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Der Pharmacia Lettre, 2014, 6 (6):373-379
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Direct and derivative spectrophotometric determination of Yttrium (III) using 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone (HNHBH) in alloy and geological samples

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ABSTRACT

2-hydroxy-1-naphthaldehyde-p-hydroxy benzoic hydrazone (HNHBH) is used as a new analytical reagent for the direct and derivative spectrophotometric determination of yttrium (III). It reacts with yttrium in basic medium (pH 8.5, ammonium chloride and ammonium hydroxide buffer) to form yellow colored (λ_{max} , 410 nm) 1:4 (Y- HNBH) complex. The colour reaction is instantaneous and the absorbance remains constant for about 24h. The molar absorptivity and Sandall's sensitivity were found to be $6.76 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0013 \mu\text{g cm}^{-2}$ respectively. The system obeys Beer's law in the range of $0.044\text{-}2.222 \mu\text{g mL}^{-1}$ of Y (III). Tolerance limits of various foreign ions were also studied. The complex was fairly stable (stability constant 2.28×10^{22}) and Second and third order derivative spectrophotometric methods were also developed for the determination of yttrium (III) which showed greater sensitivity and selectivity. The proposed method was applied for the determination of yttrium (III) in some nickel based alloy samples and in certain geological samples. The method has high sensitivity, selectivity precision and accuracy.

Keywords: yttrium (III), HNBH, Direct and derivative spectrophotometry, alloys and geographical samples

INTRODUCTION

Yttrium (III) oxide is the most important compound of yttrium. It is widely used to make YVO_4 : Eu and Y_2O_3 : Eu phosphors that give the red colour in colour television picture tubes. Yttrium-iron garnet is a very effective microwave filter. Yttrium-aluminium garnet has a hardness of 8.5 and used as simulated diamond. Iron, aluminium and gadolinium garnets of yttrium have interesting magnetic properties. Yttrium-iron garnet is a very efficient as an acoustic energy transmitter and transducer. Yttrium-aluminium garnet, yttrium lithium fluoride and yttrium vanadate along with dopants such as neodymium or erbium are used as infrared lasers. Cerium doped yttrium aluminium garnet crystals are used as phosphors to make white LEDs. Yttrium-90 microspheres have shown promise as treatment for unresectable *hepatocellular carcinoma*. The superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_y$, which was synthesized at University of Houston showed remarkable superconductivity [1] above 90 K, in which Yttrium is a key element. This was amazing feature because it can operate at above liquid nitrogen boiling point (-195.9°C).

The literature survey showed that yttrium analysis has been studied very sporadically using spectrophotometry. Only handful of methods were reported during the last 50 years. Of these, most of the methods are less sensitive [2-9] and less selective [8] and also involve extraction into harmful organic solvents[3,9] Hence, there is a great need for the development of more sensitive, selective and simple methods for the effective determination of microgram amounts of yttrium in the nuclear waste. We are now proposing simple, highly sensitive and reasonably selective direct and derivative spectrophotometric methods for the determination of yttrium. The methods were also applied for the analysis of alloy samples and geological materials.

MATERIALS AND METHODS

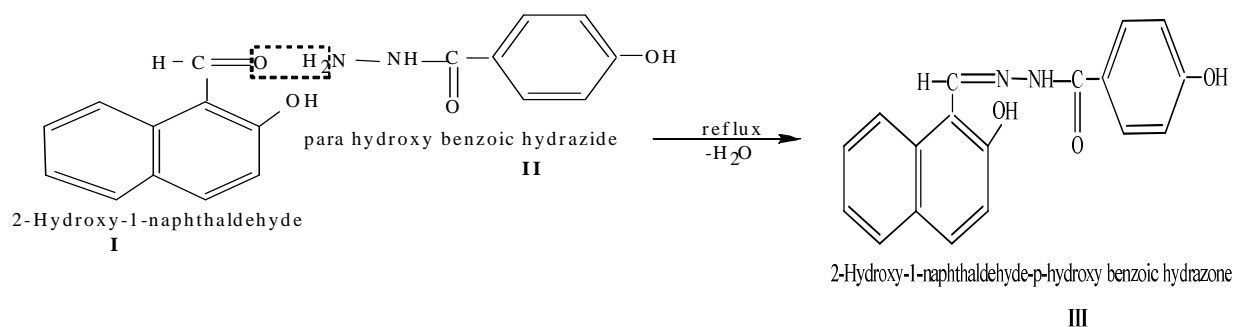
Schimadzu 160A UV-visible spectrophotometer (PerkinElmer Singapore Private Limited, Singapore) equipped with 1.0 cm quartz cell and an ELICO model LI - 610 pH meter (M/s ELICO private limited, Hyderabad, India) were used in the present study.

