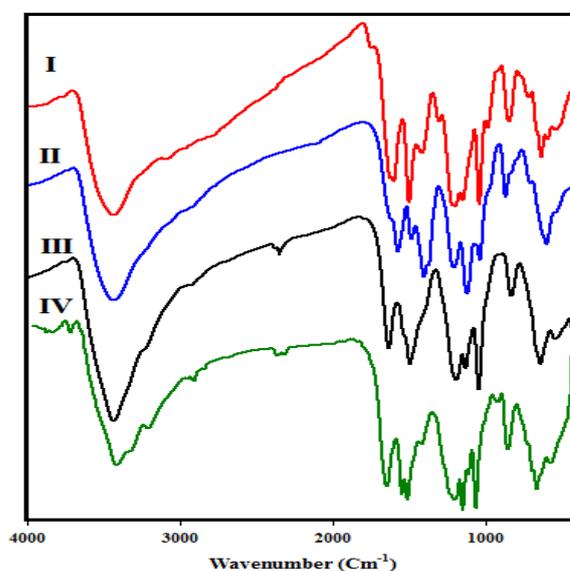


Figure 1: IR spectra of the four chromotropic acid azo dyes.

¹H-NMR results of the prepared chromotropic azo dyes

The ¹H-NMR spectrum of azo dye I is shown in Figure (2) and discussed in details below. But in case of dye II, III, and IV the spectra were unclear which may be due to the precipitation of the azo dye in DMSO at high concentration ²⁰.

The protons of CH₃ groups (sulfadimidine moiety) appear in the range from 2.2 and 2.6 ppm. The signals of the sulfonic acid groups (SO₃H) ²¹ (chromotropic acid moiety) appeared as a broad signal at 3.8 ppm and lost on deuteration. The signal of the primary aromatic amino group of sulfadimidine that would appear at approximately 6.0 ppm (sulfa moiety) ²² completely vanished which makes strong evidence on the occurrence of the coupling reaction. The aromatic protons ²³ appear in the range from 6.7-8.0 ppm. The proton of the SO₂ NH (sulfonamide nitrogen) appears at 8.2 ppm as a broad signal which lost on deuteration. The signal observed at 12.7 ppm may be assigned to the proton of OH group at position 5, and the signal at 14.9 ppm may be assigned to the proton of the OH group at position 4 as it is more deshielded due to intramolecular hydrogen bonding with the azo group. The disappearance of the signals of SO₃H, OH and NH protons on deuteration confirms that they are ionizable protons.

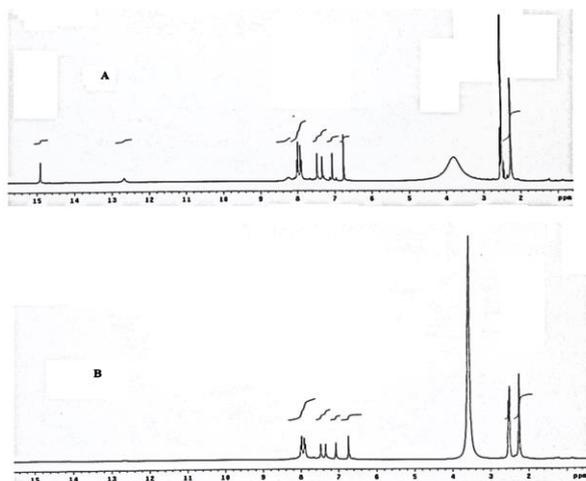


Figure 2: ¹H-NMR spectrum of dye I in DMSO (A) and in D₂O (B).

UV-VIS spectra of the four azo dyes

The spectra of the four prepared chromotropic acid azo dyes in water is shown in Figure (3). The absorption spectra of dyes (I-IV) are characterized by a main broad strong band absorbing maximally at 515, 530, 525 and 525 nm, for dye I, II, III, and IV, respectively. This band is assigned as π-π* transition within the azo group influenced by charge transfer in whole molecule. There is a weak band at range 355-390 nm which is due to π-π* transition within the H-chelate resonance ring ⁽²⁴⁾ as shown in figure (3). There is another band appears at 305 nm in the four dyes this band is due to π-π* transition in the aromatic naphthalene nucleus in dyes molecules.

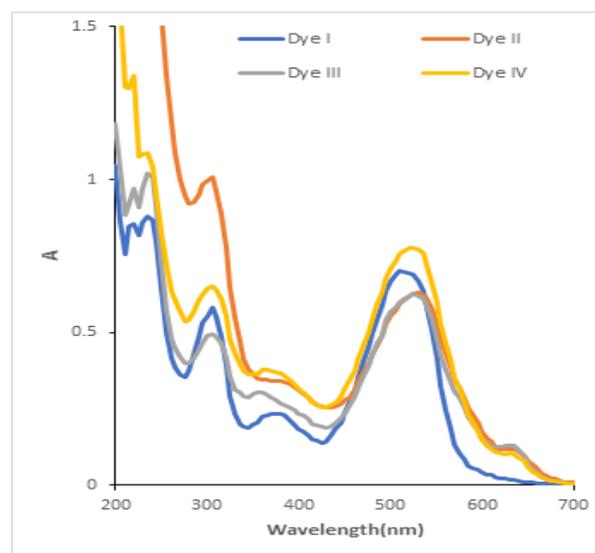


Figure 3: Absorption spectra of 5×10^{-5} mol/L of the four chromotropic acid azo dyes in water.

