



Spectrophotometric Determination of Cerium(III) in Some Industrial and Plant Samples Using New Synthesized Azo-dye Reagent: Synthesis and Characterization



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NEW spectrophotometric method was proposed for the rapid and accurate determination of Ce(III) using a new synthesized sulfacetamide azo-dye reagent [N-(4-((2,3-dihydroxy-5-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)phenyl)diazanyl) phenylsulfonyl)acetamide] [DTPPA]. The reagent was characterized by IR, ¹HNMR and mass spectra. The developed method was based on the reaction of Ce(III) with DTPPA reagent to form brown colored complex in an alkaline medium using borate buffer at pH = 9 with absorption maximum at 560 nm. The method was enhanced by the use of cationic surfactant of cetylpyridinium bromide (CPB). Different factors affecting the formation and stability of the complex such as reagent concentration, time, temperature, solvents and order of addition were also studied. The composition of the complex was found 1:2 (metal: ligand) by both Job's and molar ratio methods. The stability constant of the complex was calculated to be 3.387×10^6 . Beer's law was obeyed in the concentration range of 5.0-100 $\mu\text{g mL}^{-1}$ of Ce(III) with molar absorptivity and Sandell's sensitivity $1.020 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.01373 \mu\text{g cm}^{-2}$, respectively. The proposed method was applied for the determination of micro-amounts of Ce(III) in some industrial and plant samples. The Ce(III) complex was also prepared in the solid state.

Keywords: Spectrophotometry, Cerium(III), Azo-dye reagent, Industrial and plant samples.

Introduction

Azo dyes are distinguished by the appearance of -N=N- azo group, which was important in the dye-stuffs industry, drugs, cosmetics, redox metalochromic indicators and biological activities including antibacterial and some pathogenic bacteria [1]. On the other hand, azo compounds were studied and widely used in many applications such as printing systems, optical recording medium and molecular memory storage owing to their accurate electronic, optical and thermal characteristics [2].

Cerium was used in many significant industries such as; nuclear reactor, alloy with chromium and nickel, microwave apparatus, fluorescent and

energy saving lamps, optical masers or lasers, television devices, in addition to agriculture and forestry. It was also used as a glass polishing compound, as a core for the carbon electrodes of arc lamps and for brilliant mantles for gas lighting [3,4]. The ore minerals of monazite, bastnasite and allanite were the most important source of cerium [5]. Cerium was accumulated gradually in water soils and soils and this lead to raising its concentrations in humans, animals and soil particles [6]. Increasing industrial use and reports on cerium toxicity made it essential to have analytical procedures suitable for monitoring of cerium in environmental and related fields. For this purpose, some suitable analytical methods were utilized for the determination of cerium

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such as electrothermal vaporization ICP-AES after high performance liquid chromatography (HPLC) separation [7], ion selective electrode [8], stripping voltammetry [9], spectrofluorometry [10], inductively coupled plasma atomic emission spectroscopy (ICP – AES) [11]. These methods were expensive, complicated and need long time. However, UV-Vis spectrophotometric methods were widely used owing to their sensitivity, rapidity, low cost, simplicity, good selectivity and wide applications. So, various analytical reagents such as; propionylpromazine phosphate [12], 4-methyl-7-hydroxycoumarin [13], 1, 3-o-hydroxyphenyl-5-phenylformazan [14], naphthol green B [15], hydrazinecarboxymide-2-[(2-hydroxyphenyl)methylene] [16], sulphanic acid [17], arsenazo-III [18], 2,4-Dimethyl pentan-3-one [19] were used for the spectrophotometric determination of cerium.

In the present study, the synthesis of a new azo-dye reagent [N-(4-((2,3-dihydroxy-5-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)phenyl) diazenyl)phenylsulfonyl)acetamide] [DTPPA] and its metal complex with Ce(III), was reported. Moreover spectral and analytical studies have been investigated for comparative purposes.

Material and Methods

Apparatus

All absorbance measurements were carried out with a (T80 UV/Vis double beam spectrophotometer, PG instruments Ltd Company, United Kingdom), spectral bandwidth 2.0 nm, with 10 mm matched quartz cells. All pH measurements were made using pH meter (Adwa pH-meter, Model AD 1030, Romania). The infrared spectra were recorded in KBr pellets on a Pye Unicam Sp-3-300 or a Shimadzu FTIR 8101 PC infrared spectrometer in the range from 4000-400 cm^{-1} (Cairo University, Cairo, Egypt). The ^1H NMR spectra were recorded on BRUKER (400 MHz) spectrometer in DMSO-d_6 solvent (Zagazig University, Faculty of Science, Zagazig, Egypt). Mass spectrometry was determined on DI Analysis Shimadzu QP-2010 Plus (Cairo University, Cairo, Egypt). C, H and N analysis was carried out on a Perkin Elmer CHN 2400. All melting points are uncorrected and were determined on a Gallen Kamp electric melting point apparatus. Molar conductivities of the solutions of the ligand and its metal complex in DMSO with concentrations of 1×10^{-3} M were measured on CONSORT K410. The completion of the reactions was confirmed using thin layer chromatography (TLC) on silica gel coated aluminum sheets.

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Reagents and solutions

All chemicals and solvents used were of analytical grade reagents and were used without further purification. Distilled water was used throughout the experiments.

[N-(4-((2,3-dihydroxy-5-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)phenyl) diazenyl)phenylsulfonyl)acetamide] (DTPPA) reagent

Stock solution of (1×10^{-3} M) of (DTPPA) was prepared by dissolving (0.0527 g, M. wt. = 527.46 g mol^{-1}) of the reagent in 100 mL ethanol.

Standard cerium solution

Stock solution of ($1000 \mu\text{g mL}^{-1}$) of cerium nitrate hexahydrate was prepared by dissolving 0.04342 g of $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, M. wt. = 434.22 g mol^{-1} in 100 mL of distilled water. Working solutions of lower concentrations were prepared from the stock solutions by appropriate dilution.

Surfactant solutions

Series of different surfactants including cetyltrimethyl ammonium bromide (CTAB), Triton X-100, sodium lauryl sulphate (SLS), cetylpyridinium bromide (CPB), tween 80 and sodium dioctyl sulfosuccinate (Aerosol GPG-E) were prepared at concentration (1×10^{-2} M) by dissolving the appropriate amount of each surfactant in 100 mL distilled water and were used without further purification.

