



Synthesis and characterization of new azo-dye reagent and using to spectrophotometric determination of samarium(III) in some industrial and blood samples

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Abstract

A new azo-dye reagent was prepared by the reaction between sulfacetamide and rutin compounds. The new synthesized reagent of (*E*)-*N*-((4-((5-(5,7-dihydroxy-3- β -[3- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyrano-syloxy]-4-oxo-4*H*-chromen-2-yl)-2,3-dihydroxyphenyl)diazenyl)phenyl)sulfonyl)acetamide [NDRGA] was characterized by FT-IR, ¹HNMR, mass spectra and elemental analysis measurements and then used for the spectrophotometric determination of Sm(III). The proposed method was based on the formation of a lemon-colored complex between Sm(III) and NDGRA reagent in an alkaline medium using borate buffer at pH = 8 with absorption maximum at 475 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 to be 1:1 (metal: ligand) by using Job's and molar ratio methods. The stability constant of the complex was calculated to be 1.1805×10^6 . The method showed a good linearity in the concentration range of 2.0–90 $\mu\text{g ml}^{-1}$ of Sm(III) with molar absorptivity and Sandell's sensitivity $1.3014 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $1.155 \times 10^{-2} \mu\text{g cm}^{-2}$, respectively. The limit of quantification (LOQ) and detection (LOD) were calculated. The interference effect of some foreign ions was also studied. The validity of the calibration curve was found useful for the determination of micro-amounts of Sm(III) in some industrial and blood samples.

Keywords Spectrophotometry · Samarium(III) · Azo-dye reagent · Beer's law · Stability constant · Industrial and blood samples

Introduction

Rare earth metal ions were used greatly in nuclear industry, new energy, native defense, aerospace, biological medicine and in agriculture (Li et al. 2016). They were used in lasers, lamps, motion picture projectors, phosphorus, magnets and X-ray condensing screens (Zolfonoun and Yousefi 2016). The natural occurrence of rare earth metal ions was based on their geological conditions. They were found in adequate amount and concentration in only few locations, also they were found in a suitable form and regulation to make their extraction and utilization economically feasible.

Geologists use rare earth metal ions as tools to facilitate the scientific research into the chemical attitude of ocean waters and the origin of ores and rocks (Mehmood 2018). In the world of technology, these metal ions were indispensable due to their magnetic, phosphorescence and catalytic characteristics. Many rare earth metal ions are radioactive materials which are hazardous as radioactive soil and water emissions. Their spectroscopic properties of rare earth metal ions for advanced new materials made them have a great attention (Makombe et al. 2018). Samarium has been used in microelectronics, glass, ceramics and nuclear industries. For instance, it has been used as an absorber in the nuclear industry and also as anesthetic with CaF_2 crystals for the use in visual lasers or masers (Soylak and Turkoglu 2000). Samarium has been used as a polishing compound and as catalyst in the gasoline cracking process; also, it has been used in the steel and iron industries to remove carbon and sulfur and some other electronegative elements (Ratre and

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Kumar 2013). Increasing industrial use of samarium has made it essential to have analytical procedures suitable for observation of samarium in environmental and related fields. For this purpose, some suitable analytical methods, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Paama et al. 2001) and inductively coupled plasma mass spectrometry (ICP-MS) (Li et al. 1999), have been utilized for the determination of samarium. Also, many spectrophotometric methods were used for the determination of samarium(III) using various organic reagents such as chrome azurol S, chlorophosphonazo III and 2-[(5-bromo-2-pyridylazo)]-5-diethyl-aminophenol (Soylak and Turkoglu 2000; Uhrovic and Lesny 2014; Ratre and Kumar 2013). In addition, it has also been determined via the complexation with disodium 2-(2-hydroxy-3-sulfo-5-nitrophenylazo) naphthalene-1,8-dihydroxy-3,6-disulfonate in the presence of cetyltrimethyl-ammonium bromide (Gadzhieva et al. 2005).

In the present study, the synthesis and characterization of a new azo-dye reagent of (*E*)-*N*-((4-((5-(5,7-dihydroxy-3- β -[3- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyloxy]-4-oxo-4*H*-chromen-2-yl)-2,3-dihydroxyphenyl)diazanyl)phenyl)sulfonyl)acetamide [NDRGA] which formed from the reaction between sulfacetamide and rutin was reported. Moreover, it was used for the rapid, simple, sensitive and highly selective spectrophotometric determination of Sm(III) in different analytical applications.

Experimental

Instrumentation

All absorbance measurements were carried out with a UV-Vis spectrophotometer (T80 UV/Vis double beam spectrophotometer, PG instruments Ltd Company, UK), spectral bandwidth 2.0 nm, with 10 mm matched quartz cells. All pH measurements were made using a pH meter (Adwa pH meter, Model AD 1030, Romania). The FT-IR spectra were recorded in KBr pellets on a Shimadzu FT-IR 8101 PC infrared spectrometer in the range from 4000 to 400 cm^{-1} . The ^1H NMR spectra were recorded on Bruker (400 MHz) spectrometer using DMSO- d_6 as solvent. Mass spectrometry was determined on DI Analysis Shimadzu QP-2010 Plus.