Determination of the dissociation constant of the prepared chromotropic acid azo dyes

Spectrophotometry can be applied for pK_a measurement as the compound has a chromophore in proximity to the ionization group, and the absorbance changes adequately as a function of pH²⁵. The dissociation constants (pK_a) of the four dyes were determined spectrophotometrically by the half height method. The absorption spectra of dyes I-IV in solution of varying pH values are shown in Figures (1S,2S). From the spectra the absorbance-pH relations at specific wavelengths were plotted and the pK_a were calculated. For mono azo dyes (I and III), Figure (1S), at pH=3, there are two bands at 300 and 520 nm, these attributed to the acid form of both dyes (H₄D). By increasing the pH till about 5 the spectra were unchanged. This confirms the fact that the ionization of the two sulfonic groups give no spectral changes as they are not directly attached to the π system of the azo dye. By increasing the pH, the absorption of the two bands decreases. This denotes the ionization of the first hydroxyl group in the chromotropic acid moiety (HD⁻³). The dissociation of the other hydroxyl group is retarded due to hydrogen bonding with the azo group and participating in azo hydrazone structure ²³, Figure (4).

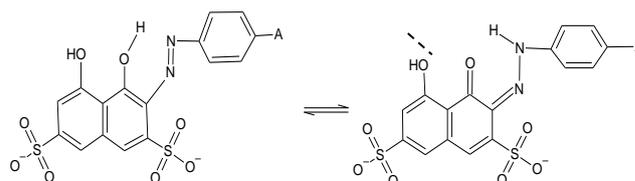


Figure 4: Hydrazone azo tautomerism

The changes occur in the spectra by further increasing in the pH were due to the ionization of the second hydroxyl group in the dye molecule (D⁻⁴). The presence of isosbestic points in the absorption spectra is an indication of the presence of equilibria. However, these points exist only up to a certain pH value above which deviation from the

isosbestic points occur. Such deviation may be taken as evidence that the first equilibrium,



is over stepped and the second equilibrium starts subsequently,



For bis azo dyes (dye II& IV), the absorption spectra are identical in the pH range from 3 to about 5 resemble the above mono azo dyes. By increasing the pH to 7, the absorption of the main band at 530 nm decreases. This change occurs at about pH 6 and 7 for dye II and dye IV, respectively. This denoted the ionization of the first hydroxyl group of the chromotropic acid moiety. Further increase in the pH to about 9 causes more decrease in the absorbance which occurs at pH 9.2 and 8.6 for dye II and dye IV, respectively. This denoted the ionization of the second hydroxyl group of the chromotropic acid moiety. So, the ionization of the two-hydroxyl groups occurs at two stages and only one of which participate in hydrogen bonding. The presence of the isosbestic points in the absorption spectra is an indication of the presence of equilibria.

The pKa values of the four dyes are summarized in Table (2).

Table 2: pKa values of dyes

| Dye | pKa ₁ | pKa ₂ |
|-----|------------------|------------------|
| I | 7.5 | 9.2 |
| II | 7.8 | 9.2 |
| III | 5.0 | 8.5 |
| IV | 6.7 | 8.6 |

Spectrophotometric studies on thorium complexes with azo dyes(I-IV)

The interaction between thorium metal ions and the prepared chromotropic acid azo dyes (I-IV) has been studied spectrophotometrically. The dye molecules chelate the thorium ions and acquire new properties different from the original dyes. These new properties were used in the identification or determination of thorium metal ions. The formation and stoichiometry of the complexes formed were studied in the visible region.

Optimization of the reaction conditions

The parameters that affect the formation of thorium complexes such as selection of suitable wavelength, effect of pH, reagent concentration, effect of solvents, time and temperature were studied.

Selection of suitable wavelength

The absorption spectra of the thorium complexes with the four dyes are shown in Figure (5). It exhibits maximum absorption at 580, 615, 600, and 605 nm for Th-dye I, Th-dye II, Th-dye III, and Th-dye IV, respectively, using the

same amount of azo dye as a blank. The complex spectrum is shifted towards longer wavelength (bathochromic shift) in comparison with the free dye. This may be attributed to increase in delocalization of the π -electrons on complexation leading to decrease in the energy gap between the excited and ground states.

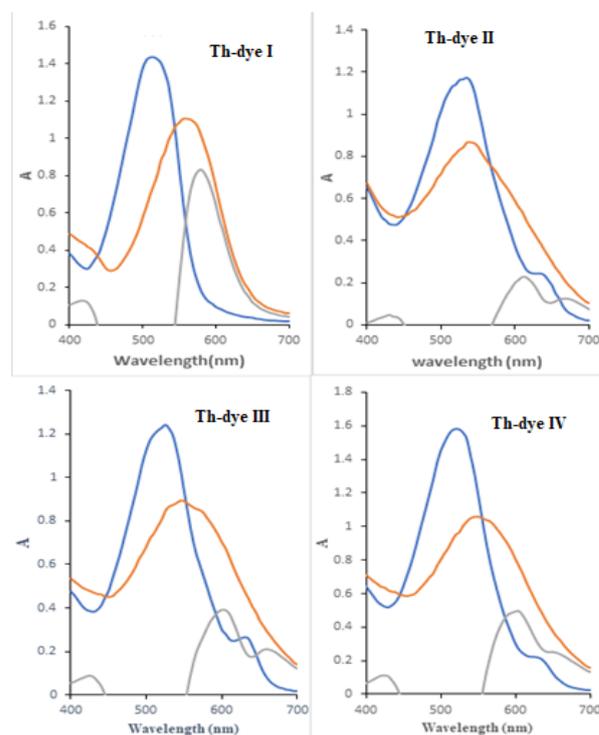


Figure 5: Absorption spectra of azo dyes (I-IV) with thorium metal, $[\text{Th}^{+4}] = 10^{-4}$ mol/L, $[\text{dye}] = 10^{-4}$ mol/L, except in Th-dye II both $[\text{Th}^{+4}]$ & $[\text{dye II}] = 2 \times 10^{-4}$ mol/L. (dye: blue, complex: orange and complex Vs dye: gray)

Effect of pH

There is no change in the color on addition of thorium to the dyes occurs in the presence of HNO_3 and HCl acids, or hexamine, acetate, phosphate and carbonate buffers. This indicates that the thorium complexes can't be formed in these media. On the other hand, the color of dyes changes from magenta red to blue color (in case of dye I) and from dark violet to dark blue in other dyes in distilled water as thorium added to the dye.

