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Direct and derivative spectrophotometric determination of La(III) using 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone

S. Satyasree*, V. Krishna Reddy and P. Raveendra Reddy

Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 055 (A.P), India

ABSTRACT

La (III) reacts with 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone (HMBAHBH) in alkaline buffer solutions (pH 7.5-9.0) forming an intense lemon yellow coloured stable complex with a λ_{max} *at 390nm. The colour reaction is highly sensitive with an* ε*,* 1.93×10^4 $Lmol^{-1}$ cm^{-1} *, detection limit 0.038* μg mL^{-1} *obeying Beer's law in the range 0.14 – 9.72* μg mL^{-1}*. The correlation coefficient (0.9999) and relative standard derivation (0.06%) indicate the good linearity for the regression curve and precision respectively. The method is reasonably selective as number of diverse ions are tolerable in large quantities in the presence of some masking agents. Stoichiometry and formation constant of the complex are determined as 2:3 (M:L) and* 3.39×10^{18} *respectively. The proposed method was applied for the determination of lanthanum in some standard lanthanum samples. Second, third and fourth order derivative spectrophotometric methods are also proposed for the determination of lanthanum. All the derivative methods are found to be more sensitive and the second derivative method is more selective than the zero order method. The second derivative method was also applied for the determination of lanthanum in standard samples.*

Keywords: Determination of Lanthanum,Direct and derivative methods,Spectrophotometry, 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone.

INTRODUCTION

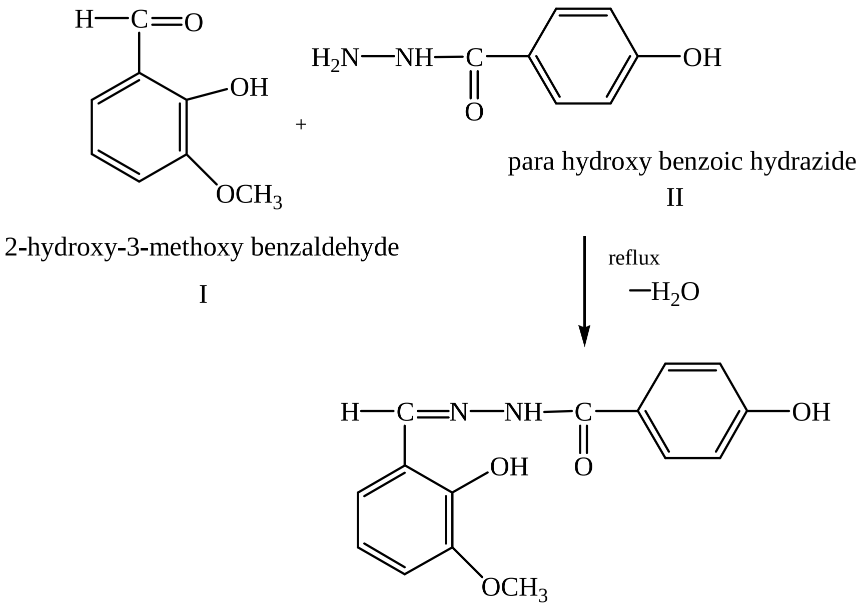
Separation and determination of rare earth metals in various geological materials and synthetic complex materials is an important task of analytical chemist. Lanthanum is highly useful as an electron dense tracer in molecular biology[1]. In recent times, cerium activated lanthanum bromide is used as scintillator which has both high light yield and best energy resolution. Lanthanum is highly useful in the manufacturing of expensive lenses as it imparts high refractive index to the glass. The most commonly used methods for the separation of lanthanides are solvent extraction and ion exchange chromatographic methods[2-4]. Survey of literature has revealed that very few spectrophotometric methods were reported till now for the determination of lanthanides. The recently proposed methods using Eriochrome Black T[5], and Arsenazo-(III)[6] are not only less sensitive but also suffer from serious interference by number of diverse ions. We are now proposing a simple, highly sensitive and reasonably selective direct and derivative spectrophotometric method for the determination of lanthanum in standard lanthanum samples employing 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone as complexing age

MATERIALS AND METHODS

The absorbance measurements were made on Schimadju, 160A UV-visible spectrophotometer with a spectral band width of 2 nm and wavelength readability of 0.1 nm employing 1cm width quartz cells. The pH measurements were made on Elico digital pH meter (L1-610) which has a temperature compensate arrangement with a reprodusability of ± 0.01 pH.