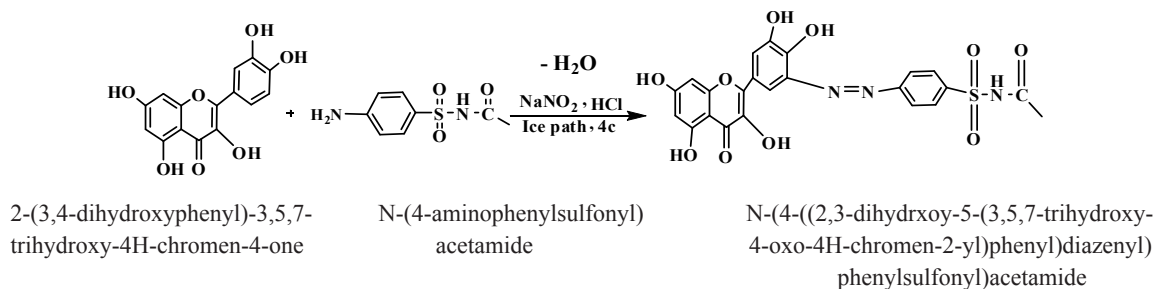
Buffer solutions

Series of buffer solutions of universal buffer (pH 2.0-11.0), borate buffer (7.0-10.0), citrate buffer (3.0-6.0), acetate buffer (3.0-6.0) and phosphate buffer (7.0-11.0) were prepared by standard methods [20-22].

Procedures

Synthesis of [N-(4-((2,3-dihydroxy-5-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)phenyl) diazenyl)phenylsulfonyl)acetamide] (DTPPA) reagent

(0.642 g, 3 mmole) of N-(4-aminophenyl-sulfonyl) acetamide was dissolved in 10 mL hydrochloric acid (1:1), and diazotized at ($0-5^\circ\text{C}$) with sodium nitrite solution (0.206 g, 3 mmole) solution in water (5.0 mL). The resulting diazo-solution was added dropwise with stirring to an ice cooled solution of (0.906g, 3 mmole) of 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one [quercetin dihydrate] which was dissolved in (10 mL) of (1 M) sodium hydroxide. The precipitate was filtered off and washed several times with (1:1) ethanol: water mixture then left to dry over CaCl_2 in a desiccator under vacuum, (Scheme 1). An orange solid with 76% yield and m.p. $234-236^\circ\text{C}$ was obtained.



Scheme 1: Synthesis of the DTPPA reagent

Synthesis of the Ce(III)-DTPPA solid complex

One mmole of DTPPA azo-dye reagent (0.527 g) was dissolved in 20 mL ethanol, then it was added dropwise to an ethanolic solution (20 mL) of 0.5 mmole [Ce(NO₃)₃·6H₂O] (0.217 g). The solution was stirred for 8 hours at room temperature till the complex was completely precipitated. The mixture was left for slow evaporation to concentrate the reaction mixture; the formed precipitate was filtered off, washed several times with double distilled water, and dried over CaCl₂ in a desiccator under vacuum. A brown solid with 84% yield and m.p. 260-262 °C was obtained.

General spectrophotometric procedures

Aliquots solutions of Ce(III) standard solution (1.0-130 µg mL⁻¹) were transferred into a series of 10 mL calibrated flasks containing 2.0 mL (1×10⁻³ M) of DTPPA reagent and followed by 5.0 mL borate buffer (pH = 9). Then, 0.5 mL of CPB surfactant was added to each flask and the volumes were adjusted to the mark with distilled water. The contents were mixed well by shaking for 2 minutes. Immediately and at room temperature, the absorbance was measured at 560 nm against the blank solution. By plotting the absorbance against the concentration of Ce(III) in µg mL⁻¹, the range of Beer's law can be determined.

Applications

Determination of Ce(III) in plant samples [Tobacco or Barley]

0.55 g of dried plant was dissolved in a mixture of [0.5 mL concentrated sulphuric acid, 1.0 mL perchloric acid and 5.0 mL concentrated nitric acid] with stirring and heating gently by rising the temperature gradually for 20 minutes. The mixture was digested by heating for 15 minutes till the white fumes were evolved. The solution was cooled and 10 mL of distilled water was added with heating to 70 °C again for 10 minutes. The solution was cooled to room temperature, diluted to fixed volume suitable

to the applicable concentration range and then the above procedures were followed. V(V) was masked by using Thiourea [23].

Determination of Ce(III) in glass: [Colored TV screen or Fluorescent glass]

A 0.5 g of glass sample was weighed and dissolved in a mixture consisting of 5.0 mL concentrated sulphuric acid and drops of HF with heating till completely dissolving and dryness. 20 mL of distilled water were added with heating again to 80 °C for 10 minutes. The solution was then cooled, diluted and analyzed as mentioned in the above procedures.

Determination of Ce(III) in monazite sand

A 0.5 g of monazite sand was dissolved in 10 mL concentrated H₂SO₄ and was evaporated to almost dryness. The residue was then diluted to 50 mL with distilled water, boiled, filtered and washed with hot water. Cerium ion was precipitated as oxalate by the addition of excess hot solution of oxalic acid till complete precipitation. The oxalate was filtered and ignited to the oxide, which was dissolved in concentrated HCl and HNO₃ and evaporated till dryness. The residue was dissolved again in 5.0 mL HCl (1M) with continued heating to 70 °C for 30 minutes. The solution was cooled, filtered, diluted and analyzed as above. Uranium (VI) was masked by using ammonium sulphate [24], while thorium (IV) was masked by using urea [25].

Determination of Ce(III) in crude phosphoric acid

5.0 mL of crude phosphoric acid were drawn and diluted to 50 mL with distilled water. The concentration of the Ce(III) was determined by the procedures described above.

Results and Discussion

Structural characterization of DTPPA reagent and its Ce(III) solid complex

The structure of DTPPA azo-dye reagent and

its solid complex was confirmed by structural data obtained using IR, ¹HNMR, UV-Vis, mass spectra and elemental analysis measurements, (Table 1).

Mass spectra

The mass spectra (Fig. 1) of the reagent showed a signal at M⁺ (m/e) = 527.30 (3.5%) attributed to parent ion and another one at m/e = 302.09 (100%) for base peak. Mol. Formula: C₂₃H₁₇N₃O₁₀S (527.46g mol⁻¹). The mass spectra of the Ce(III) complex showed a signal at m/z: 1272.02 (100.0%), 1273.02 (51.0%), 1274.02 (32.4%), 1275.02 (10.2%), 1274.01 (9.1%), 1275.01 (4.8%), 1273.01 (4.2%), 1276.02 (2.8%), 1276.03 (2.5%), 1275.03 (2.1%), 1276.01 (1.5%), 1277.02 (1.1%).