Effect of dye concentration

The effect of reagent concentration on the intensity of the color formation was studied by the addition of varying volumes (0.2-3.0 mL) of the prepared dyes (10^{-3} mol/L) to a constant concentration of thorium metal ions (1 mL of 10^{-3} mol/L) in a 10 mL volumetric flask. Then the absorbance of the solution was measured. The results showed that the best concentration of dyes was 10^{-4} mol/L. The data are shown in Figure (3S).

Effect of time

Under the above-mentioned conditions, the effect of time on the formation and stability of the formed complexes was studied by measuring the absorbance of the complexes at increasing time intervals. The results show in all cases that the complexes are formed instantaneously and remain constant for more than 24 hours.

Effect of solvent

The effect of some common solvents as water, ethanol, acetone and dimethyl formamide (DMF) was studied to choose the most suitable solvent. In case of DMF there was no change in color of all dyes (i.e., no complex was formed). Also, the Th complex with dye II in ethanol didn't form. It was found that acetone and ethanol give lower absorbance values than water in all dyes. So, the best solvent for the formation of thorium dye complex was water.

Effect of temperature

The effect of temperature on the stability of Th complexes was studied by measuring the absorbance of the formed complex at different temperatures, 25, 35, 40, 45, 50, 55 and 60 °C. The results show that the highest absorbance value was at room temperature. As shown in Figure (6), the absorbance decreases by increasing the temperature. So, the best temperature for the complex to be formed was 25°C.

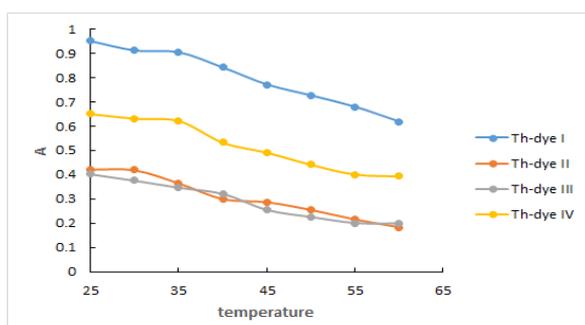


Figure 6: Effect of temperature on the absorbance of thorium complexes, $[Th^{4+}] = 1 \times 10^{-4}$ mol/L except in Th-dye II it was 1.5×10^{-4} mol/L, $[dye] = 1 \times 10^{-4}$ mol/L, except $[dye II] = 1.5 \times 10^{-4}$ mol/L.

The stoichiometry of the complexes

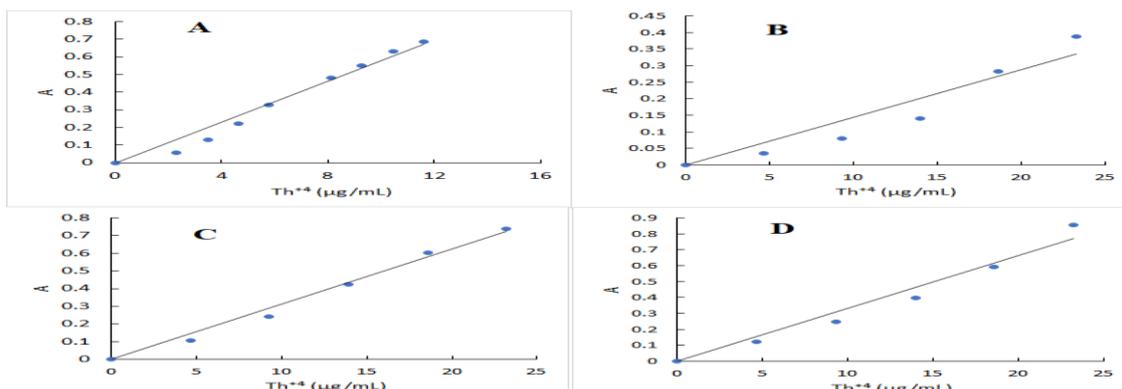


Figure 7: Obedience to Beer's law for Th^{4+} complex with dye I(a), dye II(b), dye III(c), dye IV(d).

The composition of thorium complexes with the azo dyes was determined by the continuous variation⁽¹⁵⁾ and the molar ratio⁽¹⁶⁾ methods which revealed the formation of 1:2, 1:1, 1:2 and 1:1 (M:L) with dyes I, II, III and IV, respectively. (Figures (4S,5S)). The stability constants ($\log \beta$) and the free energy change (ΔG) of formation of the complexes were calculated using the results of continuous variation method and were given in Table (3). The reaction between Th(IV) and azo dyes are spontaneous due to the negative values of ΔG . The complexes with mono azo dyes (I, III) are more stable than that with bis azo dyes (II, IV) as indicated by their higher values of $\log \beta$.