Chemical and materials

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

Alcoholic solution of (1×10^{-3} M) of (*E*)-*N*-((4-((5-(5,7-dihydroxy-3- β -[3- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyloxy]-4-oxo-4*H*-chromen-2-yl)-2,3-

dihydroxyphenyl)diazanyl)phenyl)sulfonyl)acetamide [NDRGA] reagent was prepared by dissolving (0.0837 g, M. wt. = 837.71 g mol^{-1}) of the reagent in 100 ml ethanol.

A (1×10^{-3} M) of samarium(III) standard solution was prepared by dissolving 0.03488 g of [Sm_2O_3 , M. wt. 348.718 g mol^{-1}] in the least amount of nitric acid (1:1) in a 100 ml measuring flask and diluting to the mark with distilled water. Working solutions of lower concentrations were prepared from the stock solutions by appropriate dilution.

Series of different surfactants including cetyltrimethylammonium bromide (CTAB), Triton X-100, sodium lauryl sulfate (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 used without further purification.

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 (Britton 1952; Bower and Bates 1955; Lurie 1978).

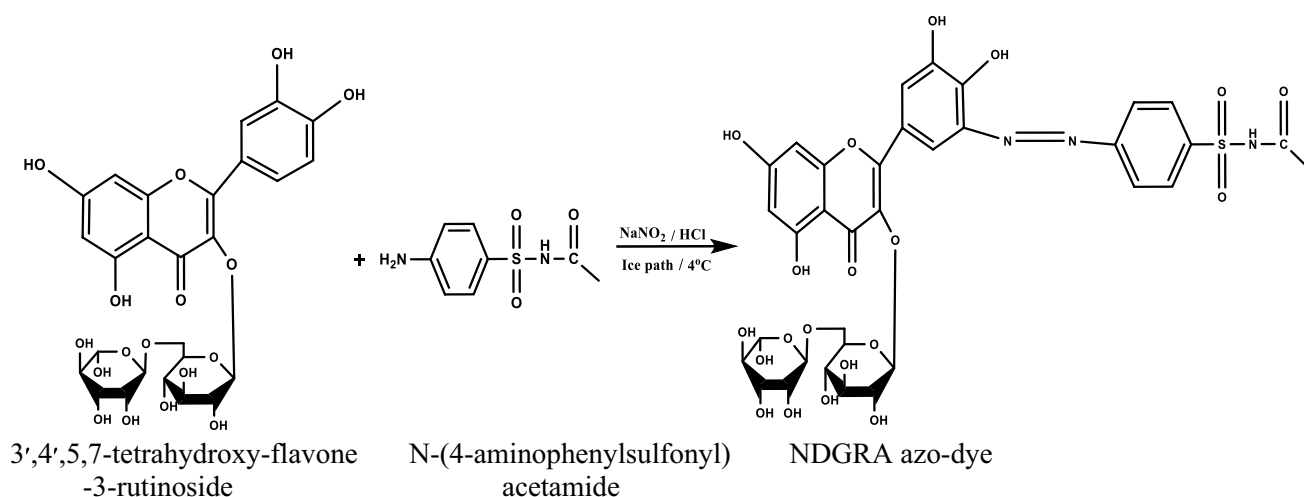
Procedures

*Synthesis of (E)-N-((4-((5-(5,7-dihydroxy-3- β -[3- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyloxy]-4-oxo-4*H*-chromen-2-yl)-2,3-dihydroxyphenyl)diazanyl)phenyl)sulfonyl)acetamide (NDGRA) reagent:*

(1.071 g, 0.005 mol) of *N*-(4-aminophenylsulfonyl)acetamide was dissolved in 10 ml hydrochloric acid (1:1), and diazotized in ice path at 4 $^\circ\text{C}$ with sodium nitrite (0.344 g, 0.005 mol) solution in water (5.0 ml). The resulting diazo solution was added dropwise with stirring to an ice-cooled solution of (3.052 g, 0.005 mol) of (3',4',5,7-tetrahydroxyflavone-3-rutinoside [rutin] which was dissolved in (10 ml) of (2 M) sodium hydroxide. The precipitate was filtered and washed with a (1:3) mixture of ethanol and water several times, then left in air to dry. The resulting compound is a solid reddish brown precipitate; yield 85%, m.p. 230–232 $^\circ\text{C}$ (Scheme 1).

General spectrophotometric procedures

Suitable aliquots of Sm(III) standard solution (1.0 – $130 \mu\text{g ml}^{-1}$) were transferred into a series of 10 ml calibrated flasks containing 1.0 ml of (1×10^{-3} M) NDGRA reagent, followed by 4.0 ml borate buffer (pH = 8). To each flask, 1.0 ml of (1×10^{-2}) cetylpyridinium bromide (CPB) surfactant was added. The volumes were adjusted to the mark with distilled water and mixed well. Spontaneously and at 20 $^\circ\text{C}$, the absorbance was measured at 475 nm against the blank solution. By plotting the absorbance against the



Scheme 1 Synthesis of the NDGRA azo-dye reagent

concentration of Sm(III) in $\mu\text{g ml}^{-1}$, the range of Beer's law can be determined.

