



Effective Spectrophotometric Quantification of Yttrium Using Clayton Yellow Dye in Different Rare Earth Concentrates

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In Loving Memory of Late Professor Doctor””Mohamed Refaat Hussein Mahran””

Abstract

A highly sensitive, direct, and precise method for the determination of yttrium (III) via spectrophotometry has been developed. This procedure relies on the formation of an orange-colored complex, exhibiting its maximum absorbance at 499 nm. This complex is formed through the reaction between yttrium (III) and Clayton Yellow (CY) reagent in a citrate buffer solution at pH 5. The FTIR analysis confirmed the yttrium-CY complex, revealing a potential interaction mechanism between reactive groups on the CY dye and the yttrium (III) ions. Several criteria were scrutinized to optimize the formed yttrium-CY complex. These included assessing the acid type, optimal pH, dye concentration, evaluating the temporal stability of the complex, and establishing the calibration curve for yttrium concentration. The complex was found to have an average molar absorptivity (ϵ) $0.54 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ with Sandell's sensitivity of 1.67×10^{-2} . Beer's law was applied within the 0.06 to $12 \mu\text{g mL}^{-1}$ range. Under ideal conditions, it has been determined that, the stoichiometry of the reaction between the CY reagent and yttrium (III) is 1:5. The limit of detection (LOD) is found to be $0.06 \mu\text{g mL}^{-1}$. Utilizing the first derivative spectrophotometric approach, the measurement of yttrium within the rare earth elements (REE) exhibited remarkable sensitivity and precision.

Keywords: spectrophotometric; Yttrium (III); Clayton Yellow; derivative spectrophotometric; rare earths Elements.

1. Introduction

The seventeen chemical elements that make up the group known as rare earth elements (REEs) are the fifteen lanthanides, scandium, and yttrium [1]. These elements are extremely valuable and are utilized in a variety of contemporary technologies, such as petrochemistry, renewable energy technologies, and communication technologies [2,3,4]. For example, lanthanum and neodymium are important for electric mobility and for enhancing the material qualities of steel alloys when combined with cerium. Future fuel cells will use zirconium dioxide stabilized by yttrium as the electrolyte material [3]. This wide range of uses, particularly in high-tech sectors, fuels the demand for REE across the world. Since they frequently occur in the same ore deposits as the lanthanides and have comparable chemical characteristics, yttrium, and scandium are regarded as rare earth elements (REEs). Though promethium, the rarest of the REE, only exists in tiny amounts in natural materials due to its lack of stable or long-lived isotopes, all of the REE are found in nature, albeit not in pure metal form [5]. There are several techniques for spectrophotometrically determining certain rare earth elements, such as the process of creating samarium chrome azulol S cetylpyridinium chloride (CPC) and complex in micellar medium [6–8], which provides a sensitive, straightforward approach for spectrophotometrically determining tiny levels of samarium. From 0.05 to 2 mg l^{-1} of samarium at 505 nm as Sm-CAS-CPC complex, Beer's law is followed. The best circumstances for determining samarium were examined

[9]. A sensitive spectrophotometric technique that was reported for the measurement of praseodymium (Pr) using 1,4-dihydroxyanthra-quinone was used to separate Pr selectively at pH 1 using D2EHPA [10]. A significant element of the REE family is yttrium. It is found in nature with heavy lanthanides and is more prevalent than them, sharing similarities in its properties. Naturally, it never shows up as a free element. It may be present in xenotime, monazite, and bastnaesite, the three primary minerals that yield lanthanides. Yttrium spontaneously ignites in air and has a silvery-metallic luster [11]. Finding out promising techniques for the quick investigation of yttrium was required due to the increasing the need for this element in the fields of nuclear chemistry and metallurgy [12]. Several techniques have been utilized for yttrium determination such as ICP-AES [13], ICP-MS [14–16], and X-ray fluorescence. A novel and accurate ion-exchange method using the DGA resin (TODGA), combined with addition of a Tm spike, which allows the separation of the REEs+Y as a whole prior to analysis using an Element XR ICP-MS [17]. Previous investigations have shown that studies focusing on yttrium analysis using spectrophotometers have been exceedingly rare over the past fifty years. Numerous chemicals have been introduced for spectrophotometrically determining yttrium, including (HNHBH) [18], 5,7-Dinitro-8-quinolinol and Basic Rhodamine Yellow [19], Spectrophotometric determination of yttrium (III) with alizarin red s in the presence of ethyltrimethylammonium Bromide [20], arsenazo(I) [21], and arsenazo(III)[22].S.A.

