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A New Spectrophotometric Method for the Determination of Uranium (VI) and Thorium (IV) in Diversified Rocks Using the Chromogenic Calcon Dye

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Abstract: Calcon dye is recommended as a chromogenic reagent in a precise and sensitive spectrophotometric approach for the detection of U(VI) and Th(IV). Calcon serves as a complexometric indicator for Al, Fe, and Zr. When combined with acetate buffer, the metal ions (U and Th) and calcon dye form a complex instantly at pH 4 for U (VI) and pH 3 for Th (IV). For two hours, the (U and Th) complex is stable. Peak absorbance (λmax) for U (VI) and Th(IV) in the complexes is 682 nm and 658 nm, respectively. The molar ratio for U- calcon and Th- calcon was 1:1 for each complex. Using XPS analysis, the preliminary complexation mechanism was verified. The impact of acid type, appropriate buffer pH, dye concentration, molar ratio, calibration curve, and tolerance limits of certain interfering ions are among the parameters of (U and Th) that are investigated in this work. For U (VI) and Th (IV), the average molar absorptivity (Ɛ) was found to be 0.89×10^4 L M^{-1} cm^{-1} and 0.67×10^4 L M^{-1} cm^{-1}, respectively. Beer's law was applied and verified between 0.1 and 15 µg U m L^{-1} and 0.25 and 20.00 µg Th m L^{-1}. Using solid ammonium chloride and ammonia solution to precipitate various ions throughout the determination process improved the selectivity of this approach. U(VI) and Th(IV) in internationally certified standard materials (Nim G, BL-2a, and DL-1a) as well as reference samples were successfully determined using the suggested method. The accuracy and precision (RSD <1%) were met with satisfaction.

Keywords: Calcon dye, Uranium (VI), Thorium (IV), Precipitation, Spectrophotometric Determination, FTIR; XPS.

1 Introduction

The absorption maxima for uranium and thorium complexes are very close to one another for most chromogenic reagents, so spectrophotometric methods for determining uranium and thorium require the separation of the two elements before and. However, a quick and sensitive method for quantitative colorimetric uranium determination was described, along with masking agents like potassium cyanide, tartaric acid, or thioglycolic acid, which could be used to determine uranium and thorium even in the presence of numerous foreign metal ions.

The following survey is restricted by reagents suitable for uranium and thorium analyses; These include; Arsenazo I and III [2-4], n-phenylbenzo-hydroxamic acid [5], 3-aminomethylalizarn-N-N diacetic acid [6], Dibromo-o-nitro-arsenazo [7], bromo cresol orange (BCO) [8], pyrimidine azo dyes[9], Chromo Azural S [10, 11], 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone [12], Eriochrome Cyanine R [13], Xipamide [14], 2-hydroxy-1-naphthaldehydep-hydroxybenzoic-hydrazone [15], Thorin [16], Alizarin Red S [17], Thoron I after separation by (E)-4-(2-hydroxyphenyl imino) pentane-2-one[18]. Specific organic dyes were used in complex materials for the uranium spectrophotometric determination, including thoronal [19], 4-(2-pyridylazo) resorcinol [20], chlorophosphonazo III [20], chrome azurol S [10], 1-(2-pyridylazo)-2-naphthol [21], guaiacol [22], Thiazole Yellow G [23], 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol [24], molybdophosphoric acid [25], N-m-tolyl-p-methoxybenzohydroxamic acid [26], 4-methyl-4-chlorodibenzoylmethane [27], 2-(2-Thiazolylazo)-p-Cresol (TAC) [28], and Eriochrome Black T [29].

An E.D.T.A. and a commercial photoelectric titrimeter are used to estimate calcium using the dye calcon (1-(2 hydroxy-1-naphthylazo)-2-naphthol-4 sulphonic acid). The effects of phosphate and magnesium interference have been eliminated. Using Eriochrome black T to determine magnesium is another option [30] Use of UV254 in the presence of H_2O_2 and $(NH_4)2S_2O_8$ as oxidants was used to

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mineralize the azo dye Calcon [31].

An innovative adsorbent known as falcon-imprinted magnetic chitosan (CIMC) nanoparticles (NPs) was successfully created. Epichlorohydrin (ECH) and glutaraldehyde (GA) were employed as cross-linkers to create the appropriate calcon-imprinted and nonimprinted agnetic chitosan nanoparticles (NPs) for the adsorption and elimination of calcon from contaminated solutions (ECH/CIMC and GA/CIMC and ECH/NIMC and ECH/NIMC etc.) [32]. Using the fluorescence sensor 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4 sulfonic acid sodium salt (Calcon), a unique fluorescent staining approach was designed [33] to detect phosphoproteins in sodium dodecyl sulfate-polyacrylamide gels. Understanding and controlling the intricate interactions between external stimuli and minute conformational changes is a challenging aspect of realizing multi-stimulation responsiveness in a single molecule. Calcon is multi-stimulus responsive to temperature, pH change, and light irradiation because of the coexistence of dynamic bonding contacts, hydroxyl group, and azo chromophore [34]. The effectiveness with which polyaniline films made via electrochemical technique can adsorb the azo dye Calcon [35].

Another study described a quick and easy way to create a polymer-metal nanocomposite for the degradation of Calcon dye by combining different concentrations of cobalt ferrite magnetic nanoparticles ($CoFe_2O_4$ MNp) with sulfonated waste polystyrene (SWPS) [36]. In a different study, the generation of green hydrogen gas (H_2) in the cathodic compartment was also investigated for the first time in conjunction with the anodic compartment's electrochemical oxidation (EO) of an aqueous solution containing Calcon dye using a PEM-type electrochemical cell powered by a photovoltaic (PV) energy source[37].

To our knowledge, no uranium or thorium study has been conducted with calcon dye. Calcon dye, the reagent under study in this work, has not yet been reported as a ligand for the spectrophotometric measurement of uranium or thorium. To determine uranium and thorium using calcon, a new and relatively simple approach was proposed in this work. The spectrophotometer, which is still widely employed because of its accessibility and ease of use, is utilized in the current work to determine uranium and thorium using calcon dye, a chromogenic reagent. As an indication for Al, Fe, and Zr complexometry, Calcon has recently been used.

2 Experimental Section

2.1. Materials

Reagents of analytical quality and chemical purity, including thorium nitrate, uranyl nitrate, sodium acetate, acetic acid, perchloric acid, nitric acid, hydrochloric acid (Panreac, Spain), sulfuric acid (Riedel De Haën, Germany), and hydrochloric acid (Stream chemicals, USA), and Calcon dye (Fluka, England, Molecular Formula: $C_{20}H_{13}N_2NaO_5S$, Molar mass: 416.39 g/mol), were used in the present work. Standard stock solutions (10^3 mg L^{-1}) of various ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zr^{4+}, Hf^{4+}, Cr^{6+}, V^{5+}, Cu^{2+}, Co^{3+}, La^{3+}, Y^{3+}, Ce^{4+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}) were of reagents of analytical quality from Merck (Germany).