Applications

Determination of Sm(III) in monazite sand

0.5 g of monazite sand was dissolved in 10 ml concentrated H_2SO_4 and was evaporated to almost dryness. The residue was then diluted to 50 ml with distilled water, boiled, filtered and washed with hot water. Samarium 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 HNO_3 and evaporated till dryness. The residue was dissolved again in 5.0 ml HCl (1 M) with continued heating to 70°C for 30 min. The solution was cooled to room temperature, filtered, diluted to fixed volume suitable to the applicable concentration range and then the above procedures were followed. Uranium (VI) was masked using ammonium sulfate (Motojima and Lzawa 1964).

Determination of Sm(III) in crude phosphoric acid

5.0 ml of crude phosphoric acid was taken and diluted to 50 ml with distilled water. The concentration of the metal ion was determined by the procedures described above.

Determination of Sm(III) in phosphate fertilizer

0.5 g of fertilizer sample was dissolved in a (1:3) mixture of concentrated ($\text{HCl}:\text{HNO}_3$) and evaporated to almost dryness. The residue was dissolved again in 10 ml HCl (1 M) and diluted with 20 ml distilled water with continued heating to

80°C for 1 h. The solution was cooled to room temperature, filtered, diluted to suitable volume by distilled water and analyzed as described above.

Determination of Sm(III) in permanent magnet

0.144 g of permanent magnet was weighed and dissolved in 5.0 ml of concentrated H_2SO_4 with heating to 80°C for 20 min. 10 ml of distilled water was added to the solution with continued heating at 70°C for 1 h. The solution was cooled to room temperature, diluted and analyzed as in previous procedures. Fe(III) was masked using sodium fluoride (Motojima and Lzawa 1964).

Determination of Sm(III) in blood

A definite volume (10 ml) of blood sample was drawn from adult human body. A 7.5 ml from this sample was centered in a centrifuge using a tube contained sodium citrate as anticoagulant to separate plasma, then center the remained 2.5 ml to separate serum. Fe(III) was masked by using sodium fluoride. The sample was then analyzed as in the above procedures.

Results and discussion

Structural characterization of NDGRA azo-dye reagent

The structure of NDGRA azo-dye reagent was confirmed by the structural data obtained using FT-IR, ^1H NMR, mass spectra and elemental analysis measurements.