Infrared spectra

IR spectrum of the free ligand and its Ce(III)

solid complex was shown in (Fig. 2). The free ligand displayed broad bands at 3394 and 3197 cm⁻¹ assigned to the stretching modes of hydroxyl (O-H) and amidic (NH) groups, respectively. The azo (N=N) group was appeared at 1516 cm⁻¹. In addition, the bands observed at 1705, 1674 and 1315 cm⁻¹ were distinguishing to ν(C=O), ν(C=O, amide) and asymmetric sulfone (SO₂) groups, respectively [26]. However in the IR spectra of Ce(III) complex, -OH group band which appeared at 3394cm⁻¹ in the ligand was migrated towards higher frequencies 3417 cm⁻¹. Also, the ν(N=N) band was shifted to lower value at 1458 cm⁻¹ due to the donation of the lone pair of electrons present on the nitrogen atom to the metal ion indicating the participation of the nitrogen atom of the azo group in the coordination [27,28]. Further, the band which appeared around 694 cm⁻¹

TABLE 1: Analytical and physical data for (DTPPA) and its Ce(III) complex.

Compounds	Yield, %	Mp, °C	Color	(Calcd.)				Λ S cm ² mol ⁻¹
				Found, (%)				
M.Wt.								
(M.F.)				C	H	N	M	
				(52.37)	(3.25)	(7.97)		0.0
DTPPA	76	234-236 °C	Orange	52.10	3.03	7.71	-	
527.46 (C ₂₃ H ₁₇ N ₃ O ₁₀ S)								
[Ce(DTPPA) ₂]NO ₃ ·H ₂ O	84	260-262 °C	Brown	(43.40)	(2.69)	(7.70)	(11.01)	77.13
(CeC ₄₆ H ₃₄ N ₇ O ₂₄ S ₂)1273.04				43.20	2.53	7.52	11.00	

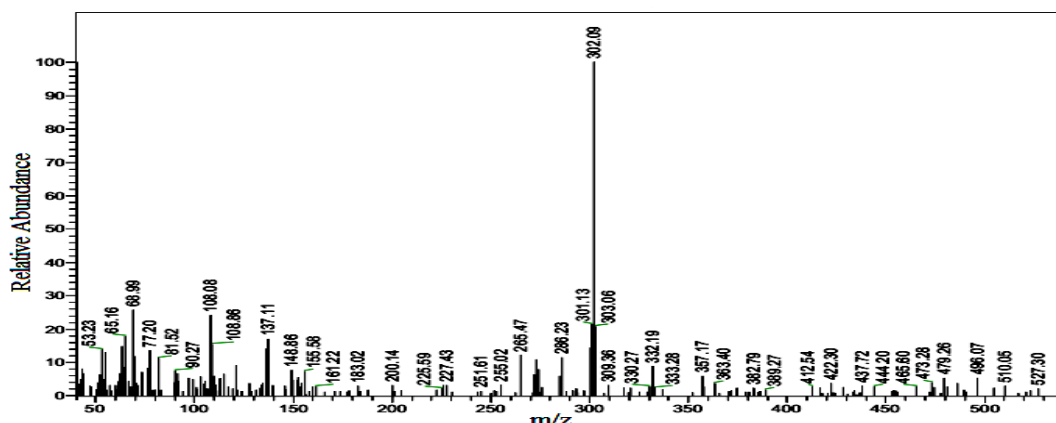


Fig. 1: Mass spectra of DTPPA azo-dye reagent

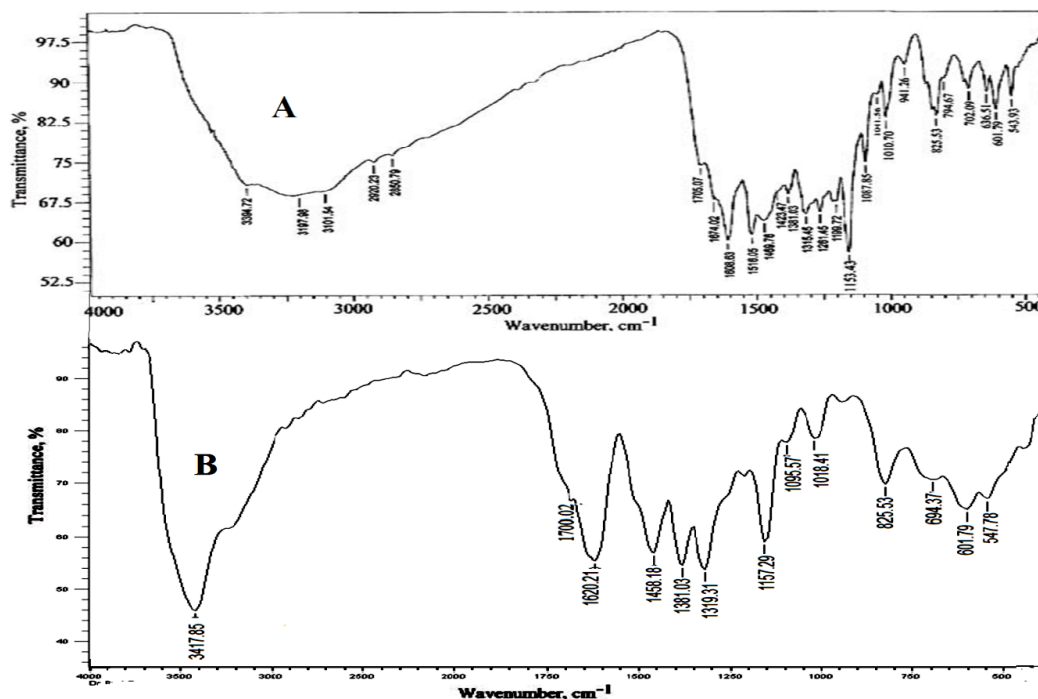


Fig. 2: IR spectra for (A) DTPPA azo-dye reagent and (B) Ce(III)-DTPPA complex.

was assignable to $\nu(\text{M-O})$ stretching mode.

¹HNMR spectra

The ¹HNMR (DMSO-d₆) spectrum data of the ligand and its Ce(III) solid complex was shown in (Fig. 3). The free reagent showed $\delta = 1.96$ (s, 3H, CH₃), 6.18 (s, 1H, Ar-H), 6.40 (s, 2H, Ar-H), 6.76 (d, 1H, $J = 6.8$ Hz, Ar-H), 6.89 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.51 (d, 2H, $J = 8.40$ Hz, Ar-H), 7.55 (s, 1H, Ar-H), 9.30 (s, 1H, OH, exchange with D₂O), 9.34 (s, 1H, OH, exchange with D₂O), 9.59 (s, 1H, OH, exchange with D₂O), 10.78 (s, 1H, OH, exchange with D₂O), 12.10 (s, 1H, OH, exchange with D₂O) and 12.48 (s, 1H, NH, exchange with D₂O). The comparison between the azo-dye reagent and its Ce(III) complex was showed that both signals was remained as it's unless the signal of two hydroxyl groups at $\delta = 9.30, 9.59$ (s, 2H, OH) in azo-dye. The chelation process was via the two OH groups as a result of the variation in the chemical shift [26].