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Receive Date: 07 March 2024, Revise Date: 01 May 2024, Accept Date: 08 May 2024

DOI: 10.21608/EJCHEM.2024.275385.9421

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Mohammed, 2018 [23] presented the extraction and spectrophotometric measurement of yttrium using TOPO and alizarin red S (ARS) reagent. A spectrophotometric method for determining Y(III) in an aqueous solution was devised, which was straightforward, sensitive, and accurate. The process involves Y(III) reacting with alizarin red S (ARS) reagent at pH 4.7 in the presence of triton-X-100 surfactants and cetyltrimethylammonium bromide (CTAB) medium to generate a red carmine complex at λ_{max} : 520 nm. Cations of an extractant are selected from the group of quaternary phosphonium or quaternary ammonium, and the anion is sec-octyl phenoxy acetate for extraction and separation of yttrium. This method used a mixed organic phase consisting of an extractant and a diluent to extract a rare earth feed liquid containing yttrium, and then washed and back extracted it with deionized water so that the consumption of acid and alkali in all the processes of extraction, washing and back extraction was avoided [24]. The separation of yttrium and dysprosium from the rare earth's product (48.15% Y₂O₃, 11.05% Dy₂O₃) obtained from a xenotime mineral concentrate was investigated. The rare earths chloride liquor is prepared followed by precipitation of yttrium using lactic acid. The optimum conditions of the yttrium precipitation are included 2M lactic acid concentration, lactic acid pH 5 with L (REEs solution) /L (lactic acid) 1/0.75 at contact time of 168 h at 25°C [25]. The reaction of yttrium with 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione(I), 5-(2'-bromophenylazo)-6-hydroxypyrimidine-2,4-dione(II), 5-(2',4'-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione(III), 5-(4'-nitro-2',6'-dichlorophenylazo)-6-hydroxypyrimidine-2,4-dione (IV), 5-(2'-methyl-4'-hydroxyphenylazo)-6-hydroxypyrimidine-2,4-dione (V) to form a dark pink complexes, having an absorption maximum at 610, 577, 596, 567 and 585 nm, respectively. The complex formation was completed spontaneously in their buffer solution and the resulting complex was stable for at least 3 h after dilution [26]. Clayton yellow dye (Thiazole azo compounds) have drawn a lot of interest due to their importance as complexing agents and sensitivity as chromogenic reagents. They have been employed in spectrophotometric analysis and several metal ion determinations. These dyes' strong selectivity and sensitivity over a broad pH range, as well as how simple and straightforward they are to synthesis and purify, make them valuable for spectrophotometric determination [27]. The suitability of employing (CY) dye for spectrophotometric evaluation of yttrium within rare earth concentrations was investigated in the present study. This investigation delved into optimizing various factors affecting complex generation and measurement, such as pH, molar ratio, initial dye concentration, λ_{max} , calibration curve, and the potential interference of other rare earth elements. Subsequent to refining the parameters previously explored for complex formation, the technique was applied to assess rare earth element concentrations extracted from specific geological materials, as well as for yttrium quantification.

2. Experimental

2.1. Materials

All of the experiments used chemically pure and of high-quality analytical reagents. Stock solution of yttrium (1000

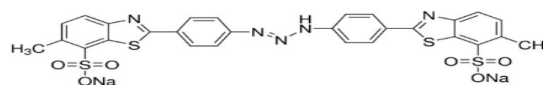
mg Y/L) were prepared using Y₂O₃ (Fluka chemical, Germany), by dissolving it in concentrated HCl and diluted with distilled water. Other reagents included perchloric acid, nitric acid, sulfuric acid, sodium citrate, and citric acid. and hydrochloric acid were Prolabo products and used as received. Analytical-grade standard stock solutions of specific rare earth elements were obtained from Merck (Germany).

2.2. Instrumentations

The Shimadzu UV-11601 double beam UV-visible spectrophotometer (Japan), was employed for the measurements. This spectrophotometer has a range of 190 to 1100 nm, a resolution of 2 nm, and a wavelength accuracy of ± 0.5 nm. pH measurements of the liquids under study were conducted using a Jenway pH meter, calibrated daily using pH buffer solutions 3, 7, and 10 solutions. The Nicolet IS10 FTIR spectrometer was used to obtain FTIR spectra, using the ATR approach. Sample preparation involved allowing the solutions to dry at room temperature on a glass slide, followed by surface analysis of the solid products.

2.3. Characteristics of the Used Dye

The dye, namely Clayton Yellow (CY) or Disodium 2, 2'-[(1E)-triaz-1-ene-1, 3-diyl]dibenzene-4, 1-diyl] bis(6-methyl-1,3-benzothiazole-7-sulfonate) was used. It was a triazene dye with the chemical formula (C₂₈H₁₉N₅Na₂O₆S₄), a molar mass of 695.720 g/mol, and has the following structural formula.



Scheme 1: The chemical structure of Clayton Yellow dye.