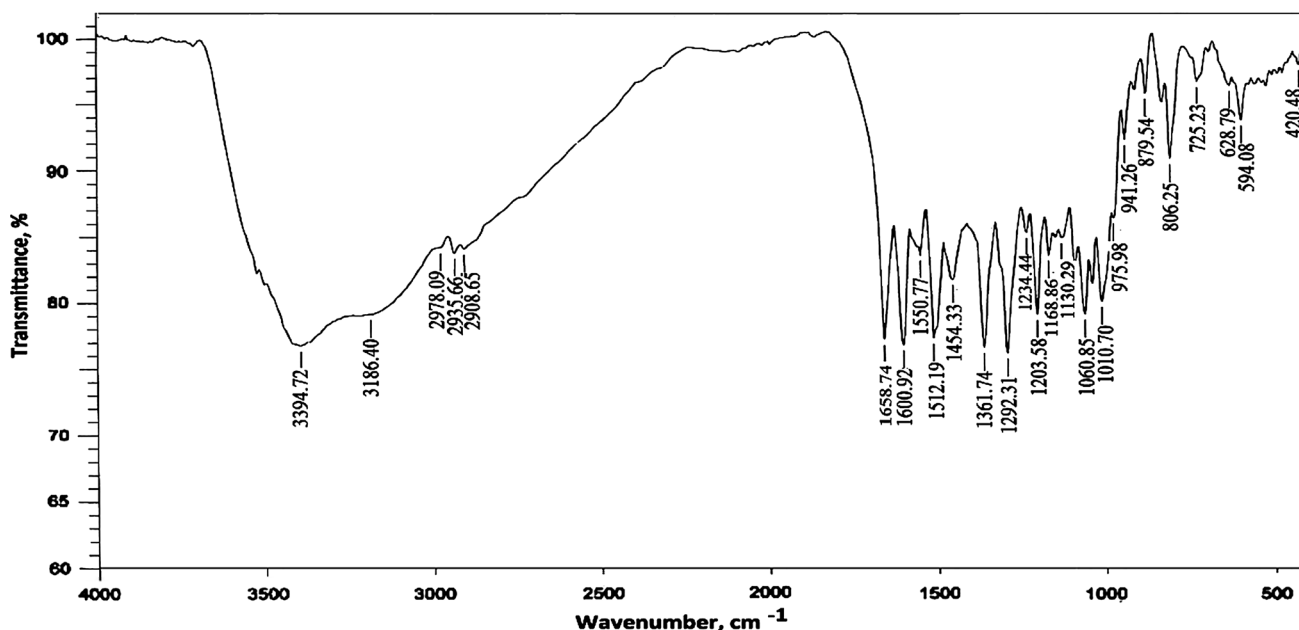


Fig. 1 FT-IR spectra of NDRGA azo-dye reagent

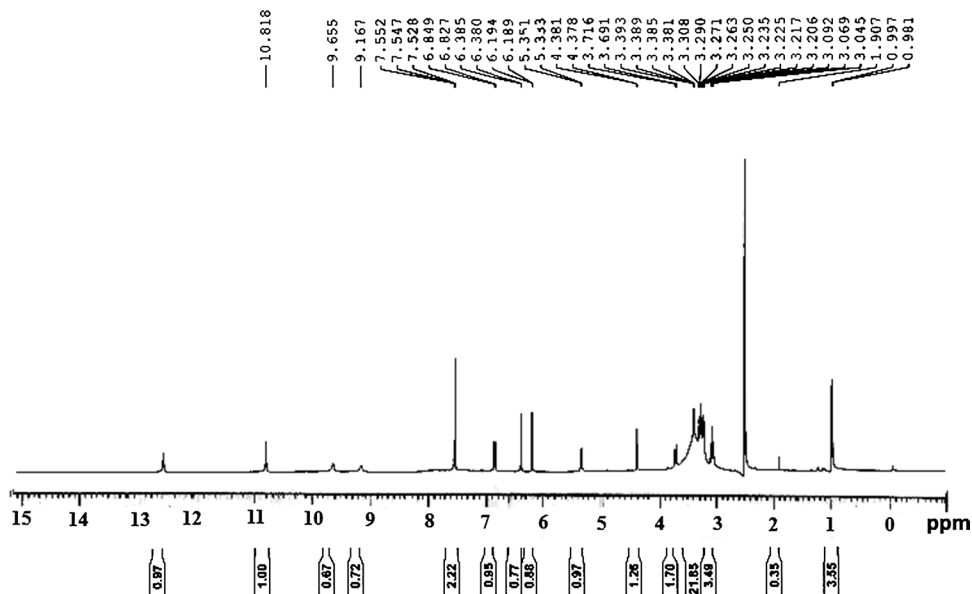
FT-IR spectra

The FT-IR spectrum (Fig. 1) of the synthesized reagent displayed a broad band at 3394 cm^{-1} for (O–H) hydroxyl groups and a band at 3186 cm^{-1} for amidic (N–H) group. It also showed bands at 1512 cm^{-1} for (N=N) azo group, 1659 cm^{-1} for α , β -unsaturated and amidic carbonyl groups and 1292 cm^{-1} for asymmetric sulfone (SO_2) group.

^1H NMR spectra

The ^1H NMR (DMSO- d_6) spectrum data (Fig. 2) of the reagent showed $\delta = 1.90$ (s, 3H, CH_3), 3.04–3.39 (m, 16H, CH_2 , 7 CHOH and 7 OH of sugar moiety), 6.69 (d, 1H, OCHCH_2), 4.37 (s, 1H, OCH), 5.33 (d, 1H, $J = 7.9\text{ Hz}$, anomeric proton of sugar H-1'), 6.18 (s, 1H, Ar–H), 6.38 (s, 1H, Ar–H), 6.82 (d, 2H, $J = 8.50\text{ Hz}$, Ar–H), 7.52 (s, 1H, Ar–H), 7.54 (d, 2H, $J = 8.50\text{ Hz}$, Ar–H), 9.16 (br, 1H, OH, exchange with D_2O), 9.65 (br, 1H, OH, exchange with D_2O), 10.81 (s, 1H, OH, exchange with D_2O), and 12.51 (s, 1H, NH, exchange with D_2O).

Fig. 2 ^1H NMR spectra of NDGRA azo-dye reagent



Mass spectra

The mass spectra (Fig. 3) of the reagent showed a signal at M^+ (m/e) = 836.30 (3.50%) attributed to the parent ion and another one at m/e = 302.00 (100%) for the base peak. Mol. formula: $C_{34}H_{35}N_3O_{20}S$ (837.71 $g\ mol^{-1}$).

Elemental analysis

Anal. calcd. for $C_{34}H_{35}N_3O_{20}S$ (837.71 $g\ mol^{-1}$): C 48.75; H 4.21; N 5.02.

Found: C 48.76; H 4.22; N 5.01.

Spectrophotometric study of Sm(III)–NDGRA complex

Absorption spectra

The absorption spectra of reagent and its complex were measured in the range of 200–800 nm against the blank solution, (Fig. 4). It was observed that Sm(III) with [NDGRA] reagent formed a lemon-colored complex at 460 nm in alkaline medium (pH = 8). The addition of cetylpyridinium bromide (CPB) surfactant resulted in an increase in absorbance with a redshift to 475 nm.