2.2. Instrumentations:

We used a Labomade double-beam UV-visible spectrophotometer model (UVD 2950) from the USA, which has a wavelength accuracy of ±0.5 nm and covers a wavelength range of 190 to 1100 nm with a resolution of 2 nm. The pH was measured using a Jenway pH meter, calibrated daily using buffer solutions with pH values of 4, 7, and 10. Thermo Fisher Scientific, Waltham, Massachusetts, USA, provided the Nicolet IS10 FTIR spectrometer, which was used to produce FT-IR spectra utilizing the ATR technique without the usage of a KBr pellet. A Perkin Elmer PHI 5600 apparatus (Waltham, MA, USA) was utilized for X-ray photoelectron spectroscopy investigations. An Mg Kα (Al Kα) radiation source with a 0.8 mm X-ray beam diameter and a 1 mm analytical zone diameter was employed in the analysis. Drying solutions on glass slides at room temperature were part of the sample preparation process, and solid products were employed for surface analysis.

2.3. Procedure

With calcon dye, uranium, and thorium react sensitively to generate complicated single and binary solutions. These compounds were made by mixing a 1 ml aliquor from 10^{-3} M calcon dye solution with either Th(IV) or U(VI) solution. After diluting the volume with double-distilled water in a 10 ml standard measuring flask, the volume was spectrophotometrically scanned in the visible range (450 to 750 nm) against a reagent blank.

2.4. Statistical and accuracy evaluation

Two purposes exist for statistical evaluation of the results obtained: (1) assessing the precision and accuracy of the analytical data; and (2) ensuring the quality of the produced concentrate. Citing the mean (X) as a standard factor for determining the precession (degree of reproducibility or random error) is a typical practice in the literature on analytical chemistry. A measuring method's accuracy (Δ) indicates how closely the results match a reference (well-known) or true value. Therefore, the following formulas are used [38-40]:

Arithmetic mean: - $X = \frac{\sum Xi}{n}$ (1)

- Standard deviation: - $SD = \left[\frac{\sum_1^n (Xi - X)^2}{(n-1)}\right]^{\frac{1}{2}}$ (2)

- Relative standard deviation: - $RSD = SD / X \times 100$ (3)

- Standard error:- $SE = \frac{SD}{\sqrt{n}}$ (4)

- The percentage error:- $\%\,Error = SE / X \times 100$ (5)

- Accuracy:- $\Delta = \pm \sqrt{\frac{d^2}{2n}}$ (6)

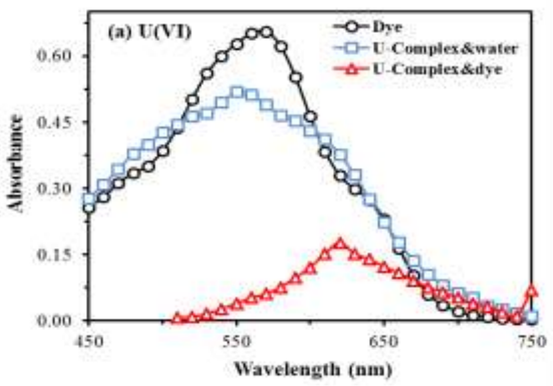
Where: Xi = is an individual measurement, n = is the number of measurements, and d represents the difference between the repeated measurements.

3 Results and Discussion

Many factors were examined to maximize the production of uranium and thorium-calcon complex. the effects of different acids, choosing the right buffer pH, the perfect concentration of calcon dye, the length of the complex, and the ideal concentration of uranium and thorium (calibration curve). Finally, studies were conducted to determine the optimal metal-to-dye molar ratio.

3.1. Calcon dye's absorption spectra and the compounds of Th (IV) and U (VI)

The spectrum of 10^{-3} M calcon dye dissolved in water is shown in Figures 1a and 1b. In the aqueous phase, the wavelength at which calcon dye absorbs the most is λmax 526 nm. When calcon dye reacts sensitively with uranium and thorium, a binary complex is produced. One milliliter of 10^{-3} M calcon dye solution and one milliliter of 10^{-3} M U (VI) /Th (IV) ions were combined to produce these complexes. After diluting the combination in a ten-milliliter volumetric flask with double-distilled water, the visible region between 450 and 750 nm was finally scanned.



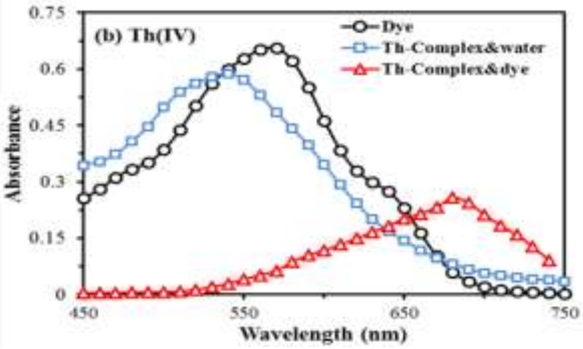


Fig.1. Absorbance spectrum of U(VI)-Calcon complex (a) and Th(IV)-Calcon complex (b).

3.2 Optimization of the relevant variables

3.2.1 Acid medium's effect

The impact of varying pH levels on complex formation was investigated for hydrochloric acid, nitric acid, sulfuric acid, and perchloric acid concentrations. To find the optimal concentration of acidic medium for the best formation of U-calcon and Th-calcon complexes, a series of 10 ml volumetric flasks were filled with aliquots of acids (0.1 ml to 3 ml) from 10^{-2} M and 10^{-4} M. A constant volume of 1 ml from each of the metal stock solution (10^{-3} M) and calcon dye (10^{-3} M) was taken. The range of 450–700 nm was used to measure the absorbance. The information retrieved in Table 1 demonstrated how the investigated acidic pH media affected the development of the uranium/thorium -calcon complex. The complex was found to have a maximum absorbance value of 624 nm for U and 1 milliliter of 10^{-2} M perchloric acid (pH 3), respectively, for Th and U. The maximum absorbance value was extracted using 0.2 milliliters of 10^{-2} M sulfuric acid or nitric acid (pH 3.69).

3.2.2. Selecting the appropriate pH buffer

To maintain the ideal acid concentration value for complex formation, a buffer solution was employed in this investigation. A buffer solution containing 0.2M sodium acetate and 0.2M acetic acid was made to produce changeable pH values of 3 and 4. Several solutions with final contents of ten milliliters or less were mixed with the buffer solution. These solutions included one milliliter of 10-3M uranium, two milliliters of 10-2M sulfuric or nitric acid, and one milliliter of calcon dye.