Electronic spectra

The electronic absorption spectra of **DTPPA azo-dye reagent** and its **Ce(III)-DTPPA complex** from 200 to 800 nm are shown in Fig. 4. Free **DTPPA** ligand showed two essential absorption bands at 330 nm and 412 nm, which may be assigned to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions, respectively [26]. These transitions were existed also in the spectra of the complexes, but they shifted to

higher values, confirming the coordination of the ligand to the metal ions. In UV-Vis. spectra, the weak band should be at 492 nm are due to ligand-Ce(III) charge transfer (CT) band in the complex, which is absence in the free ligand. However, the weak broad band at 578 nm is due to different d-d transitions of the metal ions as mentioned [29,30].

Spectrophotometric study of the complex in solution

Absorption spectra

The absorption spectra of reagent and its complex were measured in the range of 200-800 nm against the blank solution. It was observed that, Ce(III) with [DTPPA] reagent form brown colored complex at 524 nm in alkaline medium. The addition of cetylpridinium bromide (CPB) surfactant was resulted in an increase in absorbance with a red shift by 36 nm, (Fig. 5).

Optimization of experimental conditions

Different factors were tested to select the optimum conditions necessary for the rapid formation and stability of the complex under investigation.

Effect of pH and buffer solutions

The effect of pH on the complex formation was studied in the pH range 1-12 by using 0.2 M NaOH and 0.2 M HCl solutions. It was observed that the suitable pH range for complete formation

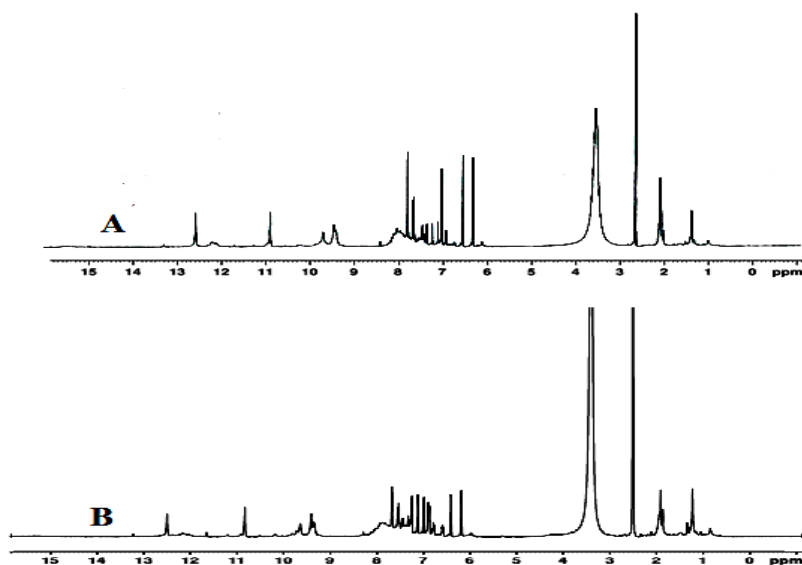


Fig. 3: ^1H NMR spectra for (A) DTPPA azo-dye reagent and (B) Ce(III)-DTPPA complex

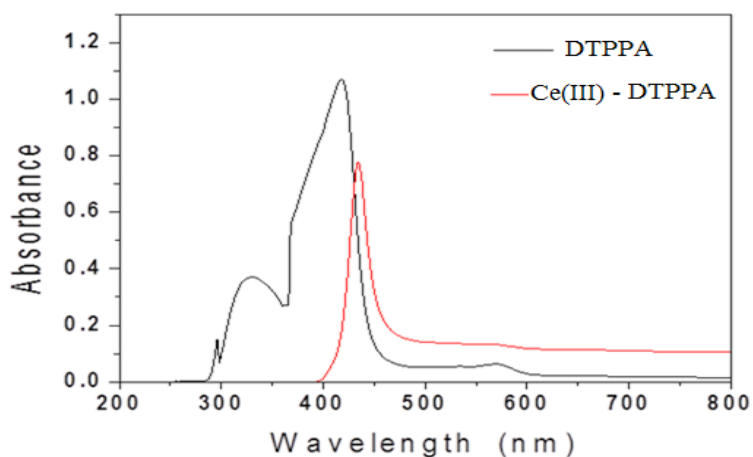


Fig. 4. Electronic absorption spectral data of DTPPA azo-dye reagent and its Ce(III)-DTPPA complex

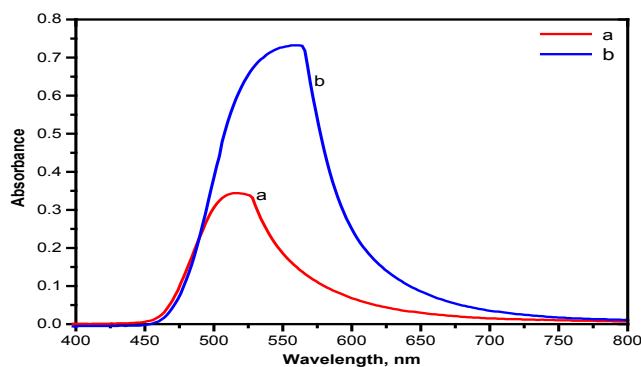


Fig. 5: Absorption spectra of (a) Ce(III)-DTPPA complex, $\text{Ce(III)} = 100 \mu\text{g mL}^{-1}$, 2.0 mL (1.0×10^{-3} M) of DTPPA against reagent blank (b) Ce(III)-DTPPA complex with 0.5 mL (1.0×10^{-2} M) of CPB against the blank solution

of the complex was from pH = 7 to 9, (Fig. 6). In more acidic or more alkaline solutions, the absorbance was decreased gradually due to incomplete formation and partial dissociation of the complex. In order to fix the pH of the media, the effect of different buffer solutions (acetate, citrate, borate, phosphate and universal) was studied. It was found that the maximum absorbance and color intensity of the complex was obtained using borate buffer (pH = 9). Further, 5.0 mL of borate buffer of pH = 9 gave the maximum absorbance value for the complex formation.

Effect of reagent concentration:

The effect of reagent concentration on the complex formation was studied by measuring the absorbance of the solutions containing fixed concentration 1.0 mL of ($1000 \mu\text{g mL}^{-1}$) of Ce(III) ion and varied concentrations (0.5 to 5.0 mL of 1×10^{-3} M) of the reagent. It was observed that the

maximum absorbance was obtained by using 2.0 mL of (1×10^{-3} M) of DTPPA reagent, (Fig. 7).