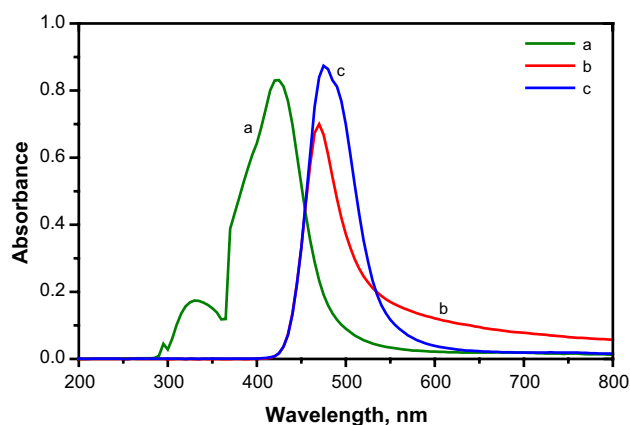


Fig. 4 Absorption spectra of **a** reagent (NDGRA) (2.0×10^{-4} M) against the buffer blank, pH = 8, **b** Sm(III)–NDGRA complex, Sm(III) = $100\ \mu g\ ml^{-1}$, 2.0 ml (1.0×10^{-3} M) of NDGRA against reagent blank, **c** Sm(III)–NDGRA complex with 1.0 ml (1.0×10^{-2} M) of CPB against the blank solution

Optimization of experimental conditions

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

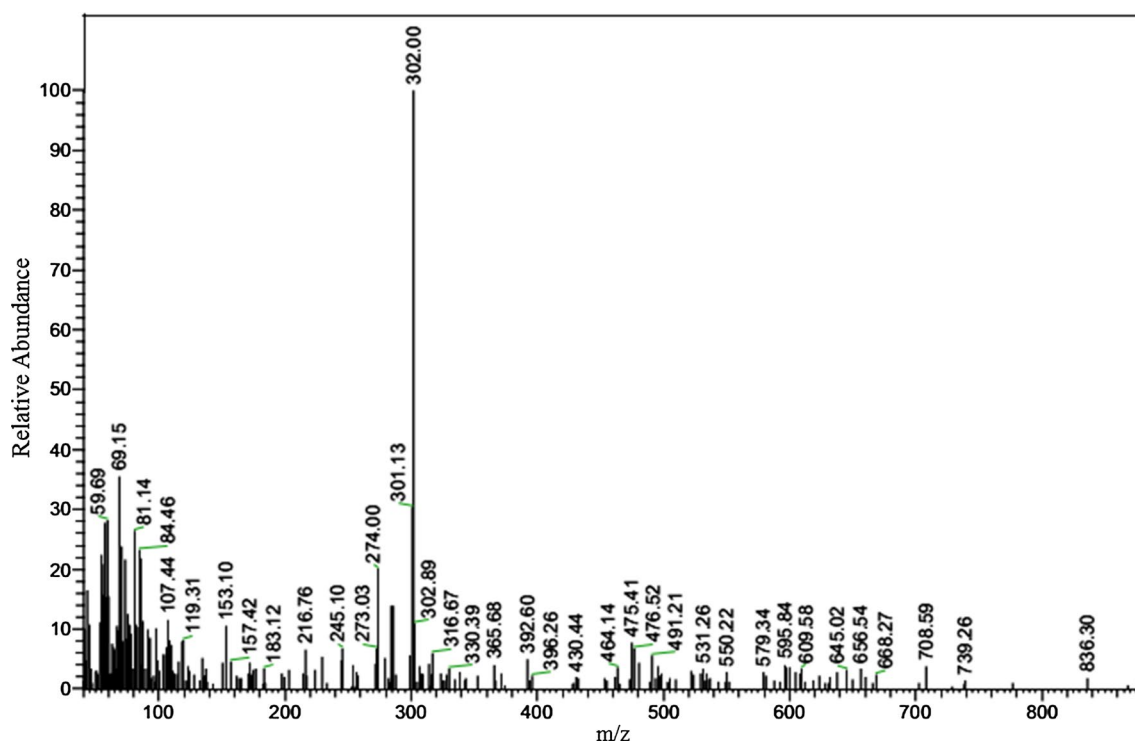


Fig. 3 Mass spectra of NDGRA azo-dye reagent

Effect of the pH and buffer solutions

The effect of pH on the complex formation was studied from pH 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 of the complex was from pH=6 to 9 (Fig. 5). In more acidic or more alkaline solutions, absorbance was decreased gradually due to incomplete formation and partial dissociation of the complex. 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=8). Further, 4.0 ml of borate buffer of pH=8 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 a fixed concentration 1.0 ml of (1×10^{-3} M) of Sm(III) ion and varied concentrations (0.5–4.0 ml of 1×10^{-3} M) of the reagent. It was observed that the maximum absorbance was obtained by using 1.0 ml of (1×10^{-3} M) of NDGRA reagent.