The wavelength range for measuring the complex's absorbance was 450–750 nm. As seen in Figs. (2), 1 ml of pH 4 acetate buffer produced the maximum absorbance. A complicated mixture containing one milliliter of 10^{-3} M thorium, 10^{-2} M perchloric acid, and 10^{-3} M calcon dye, each finished to ten milliliters in final volumes. The absorbance of the complex was measured at wavelengths ranging from 450 to 750 nm, as shown in Figs (2). With

Table 1. Impact of acid type on Th (IV) and U (VI) absorbance measured with Calcon dye (at λTh: 658 nm & λU: 682 nm).

Element	Acid vol., (ml)			HCL		HNO_3		H_2SO_4		$HClO_4$	
				Absorbance							
		pH		10^{-2} M	10^{-4} M	10^{-2} M	10^{-4} M	10^{-2}M	10^{-4} M	10^{-2} M	10^{-4} M
U(VI)	0.10	4	6	0.032	0.046	0.110	0.045	0.108	0.075	0.006	0.039
	0.20	3.69	5.69	0.038	0.073	0.128	0.063	0.126	0.094	0.013	0.065
	0.30	3.52	5.52	0.041	0.081	0.112	0.090	0.111	0.107	0.021	0.080
	0.50	3.30	5.30	0.056	0.100	0.094	0.108	0.091	0.065	0.033	0.099
	1.00	3	5	0.043	0.086	0.080	0.087	0.068	0.048	0.019	0.078
	2.00	2.69	4.69	0.028	0.064	0.059	0.062	0.051	0.023	0.008	0.059
	3.00	2.52	4.52	0.011	0.037	0.038	0.054	0.027	0.016	0.003	0.040
Th(IV)	0.10	4	6	0.007	0.014	0.011	0.009	0.008	0.014	0.007	0.008
	0.20	3.69	5.69	0.014	0.024	0.017	0.019	0.015	0.016	0.018	0.012
	0.30	3.52	5.52	0.022	0.016	0.020	0.023	0.018	0.024	0.023	0.019
	0.50	3.30	5.30	0.041	0.012	0.036	0.051	0.022	0.020	0.048	0.036
	1.00	3	5	0.049	0.010	0.019	0.026	0.016	0.017	0.069	0.022
	2.00	2.69	4.69	0.028	0.007	0.008	0.022	0.011	0.014	0.042	0.013
	3.00	2.52	4.52	0.013	0.002	0.003	0.009	0.005	0.010	0.019	0.002

2 milliliters of acetate buffer, the maximum absorbance was Achieved.

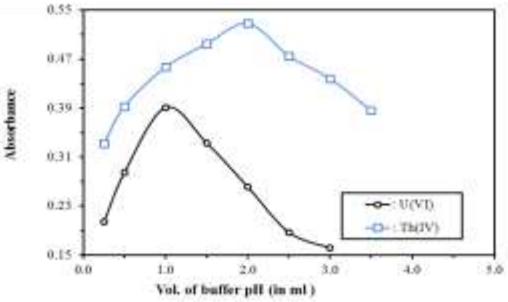


Fig. 2: The impact of buffer pH on Th(IV) and U(VI) absorbance.

3.2.3. Impact of concentration of Calcon dye on Th (IV) and U (VI) complex absorbance

Since a concentration that is either too high or too low might cause the calibration curve to deviate from Beer's law, the concentration of calcon dye should be optimized. To some extent, the dye wouldn't form complexes with other ions that might be present in the aqueous solution if the dye concentration was optimized in addition to the pH value. To investigate the impact of dye concentration, a set of varying volumes of 10^{-3} M calcon dye was introduced to a 10 ml volumetric flask along with fixed volumes of one milliliter from 10^{-3} M U, 0.2 ml from 10^{-2} M sulfuric acid or nitric acid, and one milliliter from acetate buffer. Next, the solution's absorbance was calculated for U at λmax: 682. Different amounts of 10^{-3} M calcon dye were applied to a series of 10 ml volumetric flasks containing fixed volumes of 1 ml from 10^{-3} M Th, 1 ml from 10^{-2} M perchloric acid, and 2 ml from acetate buffer in the other measuring flask. Next, the solution's absorbance was calculated for Th at λmax: 658. The data were presented in Fig. (3), where under the previously indicated experimental circumstances, the maximum absorbance of U occurs at 1.5 ml from 10^{-3} M Calcon dye, and the maximum absorbance of Th binary complex occurs at 2.5 ml from 10^{-3} M Calcon dye.

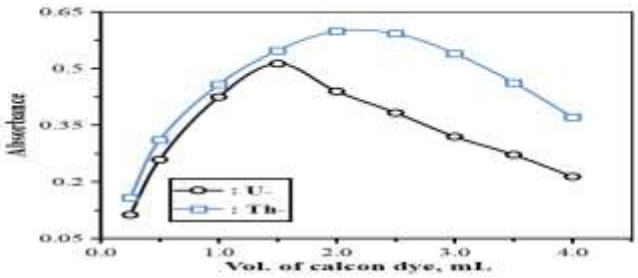


Fig. 3. Impact of Calcon dye on Th(IV) & U(VI) complex absorbance

3.2.4. Ratio of the "metal Calcon" compound

The molar ratio approach and the continuous variation method were used to estimate the molar ratio between the dye and metal ions (U or Th). The continuous variation approach, also known as Job's method [41], involves varying the molar ratio of the metal and dye while keeping the total moles of both constituents constant. This is achieved by varying their molarities. Each metal and dye had a concentration of 10^{-3} M. Here, maintaining a consistent end volume ensures a constant total number of moles of metal and color. It is abundantly clear from the data shown in Fig. 4 that metals Th (IV) and U (VI) complex with calcon dye at a 1:1 molar ratio.

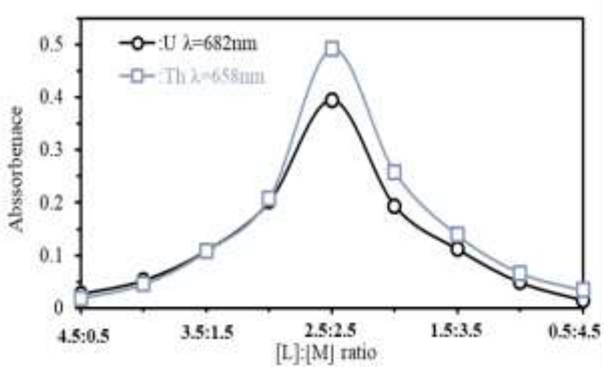


Fig. 4. Molar ratio of Calcon dye to metal U(VI) and Th(IV).