Effect of time

In order to study the effect of time on stability of the formed complex, the absorbance readings of the complex were recorded at different time in the range from 1.0 to 120 min and after 24, 48 hours at room temperature. The complex was formed spontaneously with maximum absorbance value after 5 minutes and remained stable up to 24 hours, (Fig. 8).

Effect of temperature

The effect of temperature on stability of the formed complex was studied in the range of $20\text{--}75^\circ\text{C}$. It was found that the color intensity of the complex was stable at room temperature ($25 \pm 2^\circ\text{C}$). On the other hand, the absorbance values were decreased at higher temperatures,

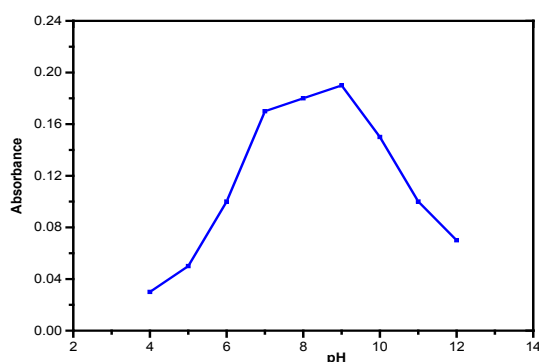


Fig. 6: Effect of pH on the complex formed between Ce(III) and DTPPA reagent; Ce(III) = $100 \mu\text{g mL}^{-1}$ and 2.0 mL (1×10^{-3} M) DTPPA reagent

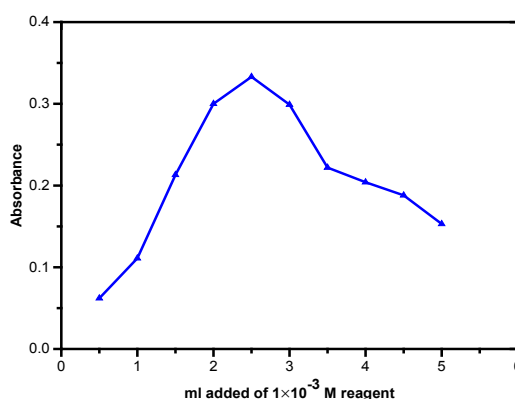


Fig. 7: Effect of reagent concentration on the complex formed between Ce(III) and DTPPA reagent; Ce(III) = $100 \mu\text{g mL}^{-1}$ and (1×10^{-3} M) DTPPA reagent

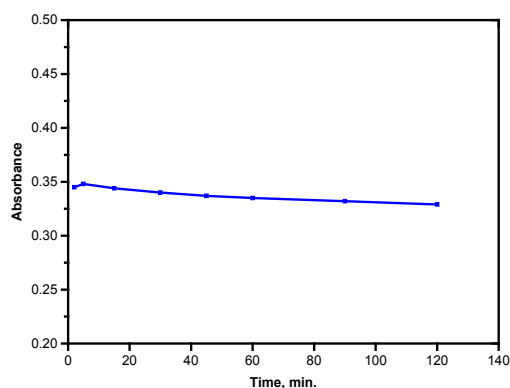


Fig. 8: Effect of time on the complex formed Between Ce(III) and DTPPA reagent, $[Ce(III)] = 100 \mu\text{g mL}^{-1}$, $[DTPPA] = 2 \times 10^{-4} \text{ M}$, $\text{pH} = 9$

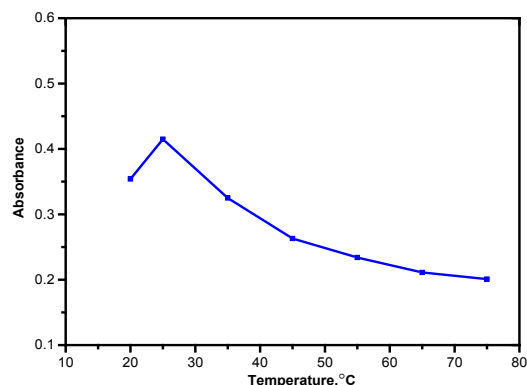


Fig. 9: Effect of time on the complex formed Between Ce(III) and DTPPA reagent, $[Ce(III)] = 100 \mu\text{g mL}^{-1}$, $[DTPPA] = 2 \times 10^{-4} \text{ M}$, $\text{pH} = 9$

(Fig. 9).

Effect of surfactants

In order to improve the sensitivity of the complex formation, the effect of different types of cationic surfactants [CTAB, CPB], nonionic surfactants [Triton X-100, Tween 80] and anionic surfactants [SLS, Aerosol GPG-E] were studied. It was observed that the absorbance was increased by CTAB, CPB and Tween 80, but the maximum value was obtained when cetylpridinium bromide (CPB) was used, (Fig. 10, A). Moreover, the effect of different concentrations ranging from 0.2 to 2.0 mL ($1 \times 10^{-2} \text{ M}$) of CPB was studied. The result was showed that the maximum absorbance was obtained by using 0.5 mL ($1 \times 10^{-2} \text{ M}$) of cetylpridinium bromide (CPB), (Fig. 10, B). At higher concentrations of CPB, the absorbance was decreased due to the appearance of turbidity.

Effect of organic solvents

The effect of different organic solvents on the absorbance of the formed complex was studied in methanol, ethanol, isopropanol, butanol, acetone, DMF and DMSO. It was evident that ethanol was the most suitable solvent for complex formation and higher absorbance value.

Effect of order of addition

Different absorbance measurements were performed by changing the order of the addition of the metal ion Ce(III), DTPPA reagent, buffer (borate $\text{pH} = 9$) and CPB surfactant. It was evident that the order (reagent-metal ion-buffer-surfactant), results in maximum absorbance. Otherwise, the other addition orders were led to

decrease in the absorbance values.

Stoichiometric ratio

In order to establish the molar ratio between Ce(III) and DTPPA reagent, Job's method of continuous variation was applied [31]. In this method, an equimolar solution of metal ion and reagent in different proportions from 0.1 mL to 0.9 mL ($1 \times 10^{-3} \text{ M}$) of the same concentration was mixed, while the total molar concentration was kept constant. The absorbance was measured at 560 nm and plotted versus mole fraction (Fig. 11, A). The composition of the complex was also confirmed by molar ratio method [32]. In this method, the concentration of metal ion was kept constant at 1.0 mL of ($1000 \mu\text{g mL}^{-1}$), while that of the reagent was differed from 0.2 to 2.4 mL of ($1 \times 10^{-3} \text{ M}$). The absorbance of these solutions was recorded at 560 nm and then plotted against the molar ratio $[\text{ligand}]/[\text{metal}]$, (Fig. 11, B). Both methods showed that Ce(III) and reagent ratio was 1:2 as indicated in (Scheme 2). The stability constant of the complex was calculated by Job's method [33] and found to be 3.387×10^6 which showed the high stability of the formed complex.