Effect of time and temperature

To study the effect of time and temperature on the stability of the formed complex, the absorbance readings of the complex were recorded at different times and temperatures in the range from 1.0 to 120 min and 15–75 °C. The complex was formed with maximum absorbance value spontaneously at 20 °C and remained stable up to 24 h, (Figs. 6

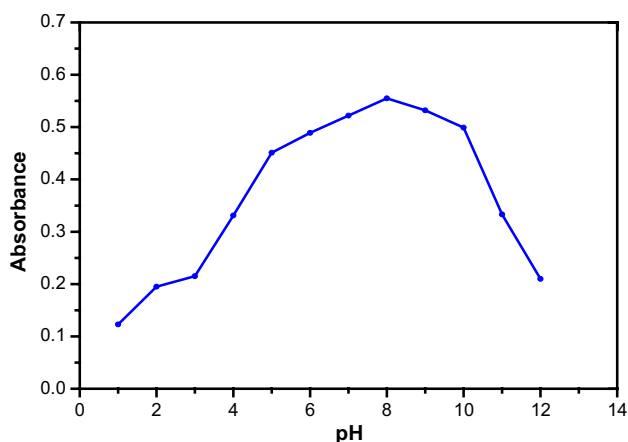


Fig. 5 Effect of pH on the complex formed between Sm(III) and NDGRA reagent; Sm(III)=100 $\mu\text{g ml}^{-1}$ and 1.0 ml (1×10^{-3} M) NDGRA reagent

and 7). On the other hand, the absorbance values were decreased at higher temperatures.

Effect of surfactants

To improve the sensitivity of the complex formation, the effect of different concentrations ranging from 0.2 to 2.0 ml (1×10^{-2} M) 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 maximum absorbance value was obtained when 1.0 ml (1×10^{-2} M) of cetylpyridinium bromide (CPB) was used

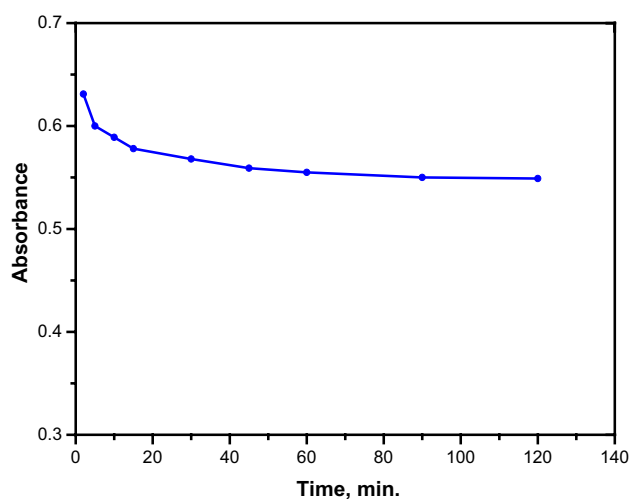


Fig. 6 Effect of time on the complex formed between Sm(III) and NDGRA reagent, [Sm(III)]= 1×10^{-4} M, [NDGRA]= 1×10^{-4} M, pH=8

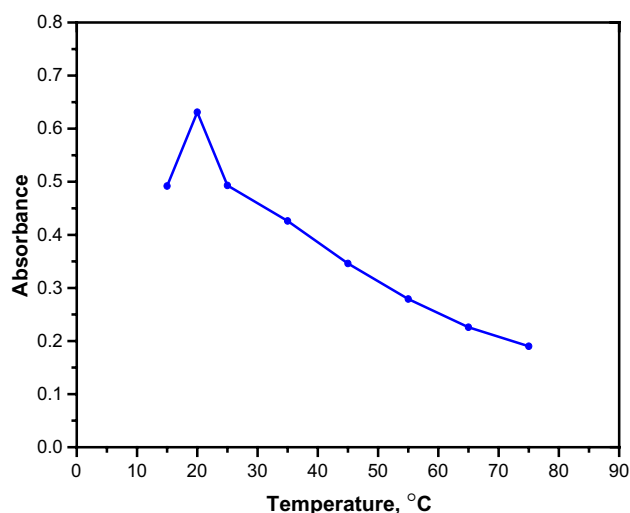


Fig. 7 Effect of temperature on the complex formed between Sm(III) and NDGRA reagent [Sm(III)]= 1×10^{-4} M, [NDGRA]= 1×10^{-4} M, pH=8