Reagents

The chromogenic reagent, 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone was synthesized in the laboratory by condensing the ethanoloic solutions of 2-hydroxy-3-methoxy benzaldehyde and p-hydroxybenzoic hydrazide on water bath for two hours. The recrystallized, light yellow coloured product with a melting point 208 – 210^0C showed IR and NMR spectral peaks at suitable positians indicating the presence of –C=N-, pehnolic –OH, and N—N—H groups in the final product. The structure of the hydrazone is therefore can be gives as



2-hydroxy-3-methoxy benzaldehyde

I

para hydroxy benzoic hydrazide

II

2-hydroxy-3-methoxy benzaldehyde-p-hydroxy benzoic hydrazone (HMBAHBH)

III

0.01M stock solution of the reagent was prepared by dissolving the requisite amount of hydrozone in dimethyl formamide. Lower concentrations were prepared by diluting the stock solution with dimethyl formamide appropriately.

La(III) solution (0.01M) was prepared by dissolving 0.4343gms of $LaCl_3$ (Sigma – Aldrich) in distilled water and diluting to 100 ml. The stock solution was standardized volumetrically[9] and diluted, as required, with distilled water.

Buffer solutions of different pH were prepared by mixing suitable volumes of 0.2M CH_3COONa + 0.2M CH_3 COOH (pH 6.0), 1M CH_3 COONa+0.2M CH_3COOH (pH 7.0), and 2M NH_4Cl +2M NH_4OH (pH 8.0 to 10.0). The pH of the resultant solutions were checked by the pH meter.

Procedure

Direct method:

Different known aliquots of La(III) solution containing variable amounts of lanthanum, taken in different 10 ml volumetric flasks, were treated with 4 ml of buffer solution (pH 8.0), 1 ml DMF, 0.9 ml of 1 x 10^{-3}M [La(III)] and 2.0 ml of 1 x 10^{-2}M HMBAHBH are added and diluted to the volume with distilled water. The absorbance of the resultant solutions was measured at 390 nm against the regent blank and plotted against the amount of lanthanum. A linear regression curve with $A_{390} = 0.1387C – 0.0023$ was obtained.

Derivative method

To the experimental solutions containing different amounts of La (III) prepared as above, the second, third and fourth derivative curves were recorded in the wavelength region 350 – 600 nm with a scan speed of 2400 nm with 9 degrees of freedom. The derivative amplitudes for the different derivative curves were measured at suitable wavelengths and plotted against the amount of La (III) which gave linear calibration plots.

RESULTS AND DISCUSSION

The yellow coloured [La(III) – HMBAHBH] complex solution showed maximum absorbance at 390 nm. The reagent blank also showed significant absorbance but much less than that of the complex at this wavelength. Hence the absorption spectrum was plotted between differential absorbance (ΔA) and wavelength as shown in Fig. 1.