Table 3: The stability constant of the thorium complexes with azo dyes

| complex | Th (IV): Dye | $\log \beta$ | ΔG (kJ mol ⁻¹) |
|------------|--------------|--------------|------------------------------------|
| Th-dye I | 1:2 | 16.20 | -92.42 |
| Th-dye II | 1:1 | 7.80 | -44.50 |
| Th-dye III | 1:2 | 15.07 | -85.99 |
| Th-dye IV | 1:1 | 8.04 | -45.87 |

Obedience of Beer's law

The obedience to Beer's law (Table 4, Figure (7)) obtained by plotting the absorbance as a function of Th(IV) concentration which gives a satisfactory measure of the sensitivity of the method. Following the proposed experimental conditions, linear regression equations were obtained. The regression plots showed that there was a linear dependence of the absorbance to the concentration up to 11.6, 27.8, 23.2 and 27.8 $\mu\text{g/mL}$ Th (IV) with dye I, II, III, and IV, respectively.

For more accurate results, Ringbom optimum concentration range was determined by plotting $\log [Th(IV)]$ in $\mu\text{g/mL}$ against percent transmittance and the linear portion of the Z-shaped curve gives the accurate range of analysis. The molar absorptivities (ϵ) values are 1.34×10^4 , 3.35×10^3 , 7.23×10^3 , 8.33×10^3 L mol⁻¹ cm⁻¹ of Th(IV) complex with dye I, II, III, and IV, respectively. Limit of detection, limit of quantification, standard deviations (S.D.) and correlation coefficients were also calculated and summarized in Table (4). It was found that Th-dye I had the highest molar absorptivity value and dye II had the lowest value.

Table 4: Molar absorptivity (ϵ), absorptivity (a), Sandell's sensitivity (S), obeyance range for Th⁺⁴ determination.

| | Dye I | Dye II | Dye III | Dye IV |
|--|--------------------|--------------------|--------------------|--------------------|
| λ_{\max} (nm) | 580 | 615 | 600 | 605 |
| Beer's law up to ($\mu\text{g mL}^{-1}$) | 11.6 | 27.8 | 23.2 | 27.8 |
| Ringbom ($\mu\text{g mL}^{-1}$) | 3.5-11.6 | 13.9-23.2 | 9.2-18.5 | 7-13.9 |
| Molar absorptivity (ϵ) ($\text{L mol}^{-1} \text{cm}^{-1}$) | 1.34×10^4 | 3.35×10^3 | 7.23×10^3 | 8.33×10^3 |
| Sandell sensitivity (ng cm^{-2}) | 17.27 | 69.4 | 32.05 | 30.12 |
| LOD ($\mu\text{g mL}^{-1}$) | 1.65 | 8.9 | 2.57 | 6.55 |
| LOQ ($\mu\text{g mL}^{-1}$) | 5.50 | 25.2 | 8.58 | 21.83 |
| Regression equation: | | | | |
| slope | 0.065 | 0.014 | 0.031 | 0.033 |
| intercept | - | - | - | - |
| correlation coefficient | 0.991 | 0.959 | 0.996 | 0.987 |
| t-value ^a | 2.08 ^b | 1.86 ^c | 1.99 ^c | 1.93 ^c |
| F-value ^a | 3.26 ^b | 64.46 ^c | 12.71 ^c | 4.78 ^c |

^a: Theoretical values of t- and F- tests at 4 degrees of freedom and 95% confidence limits are 2.78 and 6.39, respectively. ^b: Th(IV) concentration 6.96 $\mu\text{g/mL}$, ^c: Th(IV) concentration 18.56 $\mu\text{g/mL}$.

Influence of foreign ions

The influence of foreign ions was studied on the absorbance of Th(IV) complexes. The concentration of foreign ions was varied to get the tolerance limit that cause a change in the absorbance value by 20%. The data are represented in Table (5). The Zirconium, phosphate, citrate, nitrate, fluoride ions prevent the interaction between thorium and the chromotropic acid azo dyes under investigation. Also, Fe(II) strongly interferes with the thorium determination. Alkali, alkaline earth, chlorides, iodide ions interfere at concentration limits above 1000 times greater than that of Th(IV) but Ca^{+2} , SO_4^{-2} , CO_3^{-2} ions

which show interference at above 300, 200 and 200 times for these cations respectively.

Statistical treatment of the results

T-test and F-test has been applied to check the accuracy and precision of the present spectrophotometric procedures ⁽²⁶⁾. A five replicates measurements of known Th(IV) concentration were measured by the suggested methods. The proposed methods was evaluated by comparison with spectrophotometric method depending on complexation between arsenazo III and Th(IV) in perchloric acid⁽²⁷⁾.

Table 5: Tolerance limit of foreign ion (cause 20% error in Absorbance reading) in the determination of 10^{-4} mol/L Th⁺⁴ using dye I at 580 nm.

| Foreign ion | Added as | Tolerance (foreign ion/Th ⁺⁴) ratio (w/w) |
|--|--|---|
| Na ⁺ | NaCl | 1000 |
| K ⁺ | KCl | 1000 |
| Ca ⁺² | CaCl ₂ | 300 |
| Mg ⁺² | MgCl ₂ | 1000 |
| Ba ⁺² | BaCl ₂ | 1000 |
| Fe ⁺² | FeSO ₄ | 1 |
| Fe ⁺³ | FeCl ₃ | 10 |
| Mn ⁺² | MnCl ₂ | 1000 |
| Zr ⁺⁴ | ZrOCl ₂ | no complex was formed |
| NH ₄ ⁺ | NH ₄ Cl | 1000 |
| F ⁻ | NaF | no complex was formed |
| Cl ⁻ | NaCl | 1000 |
| I ⁻ | KI | 1000 |
| SO ₄ ⁻² | Na ₂ SO ₄ | 200 |
| CO ₃ ⁻² | Na ₂ CO ₃ | 200 |
| NO ₃ ⁻ | NaNO ₃ | no complex was formed |
| NO ₂ ⁻ | NaNO ₂ | 1000 |
| Citrate(C ₆ H ₅ O ₇) | Na ₃ C ₆ H ₅ O ₇ | no complex was formed |
| PO ₄ ⁻³ | NaH ₂ PO ₄ | no complex was formed |