Reagent and solutions

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment. Glass vessels were cleaned soaking in acidified solutions of $K_2Cr_2O_7$ followed by washing with con. HNO_3 and were rinsed several times with high purity deionized water.

2.1 Preparation of 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone (HNHBH):

The reagent (HNHBH) was prepared by simple condensation of 1 mol of 2-hydroxy-1-naphthaldehyde and 1 mol of p-hydroxybenzoic hydrazone. In a 250-ml Erlenmeyer flask, a hot ethanolic solution of 2-hydroxy-1-naphthaldehyde (5ml, 0.0438mol in 5ml of ethanol), thiosemicarbazide (4g, 0.0438 mol, dissolved in 10 ml of hot water) were taken in 250-ml round bottom flask. Suitable quantity (~ 2ml) of glacial acetic acid was added to the reaction mixture and refluxed for 3 hours. [10] On cooling the reaction mixture, the reddish brown coloured solid obtained was then separated by filtration, washed and dried. The product was recrystallized from aqueous ethanol in the presence of norit and dried in *vacuo*, yield 4.2 g; m.p.273⁰c as shown in Scheme 1.



Scheme-1

2.2 Characterization:

The compound was characterized by IR and ¹H-NMR spectral data. Infrared spectrum of HNHBH shows bands at [3467(m) and 3185(m,br)], 3292(m), 3207(m), 1735(s), merged peaks at 1635 and 1608(m), 1466(s), 1383(w), 1455 to 1591, 1256(δ) and 1280(δ) 746, 764 cm⁻¹ respectively corresponding to ν OH stretching, ν (N-H) stretch, ν (C-H) bond, ν (C=N) stretching, ν (C-C) aromatic ring, δ phenolic (>C=O) stretching and naphthalic (>C=O) stretching vibrations respectively, δ (C-H)-oop bend (aromatic) vibrations. ¹H-NMR spectrum of HNHBH (CDCl₃+ DMSO-d₆) showed signals at 12.10 (2H,s), 10.50 (1H, s), δ9.49 (1H,s), 7.91(4H, s), 6.93-7.65 (5H, m), 8.20(1H, d) due to -OH(phenolic and naphthalic), -NH, -CH, phenyl, naphthyl, naphthyl (influenced by the adjacent -CH proton of azomethine group).

2.3 HNHBH solution

The reagent solution (0.01M) was prepared by dissolving 31 mg of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 12h.

2.4 Yittrium (III) Solution:

A Stock solution (1 x 10⁻² M) of trivalent yittrium was prepared by dissolving 0.303 g of YCl₃ (Sigma-Aldrich) in deionized water containing few drops of concentrated hydrochloric acid and made up to the mark in a 100-ml volumetric flask. Aliquots of this solution were standardized [11] with EDTA using xylenol orange as an indicator. Dilute solutions were prepared from this stock solution.

Solutions of large number of inorganic ions and complexing agents were prepared from their Analar grade or equivalent grade water soluble salts. In the case of insoluble substance, special dissolution methods were adopted [12]

2.5 Buffer Solution

Buffer solutions of various pH values were prepared by mixing 1 M hydrochloric acid and 1 M of sodium acetate (pH 1.0-3.0), 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0), 0.2 M acetic acid and 1 M sodium acetate

(pH 7.0) and 2M ammonium chloride and 2 M ammonium hydroxide (pH 8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter. Suitable portions of these solutions are mixed to get the desired pH.