2.4. Samples and Sample Preparation Procedure

Monazite and xenotime samples were given by the Nuclear Materials Authority, Egypt. A sulfuric acid digesting process was chosen to dissolve the materials [28–32]. The sulfate liquors used in this investigation were made in a closed reactor with constant stirring while the sample was digested at a high solid/acid ratio (1:3) using conc. sulfuric acid. The mixture was agitated at 220°C for three hours. After the slurry was filtered, the filtrate was diluted by adding distilled water. After the ore was digested, a thick gray paste was produced that cooled and diluted water by 20 times the ore's weight over a minimum of two hours. Cooling was necessary to in order to prevent the increase of temperature to more than 17°C; as the temperature drops, rare earth sulfates become more soluble.

2.5. Statistical and Accuracy Evaluation

Analytical data's accuracy and precision are estimated in the current work using statistical approaches. The mean (\bar{X}) is frequently used as the standard factor for precision estimates (degree of repeatability or random error) in analytical chemistry literature. The definition of accuracy (Δ) in a measurement procedure is the degree to which

findings are similar to real or reference (well-known) outcomes. As a result,

[33–38] uses the subsequent formulas:

$$\text{Arithmetic mean: } - \bar{X} = \frac{\sum X_i}{n} \quad (1)$$

Where:

X_i = is an individual measurement.

n = is the number of measurements.

$$SD = \left[\frac{\sum (X_i - \bar{X})^2}{(n-1)} \right]^{1/2} \quad (2)$$

Standard deviation:

$$\text{Relative standard deviation: } - RSD = \frac{SD}{\bar{X}} \times 100 \quad (3)$$

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

$$\text{The percentage error: } - \% \text{ Error} = \frac{SE}{\bar{X}} \times 100 \quad (5)$$

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

Where d represents the difference between the repeated measurements.

3. Results and Discussion

3.1. Spectrum of Clayton Yellow Dye and Complex

Fig.1 shows the colored spectrum of 10^{-3} M dissolved CY dye in water. The maximum absorption wave length of CY dye in aqueous phase was at λ_{\max} 412 nm. Yttrium forms a binary complex with the sensitive reaction of CY dye. To create this complex, mix 1 mL of 10^{-3} M CY dye solution with 1 mL of 10^{-3} M Y(III) ions. Dilute the mixture using a 10-ml measuring flask filled with distilled water, and then scan in the visible range of 350–650 nm.

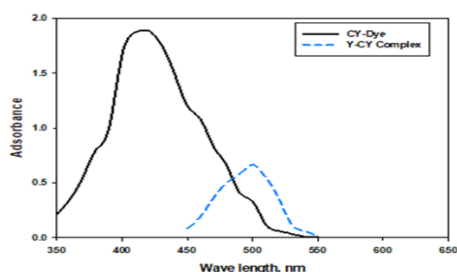


Fig. 1 displays the spectrum of 10^{-3} M Clayton Yellow dye dissolved in water. (1mL of 10^{-3} M CY dye solution with 1 mL of 10^{-3} M Y (III))

3.2. Optimization of the Relevant Factors

3.2.1. Impact of Acid Medium:

Different concentrations (pH) of hydrochloric acid, perchloric acid, nitric acid, and sulfuric acid on complex formation were studied. A series of 10 ml volumetric flasks were filled with aliquots ranging from 0.1 ml to 3 ml of different acids from 10^{-2} M and 10^{-3} M at room temperature (25 ± 2) °C in order to determine the appropriate concentration of acidic medium. These were taken from both the CY dye (10^{-3} M) and the yttrium stock solution (10^{-3} M). Every acid concentration's absorbance was measured

between 350 and 650 nm. The acquired information is displayed in Table (1). Using 0.3 ml of 10^{-3} M hydrochloric acid (pH \approx 5), the complex's maximum absorbance value was determined at λ_{\max} 499 nm. Thus, it was decided that the best medium complex for creation would be hydrochloric acid. A volume of 0.3 mL of 10^{-3} M hydrochloric acid (pH \approx 5) was added for each of the following measurements.

Table 1: Impact of acid type in Y absorbance using CY dye (1 mL of 10^{-3} M Y ions, room temperature and 10^{-3} M CY).