The results showed that Th-dye I and Th-dye IV provided comparable accuracy (t-test) and precision (F-value), since the calculated values were less than the theoretical data (Table (4)). So, it can be concluded that there is no determinant error in the suggested procedure. But Th-dye II and Th-dye III have the F-value exceeds the tabulated value, therefore it is not precise. The values indicate that the procedures of standard calibration curve with dye I and IV is extremely reliable in the determination of Th (IV) metal ions.

Spectrophotometric titration of Th (IV) with EDTA or fluoride ion using dye I as an indicator

Dye I, III, IV were used successfully as indicators for spectrophotometric titration⁽¹⁷⁾ of thorium metal ions. In 10 mL volumetric flasks, 1 mL of 10^{-3} mol/L dye I, dye III or dye IV solution and a Th (IV) concentration range 9.28-23.20 $\mu\text{g/mL}$ was pipetted into each series. Then successive volumes of 10^{-3} mol/L EDTA or 4×10^{-3} mol/L sodium fluoride solution (NaF) were then added. The volumetric flasks were completed to the mark with distilled water and the absorbances are then measured at 580, 600, and 605 nm using the same volume of dye I as a blank. The absorbance versus volume of EDTA or F⁻ (mL) plots are constructed. The plot consists of two straight lines intersecting at the end point was obtained. It was

found that using dyes I, III and IV as metallochromic indicators, with EDTA or fluoride ion as a titrant, in the spectrophotometric titration of Th (IV) shows a good response. With the aid of this method up to 23.2 $\mu\text{g/mL}$ of Th(IV) can be determined with fair accuracy and precision. Representative curves are shown in Figures (6S-8S). The results were summarized in Tables (6, 7).

Table 6: Th (IV) determination by spectrophotometric titration with EDTA using dye I, III and IV as indicators.

| | Taken($\mu\text{g/mL}$) | Found($\mu\text{g/mL}$) | Recovery \pm S.D. |
|---------|---------------------------|---------------------------|---------------------|
| Dye I | 9.28 | 9.33 | 100.54 \pm 0.002 |
| | 11.60 | 11.83 | 101.93 \pm 0.005 |
| | 13.92 | 14.15 | 101.65 \pm 0.002 |
| Dye III | 13.92 | 13.69 | 98.3 \pm 0.006 |
| | 18.65 | 18.10 | 97.5 \pm 0.002 |
| | 23.20 | 22.74 | 98.0 \pm 0.006 |
| Dye IV | 13.92 | 17.17 | 123.33 \pm 0.020 |
| | 18.65 | 19.95 | 107.5 \pm 0.023 |
| | 23.20 | 25.52 | 110.0 \pm 0.058 |

Table 7: Th(IV) determination by spectrophotometric titration with F⁻ using dye I as indicator.

| | Taken($\mu\text{g/mL}$) | Found($\mu\text{g/mL}$) | Recovery \pm S.D. |
|---------|---------------------------|---------------------------|---------------------|
| Dye I | 9.28 | 9.51 | 102.48 \pm 0.005 |
| | 11.60 | 11.14 | 96.03 \pm 0.005 |
| | 13.92 | 14.04 | 100.86 \pm 0.003 |
| Dye III | 13.92 | 13.92 | 100.0 \pm 0.006 |
| | 18.65 | 18.79 | 101.3 \pm 0.006 |
| | 23.20 | 22.74 | 98.0 \pm 0.006 |
| Dye IV | 13.92 | 13.79 | 98.33 \pm 0.005 |
| | 18.65 | 18.10 | 97.50 \pm 0.01 |
| | 23.20 | 23.2 | 100.0 \pm 0.10 |

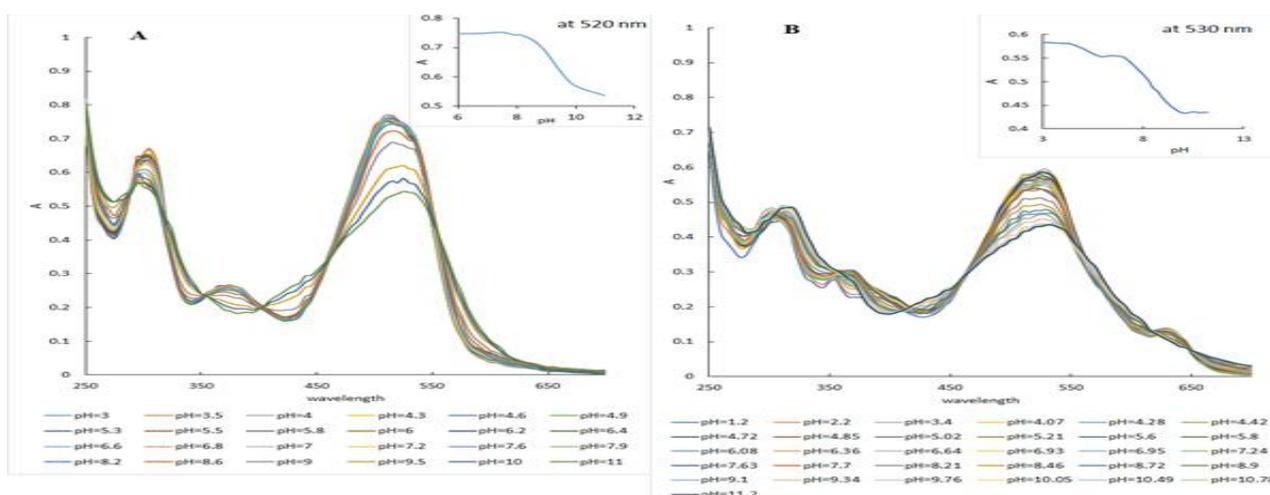


Figure 1S: Absorption spectra of 5×10^{-5} mol/L of dye I (A) and dye (III) at different Ph