3.2.5. Impact of addition sequence

To achieve the highest absorbance value, the complex formation sequence had to be optimized. In this way, four distinct addition sequences were examined at the ideal previously identified criteria for the creation of complexes. The data shown in Table 2 determined that adding metals, acid, dye, and buffer or dye, acid, buffer, and metals in the order that recorded the highest absorption values was the ideal sequence. In contrast to Th, the ideal addition order for U is different where:

Table 2. Impact of adding order on the complex's absorbance

Addition sequence	Abs. U(VI)	Abs. Th(IV)
Dye- metal- acid -buffer	0.267	0.433
Metal -acid - buffer-dye	0.442	0.586
Metal -acid - dye-buffer	0.396	0.627
Dye-buffer- acid- metal	0.341	0.375

3.2.6. Duration time's impact on metal (U/Th) complex stability

The uranium and thorium calcon complex were examined for stability over time, with absorbance measurements made every five minutes. As illustrated in Fig. (5), it was discovered that the complex formed quickly and remained stable for two hours following the preparation of the addition sequence.

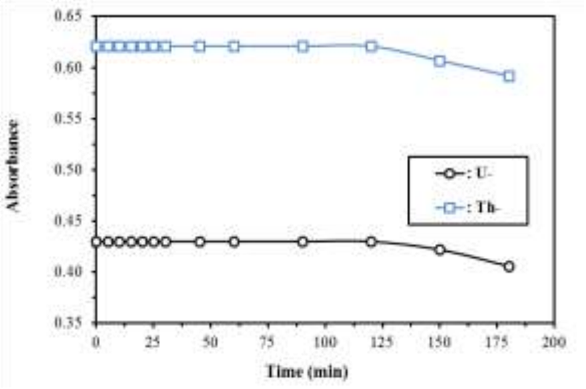


Fig.5: Duration time's impact on the U (VI) & Th (IV) complex's stability.

3.3. Constructing a calibration curve

Following an extensive examination of the key variables affecting the best calcon spectrophotometric estimation of U (VI) and Th (IV), the concentration range (minimum and maximum) was found to be sufficient above which no more U and Th complexes with calcon dye could be formed or identified. However, utilizing the optimum settings that were tested, it was not possible to measure U and Th below this range (the detection limit). All of these limits for the U-complex and Th-complex will be defined by the spectrophotometric calibration curve. It is necessary to perform this spectrophotometric determination of both metals U and Th within the range of concentrations where Beer's law is applicable. To do this, a series of solutions with varied concentrations of either Th or U were created, along with fixed volumes of 1.5 ml and 2.5 ml of 10^{-3} M Calcon dye for U and Th, respectively. Every produced solution was measured at the suggested wavelength and compared to the appropriate blank solution after being adjusted to pH 4 (acetate buffer) for U and pH 3 (acetate buffer) for Th. The data obtained are displayed in Figure (6). It is abundantly clear from the collected data that 15 mg/L U and 20 mg/L Th is the highest concentration limit that was reached. The average molar absorptivity (Ɛ) of the uranium and thorium complexes was determined to be 0.89×10^{4} L M^{-1} cm^{-1} and 0.67×10^{4} L M^{-1} cm^{-1}, respectively, based on this straight line. Between 0.1 and 15 mg/L U and 0.25 to 20 mg/L Th, Beer's law was followed.

3.4. The interfering ions' tolerance ratio on the spectrophotometric determination of U and/or Th dye

Investigating the interference impact of a few related elements with uranium and thorium was vital. Through the use of the previously adjusted additions (0.2 ml from 10^{-2}M sulfuric acid, 1 ml from acetate buffer solution, and 1.5 ml from 10^{-3}M calcon dye), the impact of various ion concentrations on uranium determination using calcon dye was investigated. 1 ml of 10^{-2} M perchloric acid, 2.5 ml of 10^{-3} M calcon dye, and 2 ml of acetate buffer solution were used for thorium.

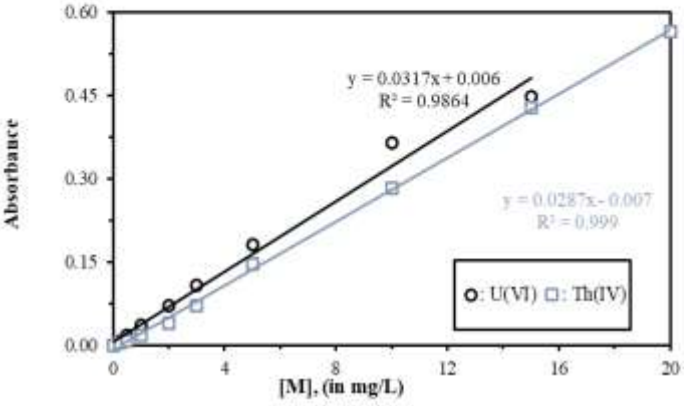


Fig. 6. U (VI) and Th (IV) calibration curve using Calcon.

The tolerance limits of interfering ions on the uranium and thorium determination using calcon dye were compiled in Table 3. The concentration of foreign ions was examined together with each ion's tolerance limit. By leaching samples and precipitating multiple ions using solid ammonium chloride and ammonia solution, the significant interference from the cations previously investigated was eliminated.

Table 3. Effect of interfering ions tolerance limits on U (VI) and Th (IV) measurement for both analytes at 1µg mL^{-1} concentration.

Element	Limit of tolerance, 1µg mL^{-1}		Element	Limit of tolerance, 1µg mL^{-1}	
	U(VI)	Th(IV)		U(VI)	Th(IV)
Fe^{3+}	100	100	Cu^{2+}	100	80
Al^{3+}	100	100	Mn^{2+}	100	80
Na^{+}	1000	1000	Cd^{2+}	100	80
K^{+}	1000	1000	V^{4+}	100	75
Ca^{2+}	500	250	Ba^{2+}	1000	750
Mg^{2+}	500	250	Ni^{2+}	1000	500
Ce^{3+}	200	100	Co^{3+}	1000	500
Sm^{3+}	200	100	PO_4^{3-}	1000	1000
Y^{3+}	250	100	Y^{3+}	750	500
Pr^{3+}	250	150			

3.5. Comparing different chromogenic reagents and spectrophotometric techniques to determine U (VI) and Th (IV)

The suggested reagent calcon is one of the most potent determinant reagents for the estimation of uranium (VI) and thorium (IV), according to a comparison of the reagent possibility (Calcon dye) under consideration for the spectrophotometric estimation of U(VI) and Th(IV) with the other methods (Table 4). Numerous metal ions contained in ore minerals, including Fe, Cr, Cu, Co, Zn, Al, Ni, V, Zr, Cu, Hg, Mn, Ce, and Mo, interfere with the previously documented spectrophotometric techniques. These procedures are laborious and time-consuming, and they call for prior separation. Furthermore, complex stability in the aforementioned approaches is low. In contrast, the currently documented approach is straightforward, non-extractive, and fairly accurate. Furthermore, compared to many of the documented ways, the precipitation method is found to be more selective.