Acid vol., (ml)	Absorbance							
	HCL		HNO ₃		H ₂ SO ₄		HClO ₄	
	10^{-2} M	10^{-3} M	10^{-2} M	10^{-3} M	10^{-2} M	10^{-3} M	10^{-2} M	10^{-3} M
0.1	0.107	0.178	0.160	0.219	0.056	0.108	0.099	0.135
0.2	0.077	0.247	0.077	0.112	0.087	0.152	0.095	0.103
0.3	0.072	0.290	0.062	0.108	0.060	0.106	0.092	0.098
0.5	0.055	0.239	0.040	0.095	0.056	0.080	0.065	0.087
1.0	0.043	0.172	0.034	0.078	0.047	0.060	0.045	0.060
2.00	0.032	0.078	0.030	0.051	0.026	0.038	0.027	0.043
3.0	0.019	0.067	0.021	0.045	0.015	0.021	0.019	0.037

3.2.2. Choice of the Suitable Buffer pH

In this investigation, the ideal acid concentration value for complex formation was fixed using a buffer solution. To achieve variable pH values of 4.6, 5, and 5.2, a buffer solution comprising 0.1 M sodium citrate and 0.1 M citric acid was prepared. Every buffer solution was added to various solutions that contained 1 mL of 10^{-3} M yttrium, 0.3 mL of 10^{-3} M hydrochloric acid, and 1 mL of 10^{-3} M CY dye, all of which had final contents of 10 mL the complex's absorbance was measured between 350 and 650 nm in wavelength. For a more thorough analysis, 0.3 mL of buffer (pH 5) was found to be ideal, as illustrated in Fig. 2.

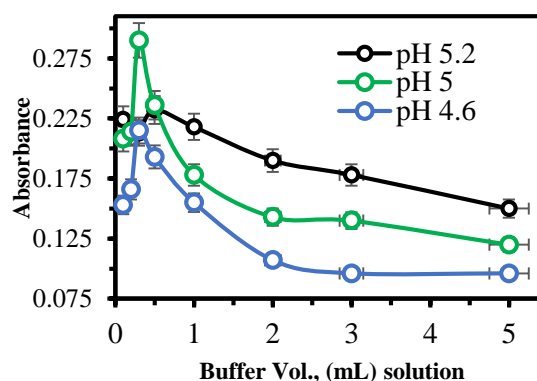


Fig. 2: Impact of varying pH levels of buffer solutions on the absorbance of Y-Clayton Yellow complex formation (1 mL of 10^{-3} M yttrium, 0.3mL of 10^{-3} M HCl, and 1 mL of 10^{-3} M CY dye and, room temperature)

3.2.3. Influence of Clayton Yellow Concentration on the Absorbance of Yttrium Complex by Molar Ratio Method

It was clearly understood that the dye concentration needed to be optimized since variations in concentration could lead to a break from Beer's law. In this experiment, a series of 10 ml volumetric flasks with fixed concentrations

of yttrium (1 ml from 10^{-3} M), 0.3 mL from 10^{-3} M HCl, and 0.3 ml from buffer (pH5) were filled with varying quantities of 10^{-3} M CY dye solution. Using double distilled water, the final volume was brought to 10 mL. At λ_{\max} 499 nm, the absorbance of every solution was determined. According to the obtained data in Fig.3, the maximal absorbance of the Y binary complex occurs at a concentration of 5×10^{-4} M CY dye (5mL from 10^{-3} M) under the stated experimental conditions. Consequently, 5×10^{-4} M of the reagent is kept for all upcoming results.

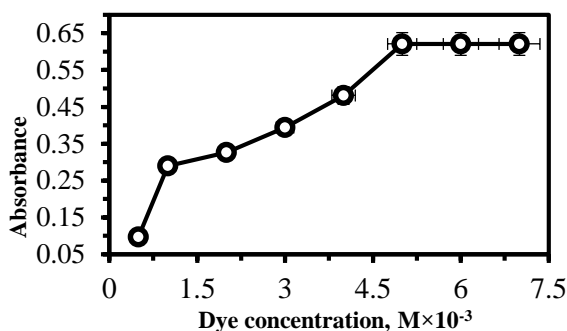


Fig.3: Impact of CY dye on Y-CY complex formation absorbance (1 mL of 10^{-3} M Y ions, 0.3 mL of 10^{-3} M HCl, and 0.3 mL from pH 5 buffer; $\lambda_{\max} = 499$).

3.2.4. Stoichiometry of the "Metal - CY" Complex

The Yoe-Jones method, also known as the Molar Ratio method, is utilized to estimate the molar ratio between metal (Y) and dye [39]. Using this approach, the ligand content varied from 1×10^{-4} M to 7×10^{-4} M, whereas the metal ion amount remained constant at 1×10^{-4} M. As a result, Different [L]/[M] ratios of aqueous metal-ligand solutions were prepared. Each of these solutions' colorimetric detection was assessed at $\lambda_{\max} = 499$, as shown in Fig.4. Upon the formation of the complex and the linear growth of absorbance with ligand (CY), the solution ultimately attained the specific molar ratio of the complex being studied. At this point, the straight line shows an inflection due to the extra ligand that was produced because of the ligand's varied absorption value at the complex's λ_{\max} . By applying the molar ratio approach, it was discovered that the ratio of CY dye [L] to metal [M] was 5/1.