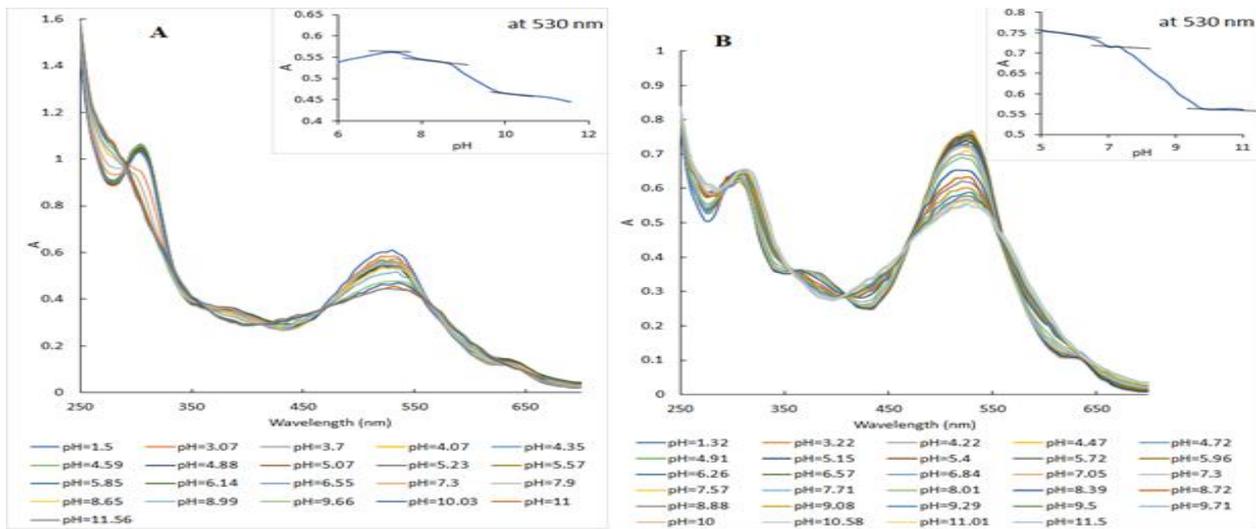


Figure 2S: Absorption spectra of 5×10^{-5} mol/L of dye II (A) and dye IV (B) at different pH

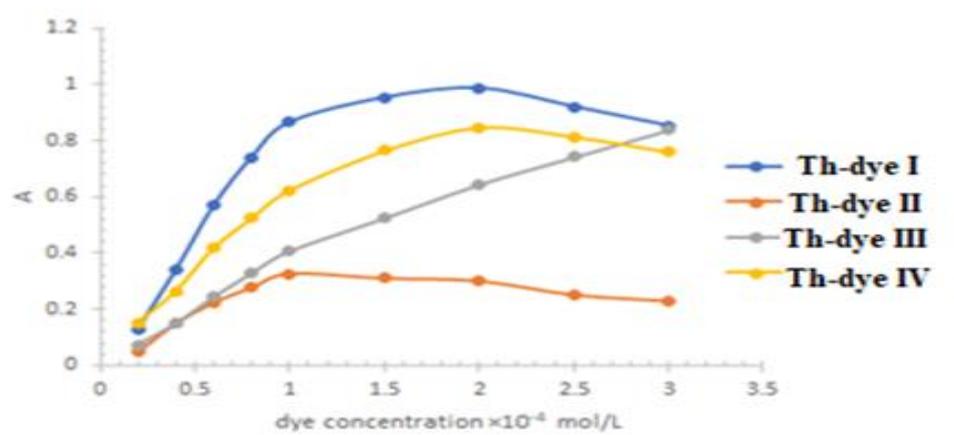


Figure 3S: Effect of azo dye concentration on the absorbance of thorium complexes, $[Th^{+4}] = 10^{-4}$ mol/L

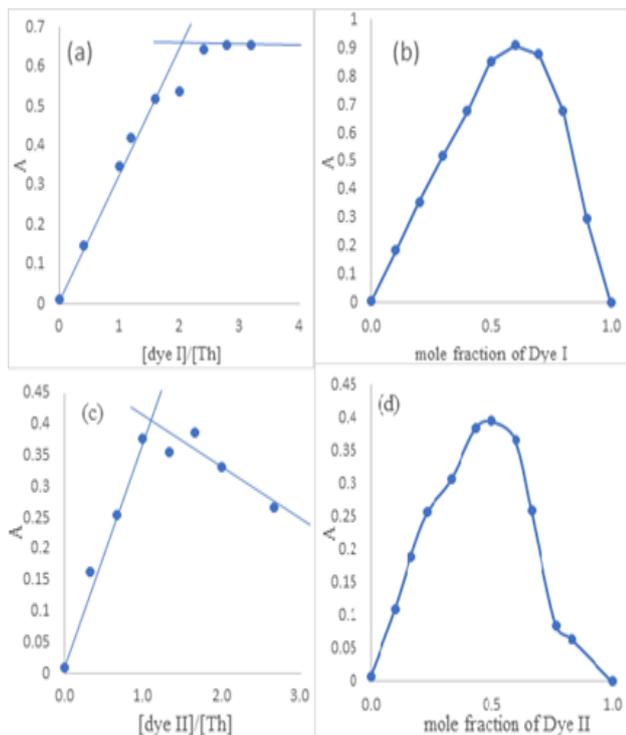


Figure 4S: Stoichiometry of Th^{+4} complex with dye I & dye II by MRM(a)&(c) and CVM (b)&(d)