2.6. Preparation of Sample solutions:

2.6 a. Preparation of nickel based alloy sample solutions [7]

0.5 grams of alloy sample was weighed and dissolved in 60 ml of a mixture of HNO_3 and HCl (1: 3). The mixture was heated to near dryness and then added 20 ml of distilled water and 2 ml of 10% oxalic acid. The pH of the solution was adjusted to 2.0-2.5 with 1:1 NH_3 solution. Then 2 ml of 10 % CaCl_2 was added and observed the formation of small amount of calcium oxalate precipitate. More amount of precipitate was formed when pH of the solution was increased to 4.0. The solution was filtered and the precipitate was washed with water. The precipitate was re-dissolved in 2 ml of 1:10 HCl and collected in to 50 ml volumetric flask. The solution was diluted to the volume with distilled water and appropriate volumes were used for the determination of yttrium. The sample solutions were treated with 500 μg of thiourea (to mask nickel) and then with suitable amount of HNHBH at pH 8.5 and the amounts of yttrium present were computed from the measured absorbance values.

2.6 b. Preparation of geological sample solutions

0.5 grams of geological sample was treated with $\text{HF-H}_2\text{SO}_4$ (10 ml each) mixture in a platinum dish, fumed on sand bath, cooled in ice, diluted with ice cold water and filtered. The residue is fused with sodium peroxide in nickel crucible and mixed with the filtrate. Yttrium is precipitated with NH_4OH , and the precipitate is dissolved in 12N HNO_3 and extraction done with 10 ml TB.P. each for 5 min. Yttrium is stripped twice in 10 ml water each for 5 min. The stripped solution is evaporated on water bath and the residue is leached with 2 ml 10% HCl and collected in to 50 ml volumetric flask. The solution was diluted to the volume with distilled water and appropriate volumes were used for the determination of yttrium.

2.7 Absorption spectrum

The absorption spectrum was recorded between differential absorbance (ΔA) and the wavelength and shown in fig.1. As the absorption was maximum at 410 nm, the analysis of Y(III) was carried out by measuring the absorbance at 410 nm against the reagent blank.

3 Recommended procedures

(a) Determination of Yttrium (III) (Zero order)

An aliquot of the solution containing 0.303 $\mu\text{g/ml}$ (or ppm) of yttrium (III), 10 ml of $\text{NH}_4\text{Cl- NH}_4\text{OH}$ buffer solution (pH, 8.5) and 1.5 ml of 0.01 M HNHBH were combined in a 25 ml volumetric flask and resulting solution was diluted to the mark with distilled water. The absorbance of this solution was read at 410 nm against reagent blank. The measured absorbance is used to compute the amount of yttrium form predetermined calibration plot.

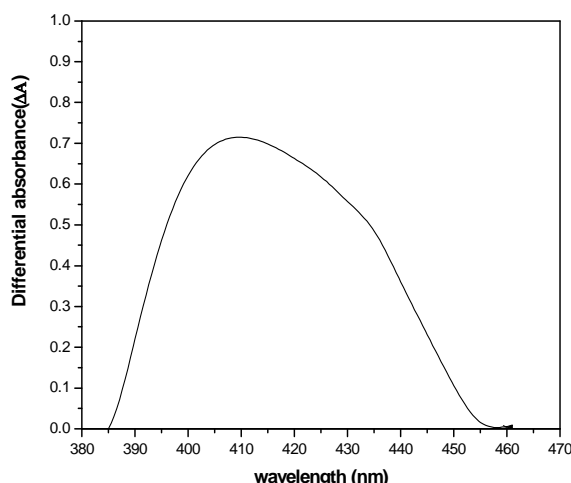


Fig.1. Absorption spectra of Y(III) – HNHBH Vs

Reagent blank	=	
[Y(III)]	=	$1 \times 10^{-5}\text{M}$
[HNHBH]	=	$1.5 \times 10^{-4}\text{M}$
pH	=	8.5

(b) Determination of Yttrium(III) using second and third derivative spectrophotometry

A sensitive second order derivative spectrophotometric method was developed for the determination of yttrium (III). For the second derivative spectra Fig. 3, the second derivative amplitudes at 415 nm (peak) and at 462 nm (valley) and third derivative curves Fig. 4 at 415 nm, 450 nm and 476 nm with zero cross at 430 nm and 462 nm were plotted against the amount of yttrium. The derivative amplitudes were measured for different concentration of Y(III) and plotted against the amount of Y (III). The plots were linear and obeyed Beer's law in the range 0.011-0.845 $\mu\text{g ml}^{-1}$ at 415 nm and 0.022-0.845 $\mu\text{g ml}^{-1}$ at 462 nm. In the second order derivative method, In third order derivative method, the determinable range was found to be 0.011-0.845 $\mu\text{g mL}^{-1}$ at all the three wavelengths (415 nm, 450 nm and 476 nm). The other analytical and statistical results of the derivative methods are presented in table 1.