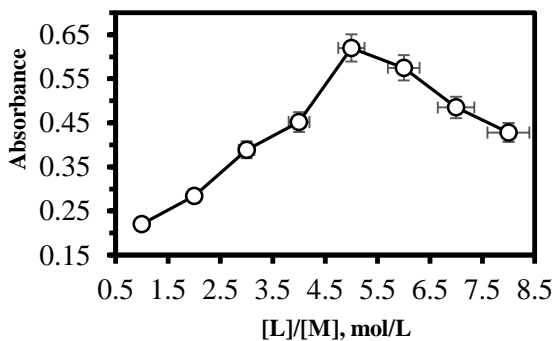


Fig. 4: Molar ratio method between CY dye and metal(Y)

FTIR Analysis:

This technique can be used to determine the function groups in the CY dye as well as the interaction between Y(III) and CY dye that occur when it complexes with Y(III) ions Fig. 5. The CY spectrum has the following distinctive bands.

- Broad band at 3456 cm^{-1} , associated with the N-H stretching vibrations [40].
- peaks at 2997 and 2881 cm^{-1} , attributed to C-H asymmetric and symmetric stretching vibrations, respectively) of $-\text{CH}_3$ group [40].
- peak at 1633 cm^{-1} , attributed to the stretching vibrations of C-C and C-N deformation mode [41].
- peak edge between $1400\text{-}1600 \text{ cm}^{-1}$, responsible for $>\text{C}=\text{N}$ stretching vibration of thiazole ring [34], [40-42].
- peaks at 1119 and 1042 cm^{-1} (weak peak), ascribed to asymmetric and symmetric stretching vibrations of SO_4^{2-} and N-H in-plane bending (and/or C-C stretching and C-H bending), respectively [34], [40-43].
- The peak at 935 cm^{-1} may be due to C-S stretching vibrations [41].

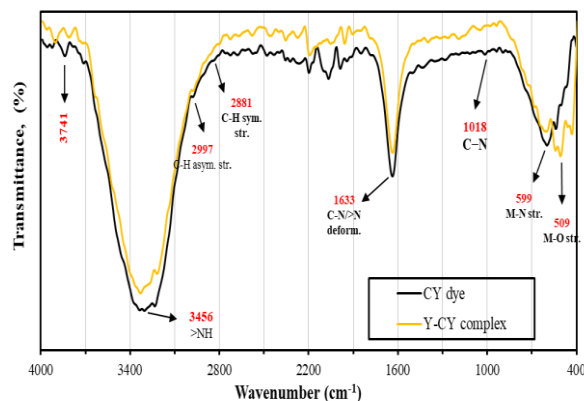


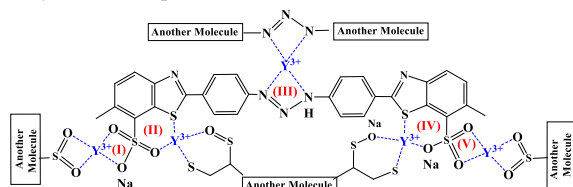
Fig. 5: FTIR spectra of the Y complex and pure CY dye

The comparison of both spectra before and after metal complexation show minimal variations, likely due to the low Y(III) concentration, making it challenging to detect these differences. Y(III) binding causes Y-CY complex spectrum changes, including typical bands disappearance, shifts, and reduced peak intensity due to $-\text{NH}_2$, $>\text{NH}$, $>\text{S}$, and SO_4^{2-} groups. The most substantial changes concern:

- the slightly changes at 3309 cm^{-1} can be directly associated with the binding of Y(III) ions, which affects the environment of NH groups,
- peaks in the region 1492 , 1428 , and 1280 cm^{-1} are strongly affected by metal Y(III) binding belonging to $>\text{C}=\text{N}$ unit [34, 44],
- the bending vibrations of the SO_4^{2-} group may be observed as weaker bands in the region around 700 to 600 cm^{-1} [34, 44],
- the appearance of new series of peaks at (681 , 640 , 599 cm^{-1}) and (542 , 509 , and 427 cm^{-1}) usually associated to the formation of M-O and M-N bond, respectively [41], and

- (e) The peak at 599 cm^{-1} in the C-S stretching vibration of CY dye spectrum is influenced by Y(III) binding, indicating its involvement in chelation [43-46].

Hence the binding mechanism can be considered as a complexation process between the N and SO_3^{2-} atoms in the CY dye and Y(III) ions, as follow in Scheme 2. The interaction (in Scheme 2) reveals that contribution modes (II and IV) form stable six-membered chelating rings, while other modes (I, III, and V) form four-membered rings. The interaction of metal ions between chains increases the stability of the complex.[34].