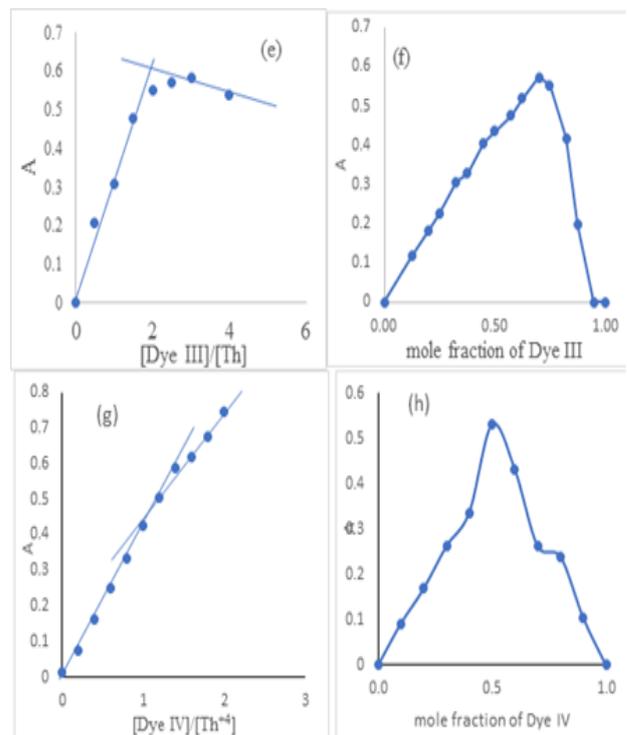


Figure 5S: Stoichiometry of Th^{+4} complex with dye III dye IV by MRM(e)&(g) and CVM (f)&(h).

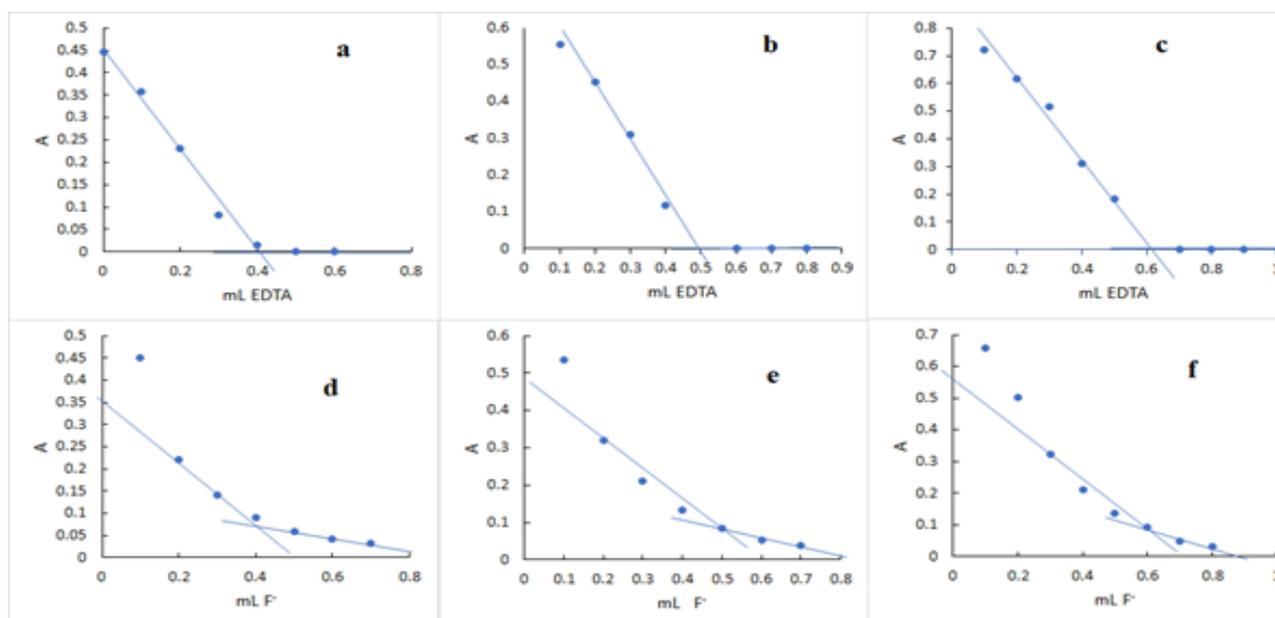


Figure 6S: Spectrophotometric titration of Th^{IV} using dye I as indicator: against EDTA, [Th⁴⁺] in (a) 9.28, (b) 11.60 and (c) 13.92 $\mu\text{g/mL}$, [EDTA]= 10^{-3} mol/L, and against F⁻ [Th⁴⁺] in (d) 9.28, (e) 11.60 and (f) 13.92 $\mu\text{g/mL}$, [F⁻]= 4×10^{-3} mol/L.