Calibration graph

The calibration graph was constructed from the spectrophotometric measurements performed after the optimization of all optimum factors of the formed complex as described above. The calibration curve was obeyed in the concentration range of 5 to $100 \mu\text{g mL}^{-1}$ as showed in (Fig. 12). A Ringbom plot was also carried out to detect the optimum range of concentration for a system that

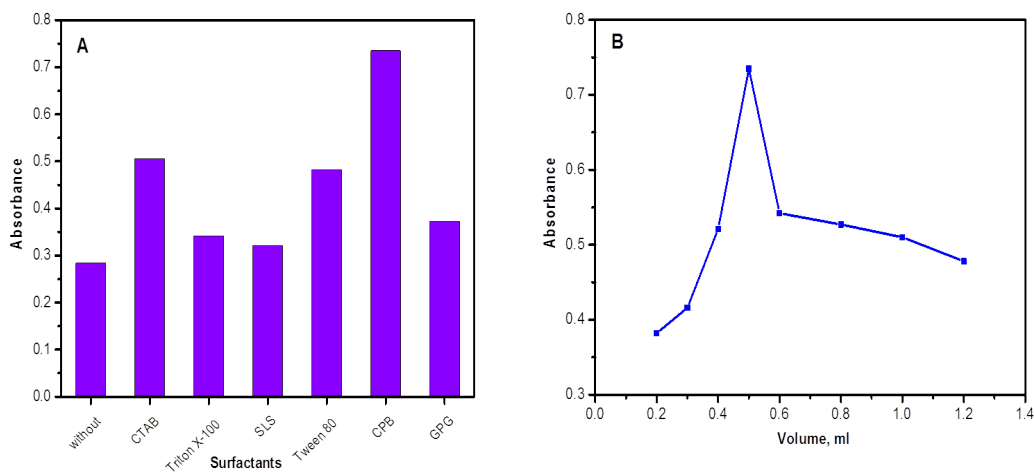


Fig. 10: (A) Effect of surfactants type and (B) surfactant volumes on complex formed between Ce(III) and DTPPA reagent, $[Ce(III)] = 100 \mu g mL^{-1}$, $[DTPPA] = 2 \times 10^{-4} M$, borate buffer (pH 9), at once and room temperature

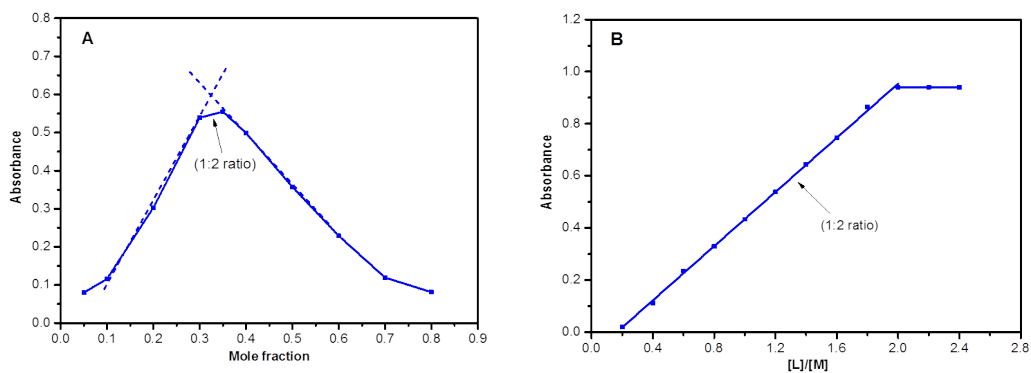
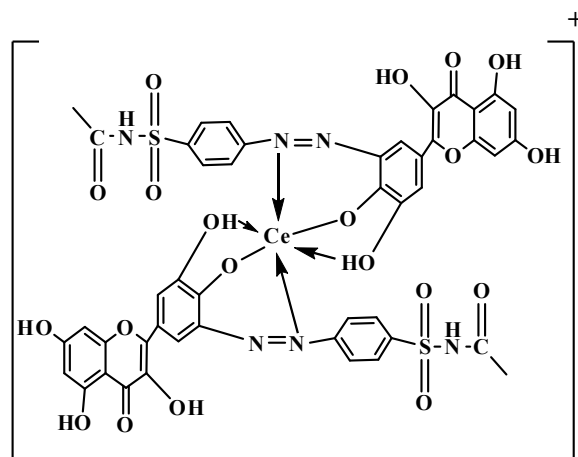


Fig. 11: Stoichiometry of Ce(III)-DTPPA complex by (A) Job's method of continuous variation (B) molar ratio method, $[Ce(III)] = [DTPPA] = 1000 \mu g mL^{-1}$, pH = 9, 0.5 mL ($1.0 \times 10^{-2} M$) of CPB



Scheme 2: The proposed coordination mode of Ce(III) with DTPPA reagent.

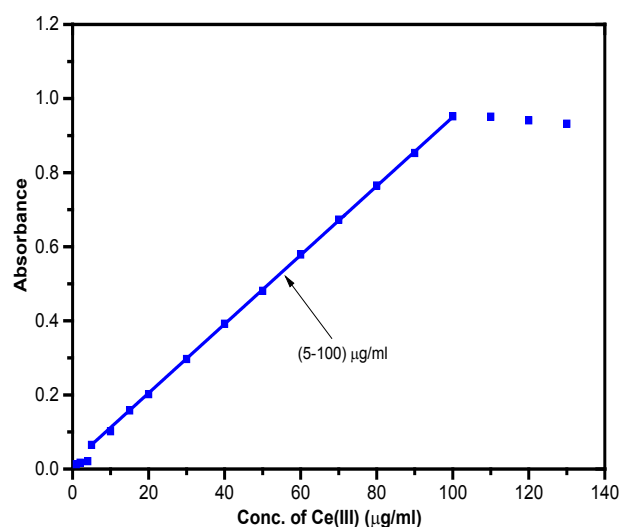


Fig. 12: Calibration graph of Ce(III)-DTPPA complex, [DTPPA] = 2×10^{-4} M, 0.5 mL (1×10^{-2} M) of CPB, borate buffer (pH 9), $\lambda_{\text{max}} = 560$ nm

obeyed Beer's law. It was achieved at intermediate concentration values ($10\text{--}100 \mu\text{g mL}^{-1}$).