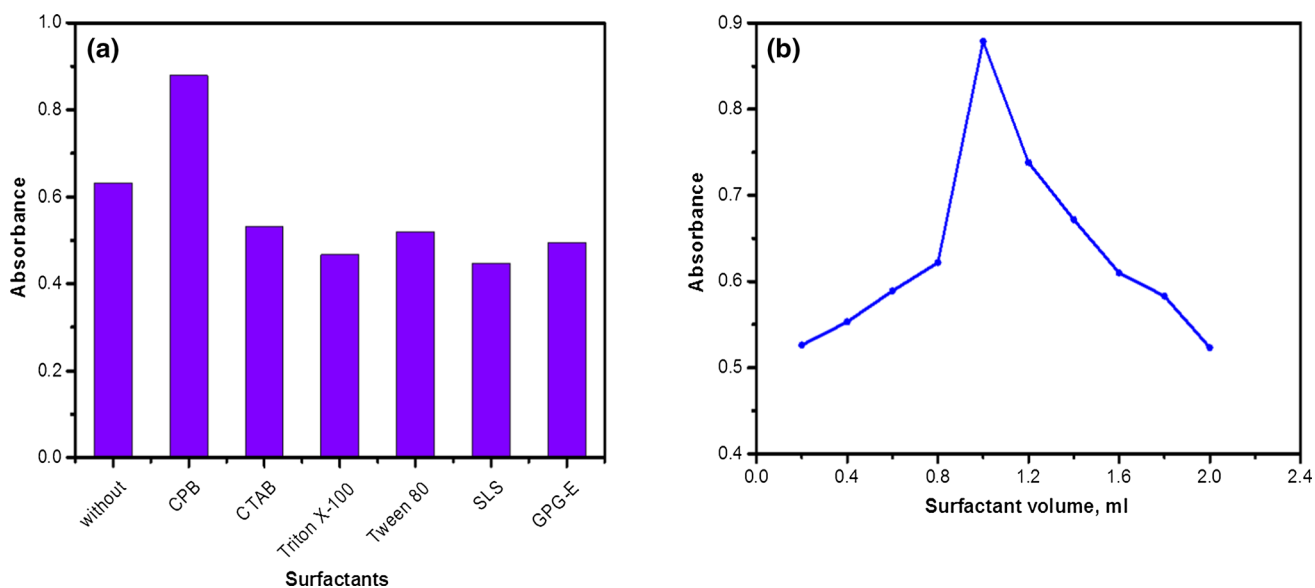


Fig. 8 **a** Effect of surfactants type and **b** surfactant volumes on complex formed between Sm(III) and NDGRA reagent, $[Sm(III)] = 1 \times 10^{-4}$ M, $[NDGRA] = 1 \times 10^{-4}$ M, borate buffer (pH 8), at once and $20^\circ C$

(Fig. 8a). At higher concentrations of CPB, the absorbance was decreased due to the appearance of turbidity (Fig. 8b).

the complex formation and higher absorbance value, while the other solvents decrease the absorbance values.

Effect of organic solvents

The effect of different organic solvents on the absorption spectra 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

Effect of order of addition

Different absorbance measurements were performed by changing the order of the addition of the metal ion Sm(III), NDGRA reagent, buffer (borate pH=8) and CPB surfactant. It was evident that the order (reagent–metal ion–buffer–surfactant) results in maximum absorbance. Otherwise, the

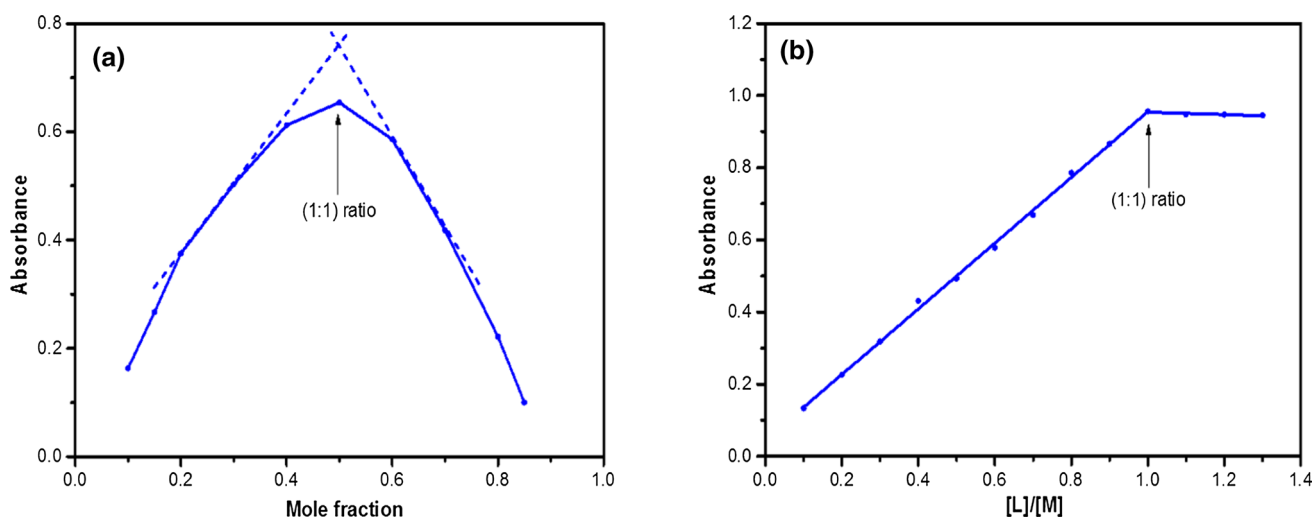


Fig. 9 Stoichiometry of the complex by **a** Job's method of continuous variation and **b** molar ratio method, $[Sm(III)] = [NDGRA] = 1.0 \times 10^{-3}$ M, pH=8, 1.0 ml (1.0×10^{-2} M) of CPB

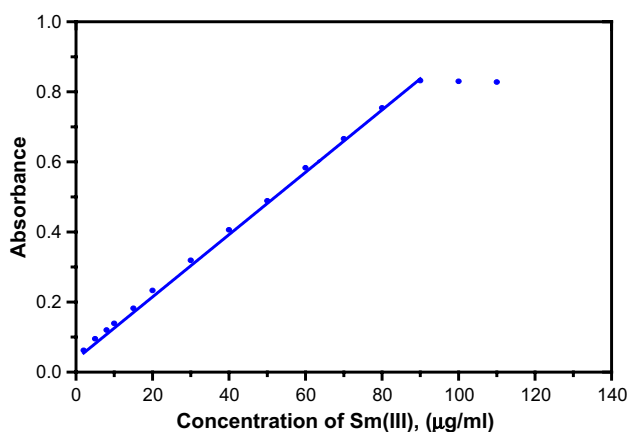


Fig. 10 Calibration curve for Sm(III)–NDGRA complex, [NDGRA] = 1×10^{-4} M, 1.0 ml (1×10^{-2} M) of CPB, borate buffer (pH 8), $\lambda_{\max} = 475$ nm