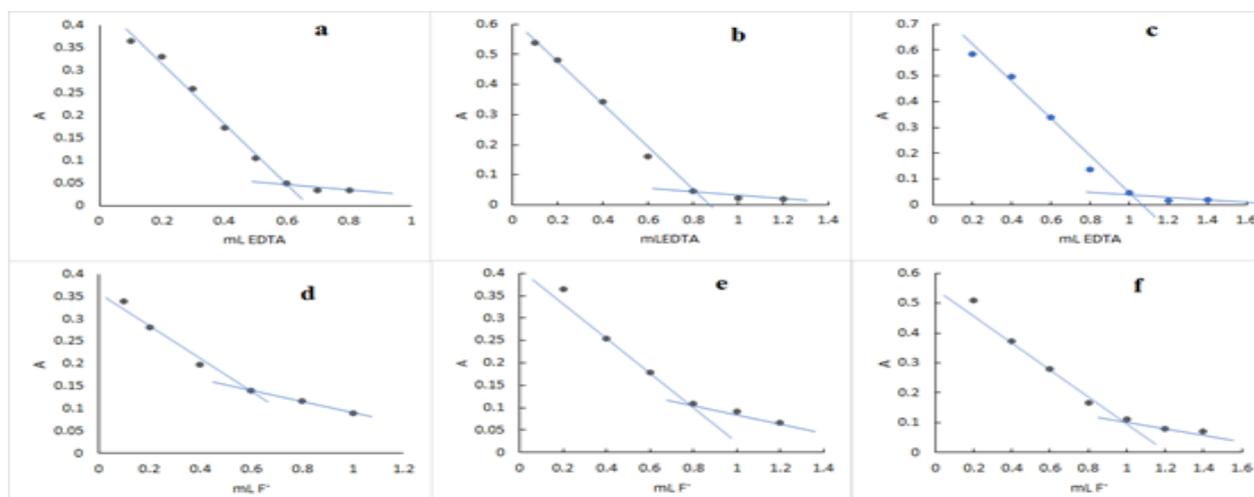


Figure 7S: Spectrophotometric titration of Th⁴⁺ using dye III as indicator: against EDTA, [Th⁴⁺] in (a) 13.92, (b) 18.65 and (c) 23.20 $\mu\text{g/mL}$, [EDTA]= 10^{-3} mol/L, and against F⁻, [Th⁴⁺] in (d) 13.92, (e) 18.65 and (f) 23.20 $\mu\text{g/mL}$, [F⁻]= 4×10^{-3} mol/L

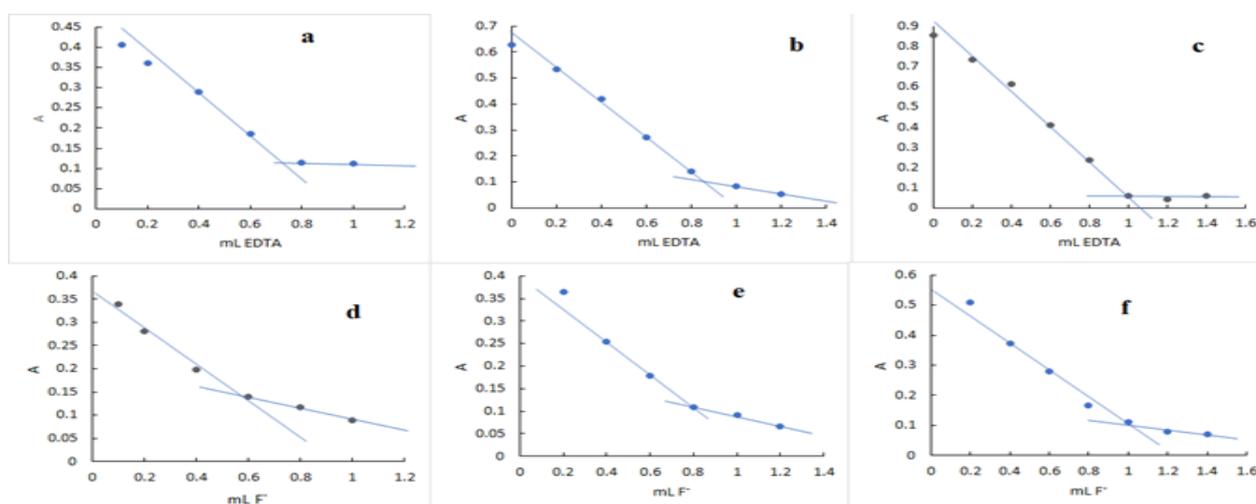


Figure 8S: Spectrophotometric titration of Th⁴⁺ using dye IV as indicator: against EDTA, [Th⁴⁺] in (a) 13.92, (b) 18.65 and (c) 23.20 $\mu\text{g/mL}$, [EDTA]= 10^{-3} mol/L, and against F⁻, [Th⁴⁺] in (d) 13.92, (e) 18.65 and (f) 23.20 $\mu\text{g/mL}$, [F⁻]= 4×10^{-3} mol/L

CONCLUSION

our new chromotropic acid azo dyes were prepared from chromotropic acid and sulfa drugs (sulfadimidine & sulfaguanidine). These azo dyes were characterized by elemental analysis, IR and ¹H-NMR. The dissociation constants were determined spectrophotometrically. the pK_{a1} values were 7.5, 7.8, 5.0 and 6.7 and pK_{a2} values were 9.2, 9.2, 8.5, and 8.6 for dye I, II, III and IV, respectively. The interaction between Th^(IV) and the prepared azo dyes were studied. The reaction conditions were optimized. The stoichiometry of the formed complexes was determined. It was found that dyes I and III Th-dye I gives the highest molar absorptivity value but Th-dye II has the lowest molar absorptivity. Dyes I, III and IV were used as a chromophoric indicator in spectrophotometric determination of thorium and also, as metallochromic indicator in thorium spectrophotometric titration.

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