3.6. Application of the proposed method

To confirm applications and validations there, the suggested approach has been applied to the spectrophotometric measurement of U (VI) and Th (IV) in a variety of samples, including certified reference materials and diverse rocks from the Gattar and Abu Rusheid region. An acidic mixture (0.5 gm of sample + 20 ml hydrofluoric acid + 10 ml sulfuric acid + 6 ml perchloric acid) was used to decompose the sample. The mixture was heated until all acidic fumes were eliminated, at which point the residue was dissolved in 10 ml hydrochloric acid 1:1 and finished in a 100 ml volumetric flask with doubled distilled water [51]. Solid ammonium chloride was added to a 10 ml aliquot sample first, followed by ammonia solution up to pH 9, at which point a precipitate of various ions was created.

Table 4. Comparison of several chromogenic reagent-based spectrophotometric techniques.

Element	Reagent	λ_{max} (nm)	Molar Absorptivity, L mol^{-1} cm^{-1}	Ref.
Th(IV)	Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH)	352	2.26×10^4	[42]
	2-hydroxy-1-naphthaldehyde-p hydroxybenzoic hydrazone	415	3.5 × 104	[43]
	5-bromosalicylaldehyde isonicotinoyl hydrazone(5-BrSAINH)	385	1.33 × 104	[44]
	Alizarin red S (ARS)	530	0.42 × 103	[17]
	2-hydroxy-3-methoxy benzaldehyde isonicotinoylhydrazone	395	1.4 × 104	[32]
	Thorin	542	0.173 × 104	[45]
	Calcon	658	0.67×10^4	*Here*
U(VI)	N-hydroxy, N, N_0diphenylbenzamidin	490	8.8×10^4	[46]
	4-(2-thiazolylazo)-6-chlororesorcinol	553	3×10^4	[47]
	Di-2-pyridyl ketone nicitinoyl hydrazone	373	2.13×10^4	[48]
	Di-2-pyridyl ketone thiophenol hydrazone	389	2.33×10^4	[49]
	Arsenazo III	650	5×10^4	[49]
	2-(2-benzothiazolylazo)phenol	585	1.03×10^5	[50]
	Calcon	682	0.89×10^4	*Here*

Here, a common buffer solution was created using the subsequent formulas:

$$NH_3 + H_2O \rightarrow NH^{+4} + OH^-$$

$$NH_4Cl \leftrightarrow NH^{+4} + Cl^-$$

After filtering the precipitate, 1% (w/v) ammonium chloride was used to wash it. Nearly all of the titanium, calcium, iron, and aluminum matrix was eliminated [51]. Because it dissolves over (OH^-), ammonium chloride functions as a common equilibrium of NH_3, reducing the concentration of OH ion and preventing $Al(OH)_3$ from dissolving. This results in the formation of soluble aluminate ions as follows:

$$Al(OH)_3 + (OH)^- \rightarrow AlO_2 + 2H_2O$$

The following procedure was used to analyze uranium spectrophotometrically in solutions: an aliquot amount of each solution was combined with 0.2 ml of 10^{-2} M nitric acid, 1 ml of buffer pH 4, and 1.5 ml of 10^{-3} M Calcon dye, and the mixture was then filled in a 10 ml volumetric flask at λmax 682 nm.

Additionally, thorium can be examined in the manner described below: an aliquot of each solution was combined with 1ml of 10^{-2} M perchloric acid, 2.5 ml of 10^{-3} M Calcon dye, and pH 3 was adjusted using diluted HCl and NaOH. The mixture was then filled in a 10 ml volumetric flask at λmax 658 nm. The accuracy of the mentioned procedure in the complex matrices for the analysis of U (VI) and Th (IV) was demonstrated by the agreement between the obtained and expected values.

Table 4. Using the currently under-study methodology, the concentrations of U (VI) and Th (IV) were determined in samples and international standards.

Sample type	Sample ID	Certified / measured value***, (mg L^{-1})	Measured [Metal], (mg L^{-1})	S.D.	S.E.	Error, (%)	Accuracy (±)
Standard sample	DL- 1a	116 U	115.8	0.29	0.17	0.14	0.012
			115.8				
			116.3				
		76 Th	75.8	0.23	0.13	0.18	0.041
			75.8				
			76.2				
	BL-2a	4260 U	4259	0.58	0.34	0.008	0.29
			4259				
			4260				
	Nim.G**	15 U	15.2	0.42	0.24	1.59	0.42
			14.6				
			15.4				
		51Th	51.6	0.69	0.40	0.78	0.69
			51.6				
			50.4				
Nature sample application	Ad 3	66 U	66	0.58	0.34	0.51	0.293
			65				
			65				
		45.6 Th	46	0.31	0.18	0.39	0.401
			46				
			45.3				
	Ad 5	48 U	48.6	0.69	0.40	0.83	0.642
			48.6				
			47.5				
		238.6 Th	239	0.58	0.33	0.14	0.581
			238				
			238				
	BH 1- 24	213 U	213	0.335	0.19	0.1	0.294
			214				
			214				
		860 Th	859	0.93	0.53	0.062	0.213
			859				
			860.6				
	BH 3- 8	136 U	135.5	0.93	0.54	0.41	0.09
			135				
			136.8				
		385Th	384	1.06	0.61	0.61	0.083
			386				
			384.4				
	L - 1	418 U	418.6	0.72	0.42	0.1	0.164
			417.6				
			419				
		57 Th	58	0.65	0.43	0.76	0.122
			56.5				
			57.4				

* Certified values provided by the certifying body, Canadian Central for Mineral and Energy Technology standards (CANMETMeasured [Metal], (mg metal L-1): Using the current method, the concentration of U and Th was found (mg metal L-1), Standard deviation, or S.D. Standard error, or S.E.

** SA Bureau of Standards P/Bag X191, Pretoria 0001 (SARM1) certified values.

*** Expected [Metal], (mg L-1) examined by XRF and Uranium lab.

This indicates that the acceptable values found by the ICP-OES and XRF procedures are comparable to the tiny reference and observed sample error percentage values achieved using this spectrophotometric approach. This claims that the results are extremely precise and accurate. Several statistical indicators, including standard deviation (S.D.), accuracy (Δ), percentage error (% E), standard error (S.E.), and error rate (%) were assessed to assess the current process (Tables 6, 7).