RESULTS AND DISCUSSION

The reagent, HNHBH is easily obtained by the condensation of 2-hydroxy-1-naphthaldehyde and p-hydroxybenzoic hydrazide. A 0.01M solution of this reagent is stable for 12h. The absorbance data measured for experimental solutions containing different known amounts of yttrium (III) fitted into a straight line equation $A_{410}=0.7402C -0.0022$. Beer's law was obeyed in the concentration range 0.044-2.222 $\mu\text{g mL}^{-1}$ of yttrium.

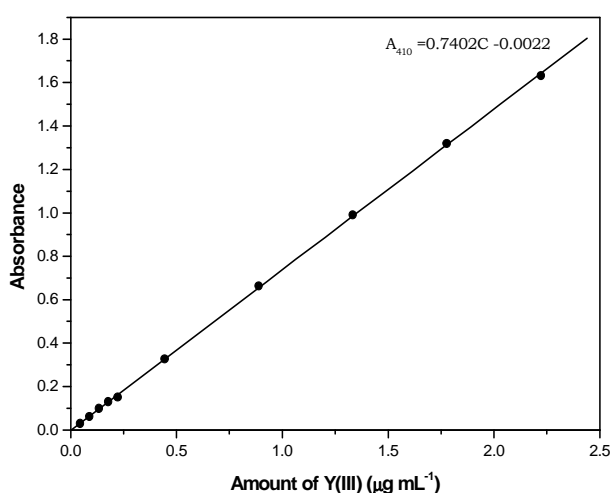


Fig.2. Applicability of Beer's law

[HNAHBH]	=	3.75 x 10 ⁻⁴ M
Wavelength	=	410 nm
pH	=	8.5

The molar absorptivity, Sandell's sensitivity, detection limit, determination limit, relative standard deviation, correlation coefficient and other statistical data of the direct method were evaluated and presented in table 1.

Table.1. Spectrochemical and Analytical characteristics of [Y (III) – HNHBH]

Characteristics	Direct method	Second derivative		Third derivative		
	410 nm	415 nm	462 nm	415 nm	450 nm	476 nm
Beer's law range ($\mu\text{g mL}^{-1}$)	0.044-2.222	0.011-0.845	0.022-0.845	0.011-0.845	0.011-0.845	0.011-0.845
Molar absorptivity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	6.76 x 10 ⁴	-	-	-	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0013	-	-	-	-	-
Angular coefficient (m)	0.7402	1.6838	0.8299	1.6957	1.6785	1.2804
Y-intercept (b)	-0.0020	-0.0005	+0.0004	+0.0005	-0.0038	+0.0003
Correlation coefficient (r)	0.9999	0.9999	0.9999	0.9998	0.9999	0.9999
Relative standard deviation (%)	1.25	0.36	0.28	0.37	0.13	0.82
Detection limit ($\mu\text{g mL}^{-1}$)	0.010	0.0028	0.0025	0.003	0.0037	0.0007
Determination limit ($\mu\text{g mL}^{-1}$)	0.030	0.0084	0.0075	0.009	0.0111	0.0021
Composition(Metal: Ligand)	1:4	-	-	-	-	-

4.1. Determination of yttrium (III)

Yttrium (III) reacts with HNHBH in Basic pH to give coloured complexes in Table1. The colour reaction is instantaneous at room temperature. The order of addition of metal ion, reagent, and buffer has no effect on the absorbance of complex. Various physico-chemical and analytical characteristics of the complex are summarized in Table 1. The stoichiometry of the complex (M: L=1:4), was determined by Job's continuous variation[13], molar ratio methods. The data obtained in Job's method were used in the calculation of stability constant of the complex,

it is found to be 2.28×10^{22} . Ammonium chloride (2M) -ammonium hydroxide (2M) buffer solution (pH 8.5 μ , 0.2 and T=300K) and equimolar (1.5×10^{-4} M) solution of Y (III) and HNHBH were used in these methods. Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference i.e., increases the tolerance limit value of foreign ions and it may be advantageously used for the second derivative determination of metal ion having peak-valley method is more sensitive and hence is adopted for the determination of Y(III).