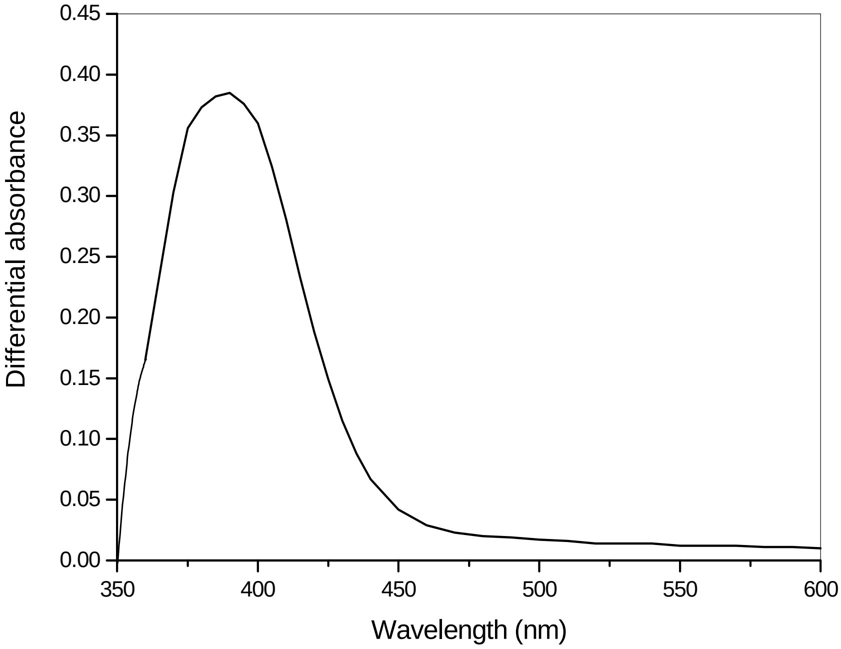


Fig. 1. Absorption spectra of [La(III) – HMBAHBH] Vs reagent blank

[La(III)] = 2×10^{-5}M
[HMBAHBH] = 4×10^{-4}M
pH = 8.0

The analytical studies were therefore carried out by measuring absorbance at 390 nm against reagent blank. Studies on effect of variation in pH on the absorbance of the experimental solution revealed that the complex shows minimum and constant absorbance in the pH range 7.5 – 9.0. The analysis was carried out at pH 8.0. A 20 fold molar excess of reagent was found to be necessary for obtaining minimum colouration. The yellow colour formation of the complex was instantaneous and the colour was found to be stable for more than 48 hours.

Table 1. Analytical characteristics of [La(III) – HMBAHBH]

Parameter	**Direct method 390 nm**	**II derivative**	**III derivative**	**IV derivative**
		437.5 nm	451 nm	412 nm
Beer's law range (μg mL^{-1})	0.1389 to 9.723	0.069 to 1.528	0.069 to 1.528	0.013 to 1.528
Molar absorptivity, ε (L mol^{-1} cm^{-1})	19,250	-	-	-
Sandell's sensitivity (μg cm^{-2})	0.0072	-	-	-
Angular coefficient (m)	0.1386	0.15759	0.18038	0.90066
Y - intercept (b)	-0.0027	-0.00001799	0.0005143	0.0001421
Correlation coefficient (γ)	0.9999	0.9999	1.0000	1.0000
Relative standard deviation (%)	0.068	0.040	0.020	0.058
Detection limit (μg mL^{-1})	0.03772	0.00586	0.0025	0.00129
Determination limit (μg mL^{-1})	0.112	0.0175	0.00752	0.00385
Composition (Metal : Ligand)	2 : 3	-	-	-
Stability constant	3.39×10^{18}	-	-	-

The regression analysis of the calibration plot between the amount of La (III) and absorbance indicated that the plot is linear in the concentration range 0.14 – 9.72 µg mL^{-1} of La (III) with a molar absorptivity of (1.93 x 10^{4} L mol^{-1} cm^{-1}) and Sandal's sensitivity (7.2 x 10^{-3} µg cm^{-2}). The detection limit (0.038 µg mL^{-1}) and determination limit (0.112 µg mL^{-1}) prove the sensitivity of the proposed direct method. The correlation coefficient 0.9999 and y–intercept (-0.0023) are the evidence of the linearity of the regression line. The RSD value (0.06%) shows the precision of the proposed method. The analytical and statistical results of the proposed method are shown in table 1. The stochiometry of the lanthanum complex was determined by Job's continuous variation method, molar ratio method and slope ratio method as 2:3 (M:L). The stability constant of the complex was calculated from the Job's method as 3.39×10^{18}.