Scheme 2: The expected mechanism of the complexation between Clayton yellow dye and yttrium ions

3.2.5. EDX Analysis:

EDX analysis Fig.6 is used to assess the chemical composition of the CY following complexation with Y(III). The findings demonstrate that Y(III) has a unique peak, which suggests that Y(III) and the CY dye have complexed. Fig. 6: EDX spectra of pure CY dye (a) and its Y complex (b).

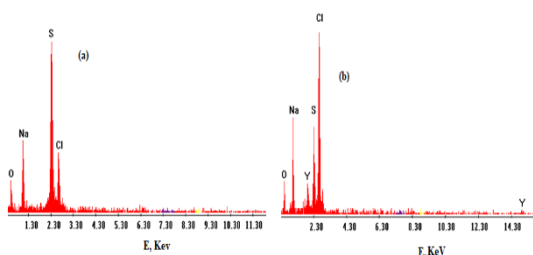


Fig. 6. EDX spectra of pure CY dye (a) and its Y complex (b).

3.2.6. Effect of Duration Time on the Stability of Yttrium Complex

The stability of the yttrium-Clayton Yellow complex was tested by measuring its absorbance every five minutes over time. The complex was shown to be stable for five minutes, following which it exhibited a gradual dissociation Fig. 7.

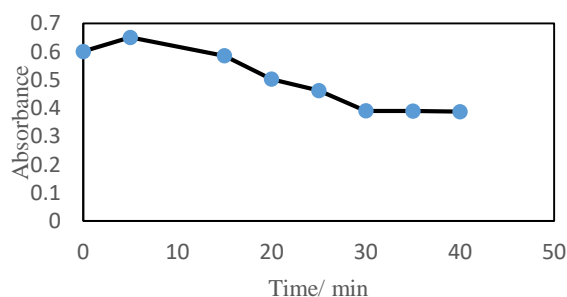


Fig. 7: Time's impact on the complex's stability. (5mL from 10^{-3}M CY, 0.3 mL of 10^{-3}M HCl, and 0.3 mL from pH 5 buffer; $\lambda_{\text{max}} = 499$).

3.3. Construction of Calibration Curve

The maximum and minimum yttrium detectable concentrations had to be established in accordance with Beer's law. To do this, a series of yttrium concentrations were created while fixing the other parameters, (0.3 mL from 10^{-3}M HCl, 0.3 mL from buffer pH (5), and 5 mL from 10^{-3}M CY dye). At the specified λ_{max} of 499 nm, each complex's absorbance was measured in relation to an appropriate blank solution. It is abundantly clear from the acquired data Fig. 8 that the maximum concentration limit for Y(III) reached is $12\text{ }\mu\text{g mL}^{-1}$. The yttrium complex's average molar absorptivity (\mathcal{E}) was determined to be $0.54 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ based on this straight line. The computed values for the molar absorptivity (\mathcal{E}), specific absorptivity (a), Sandell index (S), the limit of detection, and Beer's law obedience range for the binary complex of Y(III) were summarized in Table (2).

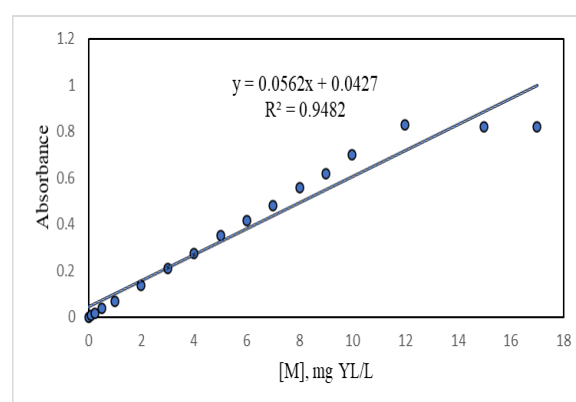


Fig. 8: Calibration curve of spectrophotometric determination of Y(III) binary complex. (5mL from 10^{-3}M CY, 0.3 mL of 10^{-3}M HCl, and 0.3 mL from pH 5 buffer; $\lambda_{\text{max}} = 499$).

Table 2: Summarizes the calculated data for binary complex of Y(III).