Statistical characteristics

The method has good reproducibility for a set of seven measurements of $50 \mu\text{g mL}^{-1}$ of Ce(III) under optimum conditions. Some different statistical parameters such as standard deviation, molar absorptivity, sandell's sensitivity, student F-test, student t-test, correlation coefficient, limit of detection (LOD) and limit of quantification (LOQ) were summarized in Table (2). The data listed in Table 2 indicated the excellent linearity, high sensitivity and good accuracy and precision of the proposed method.

Effect of diverse ions

The effect of 100 folds molar excess of many interfering ions which were added relative to ($40 \mu\text{g mL}^{-1}$) of Ce(III) was tested in the determination of the metal ion with DTPPA reagent. Then the absorbance was measured as the procedures mentioned above. It was evident that, Cd(II), Cr(III), Fe(III), As(III), Mg(II), Hg(II), Zn(II), Al(III), La(III), Nd(III), Pr(III), Sm(III), Sr(III), Gd(III), Y(III), Cu(II), Pb(II), Mo(VI), PO_4^{3-} , NO_3^- , SO_4^{2-} and Cl⁻ do not interfere in this determination, while Th(IV), Co(II), V(V), Ni(II), U(VI) and Ba(II), CO_3^{2-} and NH_4^+ interfered seriously.

Analytical applications

The proposed method was applied for the determination of Ce(III) in monazite sand,

crude phosphoric acid, tobacco, barley, colored TV-screen and fluorescent glass. The results listed in Table (3) showed good agreement with the recommended method and indicated the applicability of the proposed method.

Comparative study of the proposed methods with other spectrophotometric methods:

The performance of the proposed method was compared with that of other existing UV-visible spectrophotometric methods (Table 4). It was clear from the table that the proposed method was simple, sensitive, selective, not complicated and required less time to complete the analysis more than many other spectrophotometric methods. Moreover, the method was free from most interfering ions and provided a wide range for the determination of Ce (III).

Conclusion

The new synthesized sulfacetamide azo-dye reagent proved as an excellent complexing agent for the spectrophotometric determination of Ce (III). The proposed method is simple, sensitive, accurate and doesn't involve extraction, heating or other special conditions. This complex was formed directly and remained stable for more than 24 hours. The absorbance of the complex was increased by using CPB as a surfactant. The statistical data proved that the method has high sensitivity and good accuracy and precision. The proposed method was successfully applied for the

TABLE 2: Statistical parameters of the proposed method

Parameters	Selected value
Molar absorptivity $L \cdot mol^{-1} \cdot cm^{-1}$	1.020×10^4
Sandell's sensitivity $\mu g \cdot cm^{-2}$	1.373×10^{-2}
Standard deviation (SD)	3.696×10^{-3}
Relative standard deviation (RSD)	7.391×10^{-3}
Standard error of the mean (SEM)	1.396×10^{-3}
Limit of detection (LOD) $\mu g \cdot mL^{-1}$	1.3100
Limit of quantification (LOQ) $\mu g \cdot mL^{-1}$	3.9699
Student's t-test	4.295
Student's F-test	1.100
Correlation coefficient	0.99996
Ringbom plot $\mu g \cdot mL^{-1}$	10-100
Intercept (a)	0.01892
Slope (b)	0.00931
S.D. of intercept S_a	0.00146
S.D. of slope S_b	2.570×10^{-5}

TABLE 3: Determination of Ce(III) in some industrial and plant samples

Sample	Proposed method ^a		Recommended Method b	Recovery %	RSD %
	Taken ($\mu g \cdot mL^{-1}$)	Found ($\mu g \cdot mL^{-1}$)			
Monazite sand	16	15.97	16.99	99.81	0.190
Crude phosphoric acid	15	14.99	14.93	99.93	0.100
Tobacco plant	18	17.96	17.90	99.77	0.231
Barley plant	14	13.96	14.09	99.71	0.288
TV screen	15	14.96	15.05	99.73	0.270
Fluorescent glass	16	15.96	15.98	99.75	0.251

^a: proposed method for determination of Ce(III) with DTPPA reagent

^b: Recommended method following to Sulaiman, et al. (2013) [34].

TABLE 4: Comparison of the proposed method with reported UV-visible spectrophotometric methods for the determination cerium:

Reagent	λ_{\max} (nm)	Beer's law ($\mu\text{g mL}^{-1}$)	Analysis time	Remark	Ref.
Propionyl promazine phosphate	513	1.0-11.0	Immediately and stable for 50 min.	Less stable. Proper analytical parameters were not fixed and it has low linear range.	[12]
1, 3-o-hydroxyphenyl-5-phenylformazan	596	0.15-2.5	5 min. and stable for 24 hrs.	Has low linear range.	[14]
naphthol green B	710	0.08–2.4	8 min.	Involved complicated steps and has low linear range.	[15]
Sulphanilic acid	490	10.0-100.0	Immediately and stable for 20 min.	Less stable and less sensitive.	[17]
2,4-Dimethyl pentan-3-one	295	1.0-10.0	15 min.	Involved extraction and complicated steps.	[19]
[N-(4-((2,3-dihydroxy-5-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)phenyl)diazanyl)phenyl sulfonyl)acetamide] (DTPPA)	560	5.0-100.0	Immediately and stable up to 24 hrs.	All proper analytical parameters were fixed. High sensitive, not complicated, rapid and have wide linear ranges.	Present study

determination of cerium (III) in monazite sand, crude phosphoric acid, barley, tobacco, colored TV-screen and fluorescent glass.

References

- Al-Adely K.J., Synthesis and spectrophotometric studies of some transition metal complexes with new azo dye 2-[2-(6-methoxy benzothiazolyl)azo]-4-nitro phenol. *Asian J. Chem.*, **24**, 5597-5601(2012).
- Kirkan B. and Gup R., Synthesis of new azodyes and copper (II) complexes derived from barbituric acid and 4-aminobenzoylhydrazone. *Turk. J. Chem.*, **32**, 9-17(2008).
- Janghel E.K. and Pervez Y., Facile spectrophotometric determination of cerium using malachite green-iodide system in geological and environmental samples. *J. Sci. Ind. Res.*, **68**, 940-944(2009).
- Tan L.V. and Ngoc Le N.T., Spectrophotometric determination of cerium using azocalixarene derivative in geological samples. *Int. J. Chem. Eng. Appl.*, **2**, 381-384(2011).
- Wahyudi T., Reviewing the properties of rare earth element-bearing minerals, rare earth elements and cerium oxide compound. *Indones. Min. J.*, **18**, 92-108(2015).
- Tavallali H., Asrari E. and Ameri Siahoe M.A., *Egypt. J. Chem.* **63**, No. 7 (2020)
- Sensitive kinetic spectrophotometric method for trace determination of cerium(IV) based on decolorization of Nile blue by potassium periodate. *Int. J. Chemtech Res.*, **1**, 359-362(2009).
- Shuai Q., Bin H., Qin Y., Ruth W. and Jiang Z., Determination of trace rare earth impurities in high purity cerium oxide by using electrothermal vaporization ICP-AES after HPLC separation with 2-ethylhexyl hydrogen 2-ethylhexylphosphonate resin as the stationary phase. *J. Anal. At. Spectrom.*, **15**, 1413-1416(2000).
- Afkhamia A., Madrakiana T., Shirzadmehra A., Tabatabaeeb M. and Bagheric H., New Schiff base-carbon nanotube-nanosilica-ionic liquid as a high performance sensing material of a potentiometric sensor for nanomolar determination of cerium(III) ions. *Sensors Actuat. B-Chem.*, **174**, 237-244(2012).
- Giridhar C., Niranjan T. and Naidu N.V.S., Simple catalytic currents at DME for trace amounts of cerium (IV) in water samples. *Chem. Sci. Trans.*, **2**, 983-991(2013).
- Yener R. and Aycicek A., New fluorometric reagents; sodium pyrophosphate, sodium trimetaphosphate and sodium tetrametaphosphate for the determination of cerium (III). *J. Fluoresc.*, **8**, 45-52(1998).
- Agrawal Y.K., Liquid-liquid extraction, separation,