The effect of various diverse ions on the determination of lanthanum by the proposed method was studied and the tolerance limits of these diverse ions were evaluated. The amount of diverse ion that caused an error in absorbance by ± 2% was taken as its tolerance limit. The results shown in table 2 indicate that most of the anions and some metal ions possess high tolerance limits. The tolerance limits of number of metal ions were substantially increased in the presence of tartrate ion as masking agent. However, Au(III), Mn(II), Cd(II), Zn(II) and Ce(IV) showed serious interferences.

Table. 2. Tolerance limits of Foreign ions

Amount of La(III) taken = 2.778 µg mL^{-1}; pH = 8.0

Foreign ion	Tolerance limit (µgmL^{-1})	Foreign ion	Tolerance limit (µgmL^{-1})
Ascorbate	875	Mo(VI)	38
Thio sulphate	560	W(VI)	28
Sulphate	480	Se(IV)	18
Nitrate	310	Pd(II)	16
Tartrate	310	Ag(I)	11
Bromide	270	Zr(IV)	10
Iodide	230	Hg(II)	8
Citrate	200	Bi(III)	3, 45[a]
Chloride	180	Tl(III)	2, 25[a]
Thiocyanate	115	Cr(VI)	2
Thiourea	90	Ru(III)	2
Oxalate	71	Au(III)	2
Carbonate	69	Mn(II)	< 1
EDTA	2	Th(IV)	< 1, 35[a]
Fluoride	< 1	U(VI)	< 1, 40[a]
Phosphate	< 1	Ti(IV)	< 1, 65[a]
		Fe(III)	< 1, 80[a]
		Cd(II)	< 1
		Co(II)	< 1, 35[a]
		Ni(II)	< 1
		Zn(II)	< 1
		Cu(II)	< 1, 50[a]
		Ce(IV)	< 1

a = in the presence of 300 µg of tartrate

To enhance the sensitivity and selectivity of the method, the absorption spectrum was derivatised twice, thrice and four times resulting in second, third and fourth derivative spectra. Investigations on the derivative spectra revealed that maximum derivative amplitude was observed 437.5nm for the second order derivative spectra. Similarly in third order and fourth order derivative spectra the maximum amplitudes were noticed at 451 nm and 412 nm respectively. The derivative amplitudes measured at the appropriate wavelengths were found to be proportional to the amount of La (III) obeying Beer's law in the range 0.069-1.528 µg mL^{-1} in second and third order derivative methods and 0.0142 -1.528 µg mL^{-1} in fourth order derivative method. The analytical and statistical results of the derivative methods are presented in table 1.

Studies on the effect of foreign ions on the derivative amplitudes of the different derivative spectra revealed that all the anions and cations which possess high tolerance levels in zero order method did not interfere in derivative methods also. Further the tolerance limits of number of metal ions which seriously interfered in zero order method were considerably increased in the derivative methods, especially in the second order derivative method (Table 3). A comparison of the results of direct and derivate methods shows that the derivative methods are more sensitive and more selective than the zero order method (Table 1).

Table.3. Tolerance limits of foreign ions

Foreign ion	Tolerance limits (in folds)			
	Zero Order	Second derivative	Third derivative	Fourth derivative
		437.5 nm	451 nm	412 nm
Mn(II)	< 1	7	interferes	interferes
Fe(II)	< 1	2	interferes	interferes
Cu(II)	< 1	1	interferes	interferes
Cr(VI)	< 1	27	4	11
Zn(II)	< 1	5	interferes	10
Cd(II)	< 1	13	19	49
Co(II)	< 1	9	interferes	interferes
U(VI)	< 1	17	1	10
Th(IV)	< 1	6	equal	equal
Ru(III)	< 1	36	8	22
Au(III)	< 1	50	20	33
Bi(III)	< 1	3	interferes	equal
Y(III)	< 1	1	interferes	interferes
Ga(III)	< 1	2	interferes	interferes
In(III)	< 1	3	6	interferes

Applications

Both direct and second order derivative spectrophotometric methods proposed were applied for the determination of lanthanum in some standard lanthanum samples. The sample solutions were prepared[8] by digesting a known amount of the standard sample in a mixture of perchloric acid and nitric acid and evaporated to dryness. The residue was dissolved in 0.5 M perchloric acid and diluted to 100ml with distilled water. Known aliquots of the sample solutions were treated with suitable amounts of reagent in pH 8.0 buffer solutions and measuring the absorbances at 390 nm (zero order) or derivative amplitudes at 437.5 nm (Second order derivative method) and from respective pre-determined calibration plots. The results presented in table 4 along with certified values show the reliability of the proposed methods in the analysis of lanthanum containing complex materials.