3.7. Metal complexes

3.7.1. FTIR analysis:

The calcon dye ($C_{20}H_{13}N_2NaO_5S$) reactive groups can be identified by FTIR spectroscopy, as can the chemical alterations that occur upon complexation with U (VI)/Th (IV) ions. The calcon spectrum shows the following distinctive bands. The N-H stretching vibrations are correlated with the broad band at 3446 cm^{-1}. The peaks located at 2914 and 2846 cm^{-1} are attributed to the −CH3 group's symmetric and asymmetric C–H vibrations. The stretching vibrations of C–C and/or C–N are attributed to the peak at 1636 cm$^{-1.}$ The calcon ring's >C=N stretching vibrations are responsible for the peak edge that arises between 1400 and 1600 cm^{-1} [58, 59]. Weak absorption peaks at approximately 1469–1406 cm^{-1} are visible in the Calcon spectra, which point to aromatic C–H bending. Peaks at 981-929 cm^{-1} are associated with the N-H wagging (N-H π) at 635 cm^{-1} [55], and the out-of-plane bending (C-H out-of-plane δ) vibration, which corresponds to para-substituted aromatic C-H groups [58-60]. The vibrations associated with CH3 asymmetric bending, CH2 bending/C–N stretching, and CH3 bending vibrations are represented by the peaks at 1460, 1417, and 1394 cm^{-1} [55, 57]. The peak observed at 1230 cm^{-1} is attributed to stretching vibrations of N–N. N–H in-plane bending (and/or C–C stretching and C–H bending) and O=S=O asymmetric and symmetric stretching vibrations in SO$_4^{2-}$group are ascribed to the distinctive peaks at 1119 and 635 cm^{-1} (weak peak), respectively [54, 58]. C–S stretching vibrations may be the cause of the peak at 925 cm^{-1}[52].

Following the complexation of metal ions (U (VI) and Th (IV)), FTIR analysis was carried out (Fig. 8). Because both U (VI) and Th (IV) complexes with dye involve reactive groups that involve both dye molecules and metal ions, their spectra exhibit similarities. The spectra of the U and Th complexes are relatively similar to that of the free Calcon dye due to their low concentration, while there are some slight differences.

i. Metal ion binding, which impacts the OH and NH group environments, has been closely linked to the area around 3219 cm^{-1} [53].

ii. Metal binding is responsible for the removal of some peaks in the 1528–400 cm^{-1} range, namely the bands in the Calcon dye spectra at 1636–1400 cm^{-1} (>C=N) and 669 cm^{-1} (C–S) [54].

iii. □M−O bonds are usually linked to new peaks at 793, 689, 571, 480, and 449 cm^{-1} [52, 59].

□The group's involvement in chelation is suggested by the loss of the 1119 cm^{-1} band in the Calcon dye–U complex spectra, which is attributed to SO$_4^{2-}$ [54].

U(VI) complexation produced a faint band about 793 cm^{-1}, but Wang et al. [60] discovered two more bands at 823 and 913 cm^{-1} as a result of linear O=U=O vibrations.

Therefore, complexation between the metal ions and the N, O, and SO3 atoms in the Calcon dye can be thought of as the binding mechanism. According to reports [59, 61], the coordination of oxygen (O) and nitrogen (N) atoms to central metal ions (Th/U) is confirmed by the values allocated to v(M-N) and from 500-400 cm^{-1} ascribed to ν(M-O).

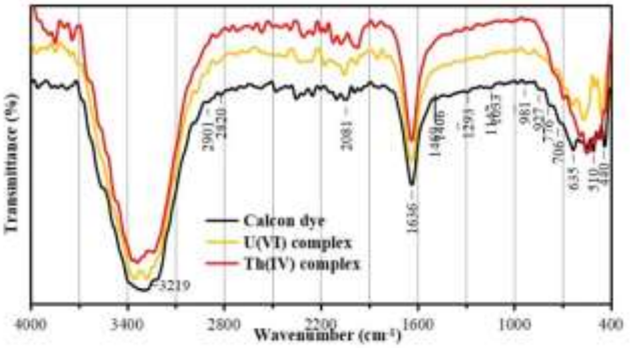


Fig: 8. The FTIR spectra of Th(IV) complex, U(V) complex, and raw Calcon dye.

3.7.2. XPS spectroscopy

In addition to defining the materials (finding particular bonds), XPS spectroscopy can be used to determine how the materials interact with metal ions after binding [52–54]. XPS analysis was utilized to ascertain the chemical makeup of both raw Calcon and its subsequent interaction with U (VI) and Th (IV) ions. This verifies the effective complexation process (Fig. 7).

As expected, the chemical compositions of all XPS spectra showed C 1s (284.92-285.15 eV), O 1s (531.12-532.69 eV), N 1s (499.63-408.04 eV), S 2p (168.89-169.27 eV) [56], and Na1s (1071.88-1072.30 eV) signals [47, 55] obtained before, and after U (VI) and Th (IV) complexation. Furthermore, the F element (F 2p signal at 686.2 eV) on the Calcon-U (VI) spectrum and the Cl element (Cl 2p signal at 199.28 eV) on the Calcon-Th (IV) spectrum was detected, which is most likely owing to impurities in the reagents. After metal complexation, the XPS spectra reveal that the presence of U 4f signal at binding energy (BE) 382.53eV) [56, 57] and Th 4f signal at BE: 335.24 eV. Fig. 8 shows the high-resolution XPS spectra of U (VI) and Th (IV). The U 4f is identified by two peaks around 392.52 eV (U 4f5/2) and 381.66 eV (U 4f7/2) can well reproduce experimental data, including relative multiplet with ΔBEs: ~10.86 eV, indicating that the oxidation state of the complexed-uranium is hexavalent U(VI) [23, 56, 58].

Furthermore, there are additional peaks indicated by a series of peaks linked to U components.: U5d5/2, U5d3/2, U5p3/2, U4d5/2, U4d3/2, and U4p5/2 at 100.18, 108.08, 201.53, 746.32, 786.18, and 1051.08 eV, respectively [55, 58]. Whilst the presence of Th 4f5/2 and Th 4f7/2 characteristic doublets at 343.85 and 334.63 eV [23], providing concrete proof of the creation of Calcon-Th (IV) and Calcon-U (VI) complexes