4.2. Interference

The effect of various cations and anions which are generally associated with the metal ion on the determination of yttrium(III) was studied by measuring the absorbance of the yttrium complex containing 0.5 μ g/ml of yttrium (III) in solution. The colour reaction is developed as described in the standard procedure. An error of $\pm 2\%$ in the absorbance or amplitude reading in the case of derivative methods considered tolerable.

Table.2. Tolerance limits of foreign ions

Amount of Y(III) taken = 0.50 μ g mL⁻¹ pH = 8.5

Foreign ion	Tolerance limit (folds)	Foreign ion	Tolerance limit (folds)
Iodide	3234	Na(I)	3380
Bromide	2618	K(I), Mg(II)	3092
Sulphate	2022	Ca(II), Ba(II)	2986
Nitrate	1502	Sr(II)	2514
Thiourea	1256	Te(IV), Hg(II), W(VI)	164
Thiocyanate	1148	Se(IV), Zr(IV)	126
Thiosulphate	840	Pb(II), Cd(II)	80
Chloride	702	Ce(IV), Au(III)	42
EDTA	242	Ir(III), Ag(I), Tl(III)	26
Tartrate	182	Th(IV), Bi(III)	20
Carbonate	160	Cr(VI)	10
Oxalate	90	U(VI)	8,190 ^b
Phosphate	60	Mn(II)	6,50 ^a
Fluoride	20	Cu(II)	2,20 ^c
		Zn(II)	2,130 ^b
		Mo(VI)	2,200 ^a
		Fe(II)	<1,16 ^c
		Co(II)	<1,40 ^a
		Sn(II)	<1,240 ^c
		Ni(II)	<1,40 ^b

*a: in the presence of 500 μ g of SCN⁻; b: in the presence of 500 μ g of thiourea
c: in the presence of 400 μ g of thio sulphate*

Table.3. Tolerance limits of foreign ions

Foreign ion	Tolerance limit(in folds)					
	Zero order	Second derivative		Third derivative		
		415 nm	462 nm	415 nm	450 nm	476 nm
Ga(III)	<1	>100	05	>100	70	10
In(III)	<1	70	80	80	20	10
Al(III)	<1	05	07	06	15	20
La(III)	<1	15	20	>100	>100	>100
V(V)	<1	>100	>100	>100	>100	30
Pd(II)	<1	35	40	70	80	45

The results are given in Table.2 &3. The data obtained in second derivative method are also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess. The tolerance limit values for many anions and cations are more in derivative methods. The interference of associated metal ions such as Co (II) and Mn(II) is decreased with 500 μ g of SCN. Larger amount of Zinc (II) and Nickel (II) do not interfere in the presence of thiourea and sulphate respectively.

4.3. Derivative methods:

In order to improve the sensitivity and selectivity of the proposed method, the absorbance data were derivatized twice and thrice and plotted against the wavelength which gave the resultant second and third order derivative curves respectively. The derivative amplitudes at certain wavelengths were found to be proportional to the amount of yttrium thus obeying Beer's law. Therefore, the method was exploited to develop second and third order derivative spectrophotometric methods for the determination of yttrium.

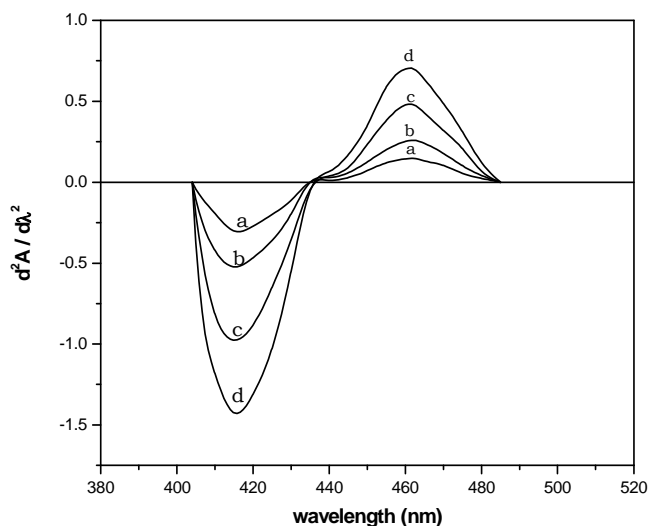


Fig.2. Second derivative spectra of Y(III) –HNAHBH

Amount of Y(III) ($\mu\text{g mL}^{-1}$) :
a. 0.178; b. 0.311; c. 0.578; d. 0.845