Table 4. Determination of lanthanum in standard lanthanum samples

Sample	**Lanthanum present (mg kg $^{-1}$)**		**Relative error (%)**
	Certified value	**Present method***	
ACV-1 (74/19)	35.0	34.50 ± 0.08	- 1.43
BCR-1 (52/19)	26.0	26.40 ± 0.10	+ 1.54

**Average of four determinations ±S.D.*

Table 5. Comparison of the results

Reagent	λ_{max} (nm)	pH/ medium	Aqueous/ Extraction	Beer's law range (μg mL^{-1})	ε x 10^4 (L mol^{-1}cm^{-1})	Interference	Ref
Eriochrome Black T, Sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-sulfonate	650 & 512	8.7	Aqueous	0-5.0	-	Fe(II), Fe(III), Ni(II), Cu(II), Zn(II), Y(III), Th(IV), U(VI)	12
Arsenazo III	600 to 680	3.3	Aqueous	-	0.18 0.017 0.003	Zn(II), Mg(II), Ni(II), Co(II), Mn(II), Cd(II)	13
1-(-2-pyrichylazo)-2-naphthol	545 & 510	9.6 / 50% Ethanol	Extraction	-	0.55	-	16
2-(2-arsenophenylazo)-7-(2,4,6-trichlorophenylazo)-1,8-dihydroxy-naphthalone-3,6-disulphonicacid	-	-	Extraction	0.2-1.6	-	-	17
Aljzarin -3-sulphonate	-	-	Aqueous	0.42-10	0.89	-	20
Neothorone	-	-	Aqueous	0-2	-	-	24
5,14-N,N'-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraazo hexa cosine(NHDTAHA)	372	$CHCl_3$	Extraction	1.2-2.0	0.77	Th(IV),U(VI), Zr(IV),Hf(IV), Sc(III)	25
2-hydroxy-3-methoxy benzaldehyde-p-hydroxy benzoic hydrazone	390	8.0	Aqueous	0.139-9.723	1.925	Bi(IV),Tl(III), U(VI), Th(IV), Ti(IV), Fe(III), Co(II), Cu(II), interference eliminated by masking agents	Present (Direct) method
2-hydroxy-3-methoxy benzaldehyde-p-hydroxy benzoic hydrazone	437.5	8.0	Aqueous	0.099-1.528	-	Cr(VI), Ru(III) and Au(III) tolerance levels greately increased	Present (Second derivative) method

A comparison of the analytical results of the proposed methods and those of some previously reported methods (table 5) indicates that the present methods, are more sensitive and selective than those proposed by Raquel *et al*,[5] Yadvendra *et al*.,[6] and Shibata, *et al*.,[7] and more sensitive than the methods proposed by Salim *et al*.[8] Zuhari *et al*.,[9] and Matsushita *et al*.,[10]. Further, the proposed methods are simple, rapid and cost effective that can be carried out in any simple analytical laboratory.

CONCLUSION

The proposed spectroscopic method of lanthanum determination involves the use of a rapidly formining an intense lemon yellow stable coloured complex.The molar absortivity and thus sensitivity is high.The method is reasonably selective as number of diverse ions are tolerable in large quantities in the presence of some masking agents. The proposed method was applied for the determination of lanthanum in some standard lanthanum samples.2nd,3rd,4th order derivative spectroscopic methods are also proposed for the determination of lanthanum.All derivative methods are found to be more sensitive and 2nd derivative method is more selective than the zero order method.

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