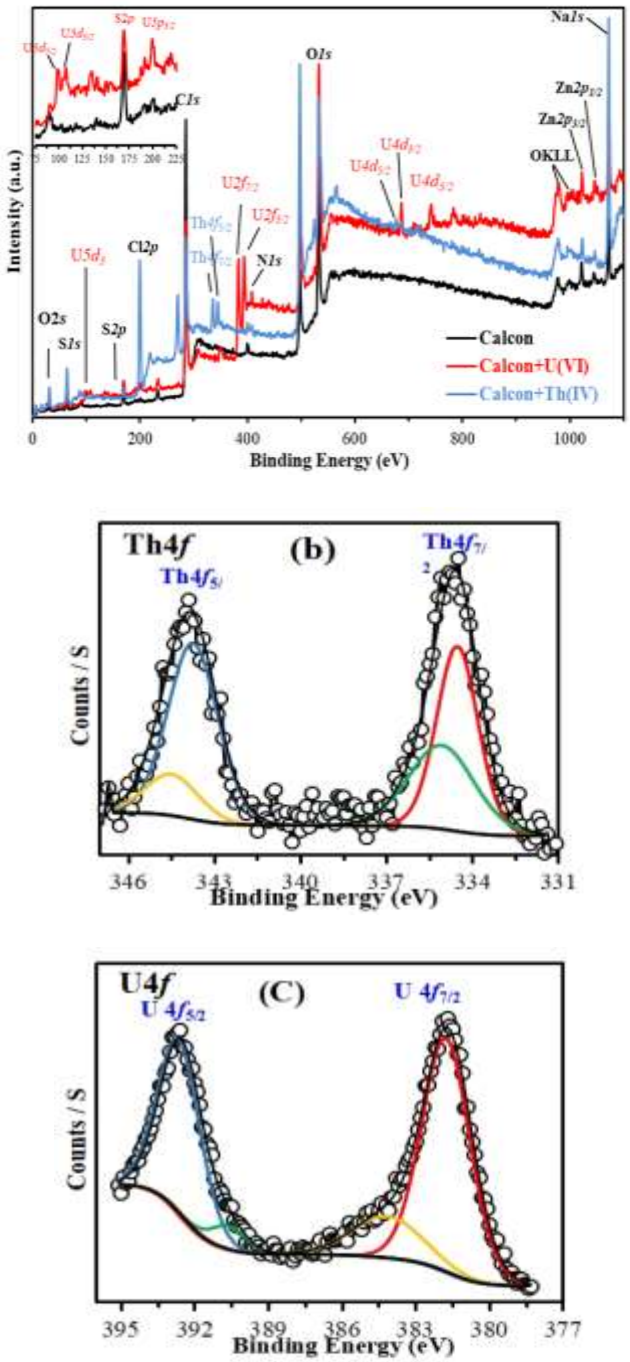


Fig 7. Th(IV)- and U(VI)-complexes, Calcon dye full XPS survey spectra (a), and core level for Th4f (b) and U 4f (c).

3.7.3. Mechanism of interaction

By using XPS to characterize the raw and reacted Calcon dye samples, the molecular interaction mechanism between U (VI) and Th (IV) with the dye was clarified. Figure 9 reports core level spectra for main elements. The same XPS spectra show certain BE shifts and dips in their respective proportions around the distinctive C 1s, N 1s, O 1s, and S 2p signals. The grafting of additional groups may have caused chemical alterations in these elements' surroundings, which could be directly linked to these modifications [45, 56]. The assignments (as well as relative atomic fractions) of the deconvoluted bands for each element signal are listed in Table 5 (which is derived from HRES spectra).

- There may be some variations in the C1s peak for raw Calcon-dye before and after U (VI) and Th (IV) complexation, according to the high-resolution C1s spectra (Fig. 9) [62].

- The O2s, N1s, and S2p peaks, which are linked to sulfur-, nitrogen-, and oxygen-containing functional groups such the S─ONa, S=O in the sulfate group, and >NH, and N=N- bonds in the azo-group of the dye molecule, show significant variations (in terms of intensities and peak positions).

Higher coordination numbers six, seven, and ten donor atoms may be involved in the coordination of (VI) and Th(IV) [23, 54]. UO_2^{2+} and $[UO_2(H_2O)_2]^{2+}$ are the two possible forms of uranium ions U(VI), but coordination complexes and thorium(IV) hexahydrate $[Th(H_2O)_6]^{4+}$ are also possible.

A possible mechanism for the metal ion complex can be suggested based on XPS investigations (Scheme 1). Metal ions connect through:

1) Two five-membered rings are formed by two ionic bonds with O-atoms (from -OH) and two coordinating bonds with nitrogen donors of the azo-group (the mode (a)).

2) Two coordination bonds (the contribution modes (b)) with the sulfate group's oxygen atom,

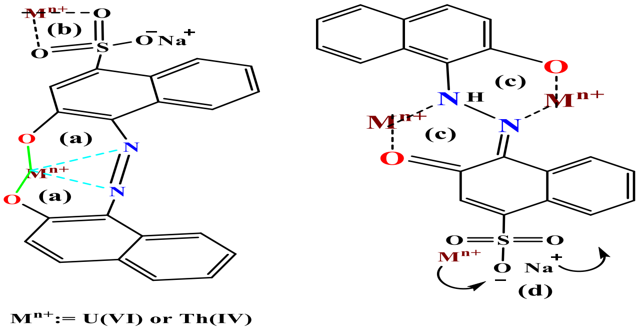
3) One stable six-membered chelating ring (the mode (c)) is formed by two coordination bonds with one N-atom from the azo group, one O-atom from the C=O group, and another O-atom from the –OH group.

4) A single, stable, six-membered chelating ring (the mode (c), is created by the combination of one ionic bond with an O-atom from the –OH group and one coordination bond with one N-atom of the azo group (–C=N). and

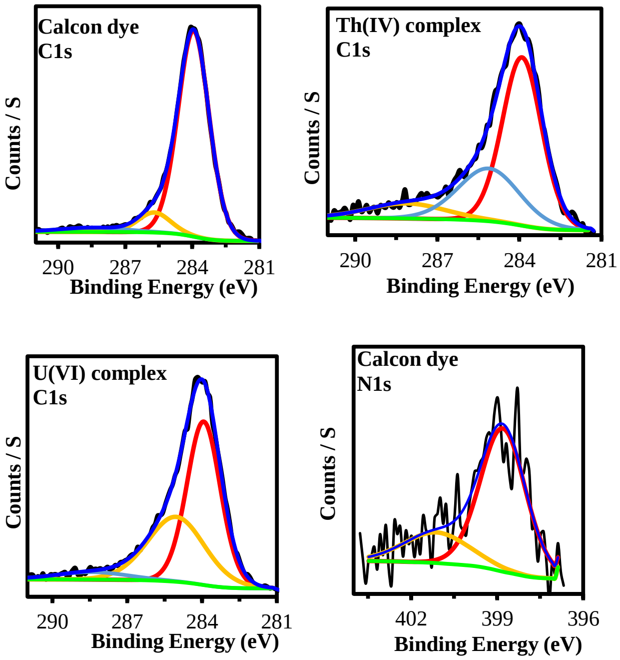
5) The cation-exchange mechanism using the Na^+ from the sulfate group is the final way of action.