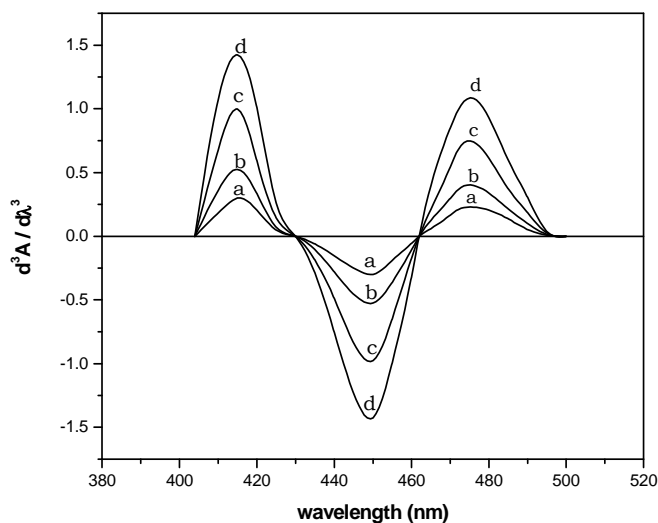


Fig.3. Third derivative spectra of Y(III) –HNAHBH

Amount of Y(III) ($\mu\text{g mL}^{-1}$) :
a. 0.178; b. 0.311; c. 0.578; d. 0.845

4.4 Applications:

To substantiate the validity of the proposed direct method, it was applied for the determination of yttrium in some nickel based alloy and geological samples. The results obtained were compared with certified values and presented in tables 4 & 5.

Table.4. Determination of yttrium in nickel based alloy samples

Sample	Amount of yttrium (%)		Relative error (%)
	Certified value	Present method *	
A-S-81	0.046	0.045 \pm 0.004	1.74
A-S-82	0.010	0.0098 \pm 0.007	2.00

*Average of four determinations \pm SD

Table.5. Determination of yttrium in geological samples

Sample	Amount of yttrium (%)		Relative error (%)
	Certified value	Found value *	
USGS G2	1.50	1.52 ± 0.04	1.33
USGS G2(6/26)	2.01	1.98 ± 0.02	1.49
USGS G2(49/50)	1.64	1.63 ± 0.03	0.61

*Average of five determinations ± SD

Table.6. Comparison of the results

Reagent	Beer's law range ($\mu\text{g mL}^{-1}$)	$\epsilon \times 10^4$ ($\text{L mol}^{-1}\text{cm}^{-1}$)	Interference	Ref
Arsenazo III	-	-	-	1
Purpurin 1,2,4-trihydroxy-anthraquinone	0.0-15.0	6.1	-	2
Chrome Azural S	-	15	-	-
Eriochrome Cyanin R	-	9.2	-	3
Pyrocatechol Violet	-	3.3	-	-
Molybdophosphoric acid	-	-	-	4
4-(2-pyridylazo)resorcinol	-	-	-	5
Bromopyrogallol red	10-50	-	-	6
5-4'-(Chlorophenylazo)-6-hydroxypyrimidine-2,4-dione	3.91-7.85	1.60	Sc(III),Eu(III),La(III), Gd(III)	7
Dibenzo-18-crown-6	0.81-16.2	0.548	-	8
2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone	0.044-2.222	6.76	Mn(II), Sn(II), (VI), Mo(VI),Fe(II),Cu(II), Zn(II), Co(II), Ni(II) interference eliminated by masking agents.	Present (direct) method
2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone	0.011-0.845	-	No influence from Ga(III), In(III) and (V)	Present (second derivative) method

CONCLUSION

The results of the present direct and derivative methods were compared with those of some of the already reported methods and presented in table 6. The comparison shows that both the direct and derivative methods proposed are more sensitive than majority of the reported methods. Further, the derivative methods are found to be more selective than large number of the reported method.

Acknowledgement

The authors thankful to Dr. B.V. Subbareddy IICT Hyderabad for providing IR, NMR and mass Spectral data. Authors also extend their sincere thanks to The Dept. of Chemistry, S.K. University, Ananatapur for the timely help.

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