Parameters	Value
Molar absorptivity (\mathcal{E})	0.54×10^4
specific absorptivity (a)	6×10^{-2}
Sandell index (S)	1.67×10^{-2}
Range obeyed	$0.06 - 12\text{ }\mu\text{g mL}^{-1}$
Detection limit	$0.06\text{ }\mu\text{g mL}^{-1}$
Standard deviation	0.0012
Relative standard deviation	0.34 %

3.4. The Tolerance Ratio of Interfering REE Elements on Y (III) Determination

Studying the interference impact of additional rare earth elements (REEs) with yttrium was essential because they might react similarly in the same circumstances. The effect of different ion concentrations on yttrium ($1\mu\text{gml}^{-1}$) measurement using CY was investigated using the previously optimized additions (0.3 ml of 10^{-3}M hydrochloric acid, 0.3 ml of citrate buffer solution pH (5), and 5 ml of 10^{-3}M CY dye). This study summarized the tolerance limits of interfering ions on yttrium determination by CY dye. The concentration of foreign ions that resulted in an inaccuracy of less than $\pm 4\%$ in the absorbance value was considered the tolerance limit of each ion. Table (3) displayed the interference concentration on yttrium, and it suggested that yttrium might be determined below these concentration limits and above, which obstructs the use of the conventional spectrophotometric method to determine yttrium. To get over the interference effect, the following methods of selective precipitation and derivative spectrophotometry were employed. In order to separate yttrium with low levels of Ce, La, and Nd, El-Awady et al., 2019 [47] report that they used sodium carbonate to easily separate yttrium from REEs sulfate leach liquor, dissolve it in hydrochloric acid, and precipitate it using oxalic acid. Therefore, using a traditional spectrophotometric method was required to investigate the interference effect of Ce, La, and Nd on Y determination.

Table 3: The maximum permissible concentration limits of REEs.

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Tm	Yb	Tb	Ho	Er	Lu
Conc. mg/L	10	10	8	10	7	7	8	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Fig. 9 shows a spectral interference of these elements on Y determination and the conventional spectrophotometry method is inapplicable for determination of Y in presence of Ce, La, and Nd. The simplest way to achieve selectivity is to derivatively modify the spectrum; this process allows for the elimination of spectral interferences and, in turn, raises the assay's selectivity. A popular technique for separating valuable signals from noisy data is the derivatization of digital data [48, 49].

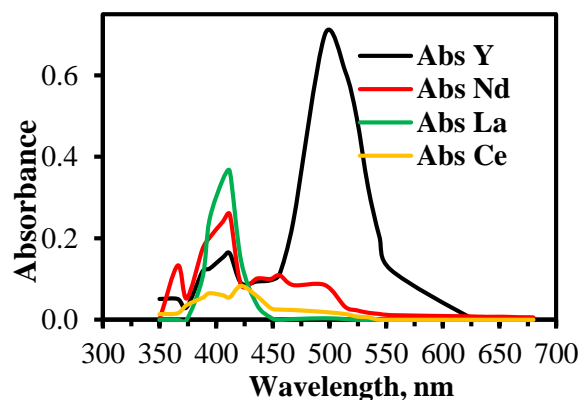


Fig. 9: Absorption spectra of Y, Ce, La, and Nd using CY conventional spectrophotometry method.

Spectrophotometers with built-in capabilities for generating derivative spectra of various orders were utilized, alongside the development of computer programs for this purpose. The spectra of the first, second, and third derivatives was investigated. It was observed that the initial derivative, as shown in Figs.10–11 increases the sensitivity by eliminating the interference effect from the other rare earth elements. It was discovered from the first derivative spectrum Figs.10-11 that Nd and Y only had substantial peaks at 378 and 476 nm, respectively. Nevertheless, in the first derivative, La and Ce have negative absorbance. Therefore, in the presence of other REE elements, the first-order derivative was the most appropriate for the selective determination of Y with CY.

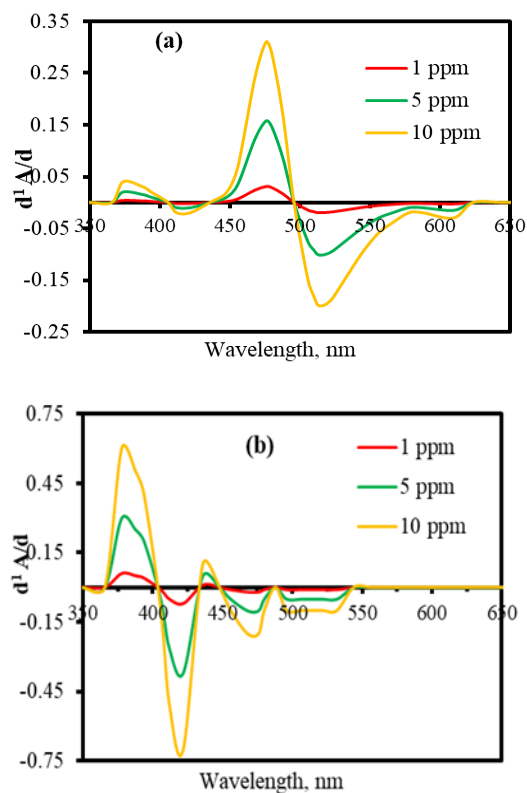


Fig. 10. First-derivative spectra of standard Y(III) (a) and Nd (III) (b) using CY dye.