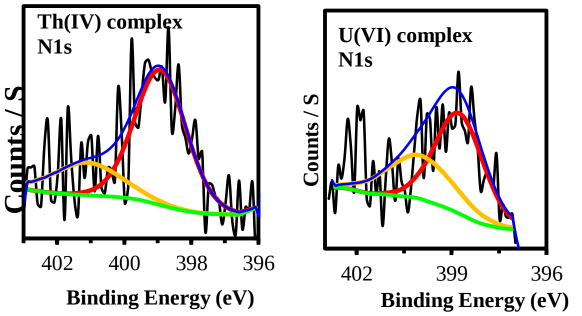
Thus, contribution modes (a, c) f Therefore, mode (b) creates a ring with four members, while contribution modes (a, c) combine to generate stable chelating rings with five and six members, respectively. whereas mode (b) produces a ring with four members, establishing a stable chelating ring with five and six members.

Furthermore, the stability of the complex produced is increased by the contact of the metal ions between two chains, which increases the number of chelate rings [52]. It is interesting to notice that the four membered contribution modes (I) and (d), which are created, are unstable and easily broken. These results are compatible with the experimental findings, which show that the generated complex is stable for the first half hour before beginning to break. This validates the anticipated mechanism.



Scheme 1. Theoretical complexation mechanism for Mn+ ($[Th(H_2O)_6]^{4+}$, and $[UO_2(H_2O)_2]^{2+}$)-modes of interactions between reactive groups on the dye and metal ion (around coordination number: 10).





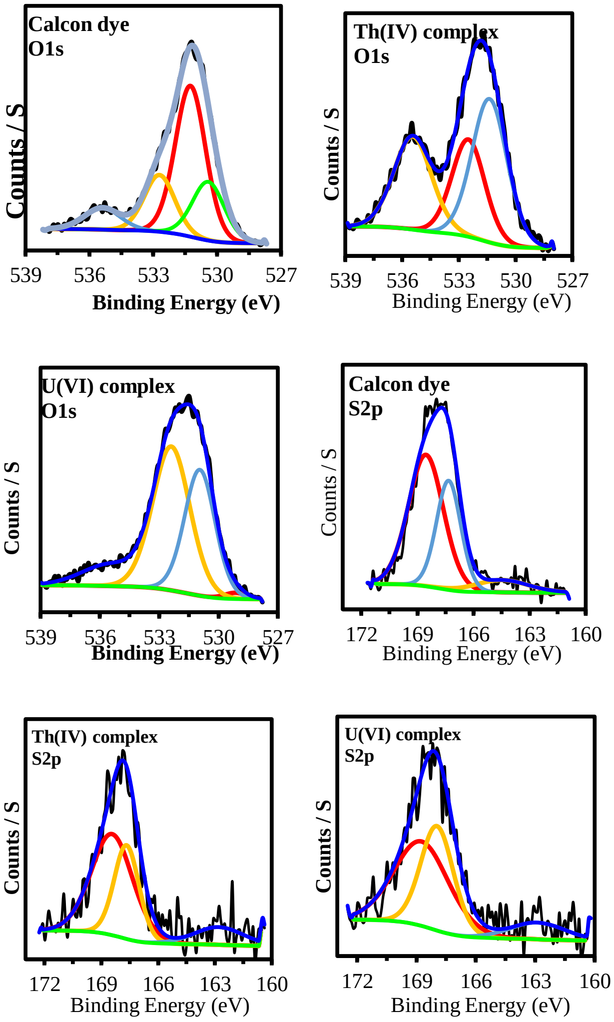


Fig. 9. Core level spectra for C1s, O1s, N1s, and S2p for Calcon dye, and after U4f and Th4f complexation.

Table 5. Examination of Calcon dye's XPS spectra, including Calcon+U (VI) and Calcon+Th (IV).

Name	Calcon		Calcon+U(VI)		Calcon+Th(IV)		Assignment
	Peak BE	Atomic %	Peak BE	Atomic %	Peak BE	Atomic %	
C1s [54]	283.94	87.41	283.93	56.47	283.9	60.0	$C_{Adv.}$, C-C,C=C-
	285.7	8.83	285.04	38.05	288.12	10.67	C-N, C=N
	288.42	3.76	288.41	5.48	285.11	29.33	C-S
N1s [58]	398.8	76.39	398.75	89.6	398.92	85.49	C-N, >N (amine)
	401.11	23.61	399.98	10.4	401.41	14.51	-N=N, N (amide)
O1s	-	-	529.15	1.45	-	-	U-O
	530.41	22.84	-	-	-	-	C=O
	531.25	56.0	530.94	41.27	531.38	61.15	C-OH
	532.7	21.16	532.39	57.28	532.49	38.85	O-H (H_2O), S-O
S2p [56]	162.47	8.58	162.88	10.45	162.79	12.07	S2$p_{3/2}$ (C-S)
	167.23	8.44	168.17	29.01	167.75	11.16	S2$p_{1/2}$ (S-O)
	168.14	82.98	168.35	60.54	168.16	76.77	S 2$p_{3/2}$ (Sulfonic)
Zn2p	1021.13	61.44	1021.88	52.46	1022.04	67.27	$2p_{3/2}$
	1044.04	38.56	1044.84	47.54	1045.09	32.73	$2p_{1/2}$
Na1s	535.39	0	535.51	0	535.43	0	NaKLL
	1071.21	100	1071.64	100	1071.54	100	Na1*s*
U4*f [55, 58]*			381.66	50.29			U 4$f_{7/2}$ ($U^{(VI)}$)
			384.15	12.96			U 4$f_{5/2}$ ($U^{(VI)}$)
			390.6	3.6			U 4$f_{7/2}$ (U^{VI})
			392.52	33.15			U 4$f_{7/2}$ (U^{VI})
Th4*f* [23]	-	-	-	-	334.63	25.46	Th 4$f_{7/2}$ (Th)
	-	--	-	-	343.85	38.97	Th 4$f_{5/2}$(Th)
	-	-	-	-	334.73	31.99	Th 4$f_{7/2}$ (Th)
	-	-	-	-	344.19	3.57	Th 4$f_{5/2}$(Th)

4 Conclusions

It was discovered that Calcon dye was sensitive and accurate for spectrophotometrically estimating Th (IV) and U (VI).

For U-calcon solution at buffer pH 4, the molar absorptivity at λmax 682 nm is calculated to be 0.89×10^4 L M^{-1} cm^{-1}, whereas for Th-calcon solution at pH 3, λmax 658 nm, it is 0.67×10^4 L M^{-1} cm^{-1}.

Molar ratio for U- calcon and Th- calcon was 1:1 to each complex.

Within the range of 0.1 to 15 mg/L U (VI) and 0.25 to 20 mg/L Th (IV), Beer's law was observed.

The analytical properties (limit of detection, precision, and accuracy) attained have shown that the newly suggested approach for determining uranium and thorium in real geological rocks and standard reference is feasible.

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