- preconcentration, and ICP-AES determination of lanthanum and cerium with N-Phenyl-(1,2-methanofullerene C₆₀)61-formohydroxamic acid. *Fuller. Nanotub. Car. N.*, **12**, 545-570(2004).
12. Masti S.P., Seetharamappa J., Melwanki M.B. and Motohashi N., Spectrophotometric determination of cerium (IV) using a phenothiazine derivative. *Anal. Sci.*, **18**, 167-169(2002).
 13. Kostova I.P., Manolov I.I. and Radulova M.K., Stability of the complexes of some lanthanides with coumarin derivatives. I. cerium (III)-4-methyl-7-hydroxycoumarin. *Acta Pharm.*, **54**, 37-47(2004).
 14. Ahmed I.S., Amin A.S. and Issa Y.M., The surfactant sensitized analytical reaction of cerium (IV) with some triphenylformazan derivatives. *Spectrochim. Acta A*, **64**, 246-250(2006).
 15. Yuying L. and Ping W., Kinetic spectrophotometric method for the determination of cerium (IV) with naphthol green B. *Rare Metals*, **28**, 5-8(2009).
 16. Lokhande R.S., Kulkarni S., Pitale S., Patil S.K. and Janwadkar S.P., Extraction and spectrophotometric determination of Ce(IV) metal ions using hydrazine carboxymide 2-[(2-hydroxyphenyl) methylene (HC22HPM) as an analytical reagent. *Int. J. Pharm. Biol. Res.*, **2**, 161-164(2011).
 17. Abdulla A.M. and Haidar O.I., Spectrophotometric determination of cerium in some ore in kurdistan region – Iraq. *J. Nat. Sci. Res.*, **5**, 132-137(2015).
 18. Khan M.H., Liaqat K., Hafeez M., Fazil S. and Riaz M., Extraction of cerium (IV) using di-n-butylsulfoxide in chloroform from nitric acid and determination with arsenazo (III) as chromogenic reagent. *S. Afr. J. Chem.*, **68**, 69-75(2015).
 19. Jawad S.K., Kadhim M.O. and Alwan, A.S., Incorporation solvation with cloud point extraction method for separation and spectrophotometric determination of cerium (III). *J. Chem. Pharm. Res.*, **9**, 85-94(2017).
 20. Britton H. T. S. "Hydrogen ions", 4th ed., Chapman and Hall, London, 28, 359-364(1952).
 21. Bower V.E. and Bates R.G., pH values of the Clark and Lubs buffer solutions at 25 ° C. *J. Res. Natl. Bur. Stand.*, **55**, 197-202(1955).
 22. Lurie J.u. "Handbook of Analytical Chemistry", 2nd ed., Mir publishers, Moscow, 1978.
 23. Qihua C., Bo G., Yuyong Z., Determination of vanadium(V) and molybdenum(VI) by means of a landolt reaction, *Talanta*, **36**, 665-668(1989).
 24. Motojima K. and Lzawa K., Potentiometric titration of free acid and uranium in uranium (VI) solutions with alkali. *Anal. Chem.*, **36**, 733-735(1964).
 25. Park, C.I., Huang, H.Z., Cha, K.W., 2001. Spectrophotometric determination of uranium(VI) with pyrocatechol violet in surfactant media. *Bull. Korean Chem. Soc.* **22**, 84-86.
 26. Ahmed F.M., Sadeek S.A. and El-Shwiniy W.H., Synthesis, spectroscopic studies, and biological activity of some new N₂O₂ tetradentate schiff base metal complexes. *Russ. J. Gen. Chem.*, **89**, 1874-1883(2019).
 27. Shafeeulla R., Krishnamurthy G., Bhojyanaik H.S. and Manjuraj T., Synthesis, Cytotoxicity, and Molecular Docking Study of Complexes Containing Thiazole Moiety. *J. Turkish chem. Soc. Sect. A chem.*, **4**, 787-810(2017).
 28. Radulescu-Grad M.E., Muntean S.G., Todea A., Verdes O. and Andelesc A., Synthesis and Characterization of New Metal Complex Dye. *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)*, **60(74)**, 37-40(2015).
 29. Aldelfy Z., Alshamkhani Z. and Al-assadi M., 2-hydroxybenzylidene-4-(4-SubstitutedPhenyl)-2-amino thiazole and their Pt(II) complexes: synthesis, characterization and biological Study, *E. J. CHEM.*, **62**, 4-5(2019).
 30. El-Shwiniy W.H. and Sadeek S.A., Synthesis, spectroscopic, thermal analyses and biological activity evaluation of new zirconium(IV) solid complexes with bidentate lomefloxacin, *E. J. CHEM.*, **61**, 27-38(2018).
 31. Job P., Formation and Stability of Inorganic Complexes in Solution. *Anal. Chim. Acta*, **9**, 113-119(1928).
 32. Yoe J.H. and Jones A.L., Colorimetric determination of iron with disodium-1,2-dihydroxybenzene-3,5-disulfonate, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111-115(1944).
 33. Tirmizi S.A., Wattoo F.H., Wattoo M.H.S., Sarwar S., Memon A.N. and Ghangro A.B., Spectrophotometric study of stability constants of cimetidine-Ni(II) complex at different temperatures. *Arab. J. Chem.*, **5**, 309-314(2012).
 34. Sulaiman S.T., Hanna G.K. and Bashir W.A., *Egypt. J. Chem.* **63**, No. 7 (2020)