Table 1 Statistical parameters of the proposed method

Parameters	Selected value
Molar absorptivity $L \text{ mol}^{-1} \text{ cm}^{-1}$	1.3014×10^4
Sandell's sensitivity $\mu\text{g cm}^{-2}$	1.155×10^{-2}
Standard deviation (SD)	3.55×10^{-3}
Relative standard deviation (RSD)	8.87×10^{-3}
Standard error of the mean (SEM)	1.34×10^{-3}
Limit of detection (LOD) $\mu\text{g ml}^{-1}$	1.3252
Limit of quantification (LOQ) $\mu\text{g ml}^{-1}$	4.0158
Student's <i>t</i> test	3.7264
<i>F</i> test value	1.120
Ringbom plot $\mu\text{g ml}^{-1}$	8–90
Correlation coefficient	0.9996
Intercept (a)	0.04442
Slope (b)	0.00884
SD of intercept S_a	4.74×10^{-3}
SD of slope S_b	9.7080×10^{-5}

other addition orders led to decrease in the absorbance values.

Stoichiometric ratio

To establish the molar ratio between Sm(III) and NDGRA reagent, Job's method of continuous variation was applied (Job 1928). In this method, an equimolar solution of metal ion and reagent in different proportions from 0.1 to 0.9 ml (1×10^{-3} M) of the same concentration were mixed, while the total molar concentration was kept constant. The absorbance was measured at 475 nm and plotted versus mole fraction (Fig. 9a). The composition of the complex was also confirmed by the molar ratio method (Yoe and Jones 1944).

In this method, the concentration of the metal ion was kept constant at 1.0 ml of (1×10^{-3} M), while that of the reagent was different from 0.1 to 1.3 ml of (1×10^{-3} M). The absorbance of these solutions was recorded at 475 nm and then plotted against the molar ratio [ligand]/[metal], (Fig. 9b). Both methods showed that the ratio of Sm(III) and the reagent was 1:1. The stability constant of the complex was calculated by Job's method (Tirmizi et al. 2012) and found to be 1.1805×10^6 , which showed the high stability of the formed complex.

Calibration curve (Beer's law)

The calibration curve 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 2–90 $\mu\text{g ml}^{-1}$ as shown in (Fig. 10). A Ringbom plot was also carried out to detect the optimum range of concentration for a system that obeyed Beer's law. It was achieved at intermediate concentration values (8–90 $\mu\text{g ml}^{-1}$).

Statistical characteristics

The method has good reproducibility for a set of seven measurements of 40 $\mu\text{g/ml}$ of Sm(III) under optimum conditions. Some different statistical parameters such as standard deviation, molar absorptivity, sandell's sensitivity, Student's *t* test, *F* test, correlation coefficient, limit of detection (LOD) and limit of quantification (LOQ) are summarized in Table 1. The data listed in Table 1 indicate the excellent linearity, high sensitivity, good accuracy and precision of the proposed method.

Effect of diverse ions

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

Table 2 Determination of Sm(III) in some industrial and blood samples

Sample	Proposed method ^a		Recommended method ^b ($\mu\text{g ml}^{-1}$)	Recovery %	RSD %
	Taken ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)			
Monazite sand	20	19.97	19.89	99.85	0.150
Crude phosphoric acid	15	14.96	14.90	99.73	0.270
Phosphate fertilizer	12	11.97	11.05	99.75	0.252
Permanent magnet	15	14.98	15.08	99.86	0.141
Human blood of leukemia patient	8	7.99	8.07	99.87	0.135

^aProposed method for determination of Sm(III) with NDGRA reagent

^bRecommended method according to Sangal et al. (1969)

Analytical applications

The proposed method was applied for the determination of Sm(III) in monazite sand, crude phosphoric acid, phosphate fertilizer, permanent magnet and human blood. The results listed in Table 2 showed good agreement with the recommended method values and indicated the applicability of the proposed method.

Conclusion

A new sulfacetamide azo-dye reagent was prepared and characterized by FT-IR, ¹HNMR, mass spectra and elemental analysis and then used for the spectrophotometric determination of Sm(III). The proposed method was simple, highly sensitive and economical, did not involve extraction, heating or other special conditions and was free from most interfering ions. Sm(III) complex was formed directly and remained stable for more than 24 h. The absorbance of the complex was increased by using CPB as a surfactant. The statistical data proved that the method had high sensitivity and good accuracy and precision. The method was successfully applied for the determination of samarium(III) in monazite sand, crude phosphoric acid, phosphate fertilizer, permanent magnet and blood samples with good results.

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