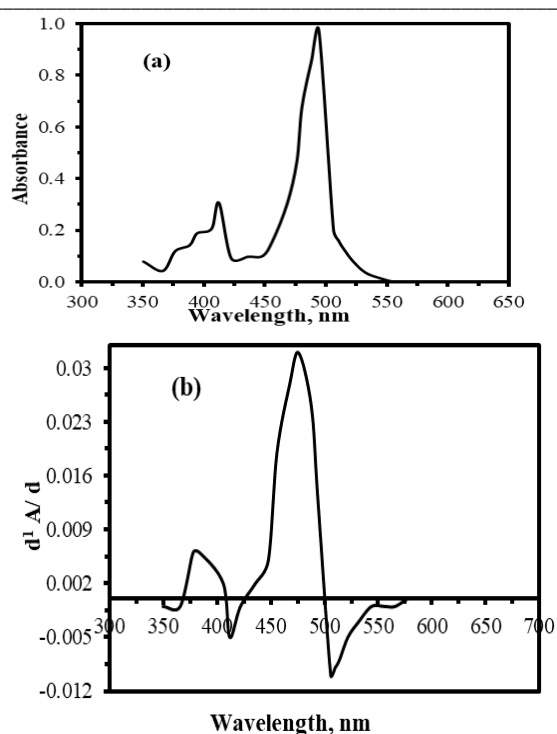


Fig. 11. Absorption spectra of a mixture of Ce, La, Nd and Y (a) and its First-derivative spectra(b) using CY conventional spectrophotometry method.

3.5. Application of the proposed method on standard geological samples

Egyptian monazite, Xenotime minerals and a rare earth oxide concentrate obtained from certified reference material (OKA-2), were employed to assess the efficacy of the proposed procedure. Firstly, a sulfuric acid digestion process was employed to dissolve each sample [28–32]. Subsequently, uranium, thorium and rare earth elements were precipitated directly from the sulfate leach liquor using 20% sodium carbonate [47]. The solution was transferred into a 250 ml glass beaker, where the majority of Th, Ce, La, Pr, Nd, Sm, and Gd were precipitated by gradually adding 20% sodium carbonate solution until the pH reached 0.5. Following the pH adjustment, the solution sample was stirred thoroughly with a magnetic stirrer for an hour at room temperature to ensure complete precipitation. Subsequently, the filtrate from each experiment was subjected to additional precipitation at a higher pH value, typically around 3, to facilitate the separation of uranium [47]. This was followed by filtration using filter paper (Whatman 41). Finally, at a basic medium (pH 9.0), the yttrium content was completely removed from the remaining solution [47]. After dissolving in HCl, this precipitate underwent refinement, followed by a secondary precipitation at pH 3.0 in the presence of oxalic acid. Subsequently, after dissolution in HCl, the yttrium (III) was quantified in the resulting concentrate using an optimally calibrated first-order derivative spectrophotometric technique with YC dye. When comparing the results obtained from the current method with those from ICP-OES, Table (4) illustrates that both samples

and certified reference materials could be accurately assessed.

Table. 4: Comparative analysis of the obtained results ICP and the present method.

Sample	Concentration of Y (%)					
	by ICP	This method	SD	SE	%E	Accuracy (Δ)
OKA-2*	0.2519	0.2517	1.0	0.57	0.023	0.01
Monazite	1.2	1.193	0.53	0.30	0.003	0.001
Xenotime	22.7	22.72	0.002	0.001	0.005	0.052

*Certified values reported by Canadian Central for Mineral and Energy Technology standards (CANMET), certifying agency

4. Conclusion

The present study suggests employing a simple spectrophotometric method for elemental determination offers a feasible alternative and low cost, to more complex analysis techniques (ICP-MS, AAS), providing a straightforward and effective approach for accurate quantification. Clayton's pioneering work enabled the first precise measurement of Y (III) amidst other rare earth elements, facilitated by the yellow chromogenic dye (CY). In the Y-CY solution within buffer at pH 5, the molar absorptivity at 499 nm is determined to be $0.54 \times 10^4 \text{ L.M}^{-1}.\text{cm}^{-1}$. Beer's law was observed within the concentration range of 0.06 to $12 \mu\text{g mL}^{-1}$ for Y(III). To mitigate interference and accurately estimate yttrium in the presence of other rare earth elements, first-derivative spectra were analyzed. The recently proposed method for determining yttrium in diverse rare earth concentrations sourced from monazite and xenotime, demonstrates feasibility, as evidenced by the attained analytical properties, including limit of detection, precision, and accuracy.

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