Synthesis of 2-Hydroxy 3-Methoxy Benzaldehyde Thiosemicarbazone (HMBATSC) and its applicatnions for direct and second order derivative spectrophotometric determination of Indium (III) in synthetic alloy samples.

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Abstract

2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone has been synthesized, characterized and its analytical applications are investigated. It reacts with Indium (III) is aqueous solution at pH 6.0 and at room temperature, to form a greenish yellow coloured metal liquid (2:3) complex with abosption maximum at 385nm and molar absorptivity 1.05×10^4 lit.mol^{-1} cm^{-1}). Beer's law is obeyed in the range of 0.5784 to 5.741 μg mL^{-1} of In(III). A method for the determination of Indium (III) by second order derivative spectrophotometry has also been proposed. Interferences of various diverse ions has been studied. The proposed methods have been successfully applied for the determination of Indium in the effluents and in synthetic mixtures.

Keywords: Indium (III), HMBATSC, DMF, Direct spectrophotometry and Derivative spectrophotometry.

Introduction

Indium is a soft silvery, white metal which looks like wine but it is chemically similar to aluminum and gallium. The main application of Indium is formation of transparent electrodes from, Indium tin-oxide which is used is

liquid crystal displays and in televisions. It is used in thin films to form, lubricated layers. Indium is very small amount is used in aluminum alloys which acts as sacrificial anodes to present passivation of the aluminum. Pure Indium in metal form is considered to be non toxic. But all the indium compounds should be regarded as highly toxic and damages the hearts, kidney and liver and may be tetratogenic. Anhydrous indium trichloride is quite toxic and indium phosphate is both toxic and the suspected carcinogen. The need arises for the development of simple and rapid methods for the quantitative determination of indium in zinc effluents and in synthetic mixtures.

Some of the conventional reagents reported for the spectrophotometric determination to indium (III) such as PAN[1], PAR[2], Pyrocatechol violet[3], xylenol orange[4] and erichrome cyanine R[5], are non selective reagents as they form coloured complexes with number of metal ions. To improve the selectivity of those methods prior separation of the analyte by solvent extraction methods was proposed. Singh et al and Agnihotri et al recently 1-(2-pyridylarzo)-2-napthol [6] and 2-(5-bromo-2-pyridylarzo)-5-diethyl aminophenol[7] for the derivative spectrophotometric determination of In(III).

Among various organic analytical reagents thiosemicarbazones continuing sulphur and nitrogen as donor atoms occupy a unique place. Thiosemicarbazones [8 - 11] are one of the important classes of reagents widely employed for the spectrophotometric determination of metal ions. In the present paper a simple, rapid, non-extractable, selective and sensitive method is reported for the spectrophotometric determination of trace amounts of Indium (III) by complexing with 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone [HMBATSC]. The reagent forms a greenish yellow coloured complex with indium (III) in acid medium at the pH 6.0. Hence, a systematic study has been made to develop a spectrophotometric method for the determination of indium (III) in zinc effluent and in synthetic mixtures.

EXPERIMENTAL

Reagents and Solutions

The reagent (HMBATSC) was prepared by literature method. 2-hydroxy-3-methoxy benazldehyde (I) (11.25 g) and thiosemicarbazide (II) (4.55 g) were dissolved in sufficient volume of methanol and the mixture was refluxed for 60 min. The contents were allowed to cool and the product was separated by filtration. The crude sample obtained ($C_9H_{11}O_2SN_3$ yield 80%) was recrystallized twice from hot methanol. Pure light yellowish green crystals of 2-hydroxy-3-methoxy benzaldehyde thiosemicarba-zone (HMBATSC) (III) (m.pt.220 – 222°C) were obtained (figure 1).

Figure 1: Preparation of HMBATSC

A 0.01 M solution of HMBATSC in dimethyl formamide (DMF) was employed in the present studies.

The infrared spectrum of the compound was recorded using Perkin-elmer 137 IR spectrometer in KBr. The peaks observed at 3458 cm^{-1} and 3342 cm^{-1} may be assigned to symmetric and asymmetric –N-H stretching frequency of primary amino group. The peak observed at 3164 cm^{-1} may be assigned to –OH stretching frequency of phenolic group due to intramolecular hydrogen bonding. The peak observed at 3028 cm^{-1} may be assigned to Ar-H stretching frequency of aromatic proton, and that observed at 1595 cm^{-1} to –C=N stretching frequency of azomethine. The peaks observed in the range 1530 – 1361 cm^{-1} were characteristic of aromatic ring stretching frequency. A strong peak observed at 1056 cm^{-1} may be assigned to C=S stretching frequency.

The 'H-NMR spectrum of the compound was recorded with DRX 300 NMR spectrometer in DMF solvent. The peak observed at δ value 8.2 (1H) was characteristic of phenolic –OH group. The peak found at δ value 7.88 (3H) may be due to aromatic protons, while that observed at δ value 4.0 (3H) due to methyl group attached to hetero atom (oxygen atom). The peak observed at δ value 6.8 (2H) may be due to –NH$_2$ protons attached to thionyl group (C=S), and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.4 may be due to –NH proton (azomethine).

Stock solution (1×10^{-2}M) of Indium Sulphate was prepared by dissolving 0.5178g of In$_2$(SO$_4$)$_3$. H$_2$O (Himedia) in 2ml of 2M H$_2$SO$_4$ and diluting to 100ml with distilled water. This solution was standardized by EDTA by using xylenol orange as indicator[12]. Working solutions were prepared daily by diluting appropriate volume of this stock solution with distilled water. All other chemicals used were of analytical grade.

The buffer solution was prepared by mixing 0.2M acetic acid and 0.2M sodium acetate pH 3.5–7.0. The pH of this solution was checked with a pH meter.

Apparatus

A shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1cm quartz cells, measuring wavelength range 200-1100 nm and slit width of 2mm

was used to measure absorbance of all analytical species. All spectral measurements were performed using the blank solution as a reference. Measurement of pH was carried out on a Phillips digital pH meter (model LI 613).

Procedure
Zero order method
In different sets of 10ml volumetric flasks, each containing 5 ml of buffer solution (pH 6.0) and 0.5ml of HMBATSC (1×10^{-3}M), varying volumes of 5×10^{-5}M indium (III) solution were added and made up to the mark with doubly distilled water. The absorbance was measured at 385nm against the reagent blank, and the calibration plot was prepared.

Second order derivative method
For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}), slit width of 1nm with 9 degrees of freedom, in the wavelength range of 350-550 nm. The derivative peak height was measured by the peak-zero method at 425 nm and observed 0 amplitude at 409 nm. The peak height was plotted against the amount of indium (III) to obtain the calibration plot.

The calibration graph follows the straight-line equation, $y = mc + b$; where c is the concentration of the solution, y is measured absorbance or peak height and m and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration, equations were calculated as $A = 0.263c - 0.0130$ for zero order data and $A_{412} = 0.293c + 0.0094$ and $A_{440} = 0.362c + 0.0295$ for second derivative data, which give the best straight lines.

Results and Discussion
The absorption spectra were recorded in wavelength region 380-500nm for the greenish yellow coloured [In(III)-HMBATSC] complex against the reagent blank and HMBATSC against buffer blank and presented in figure 2.
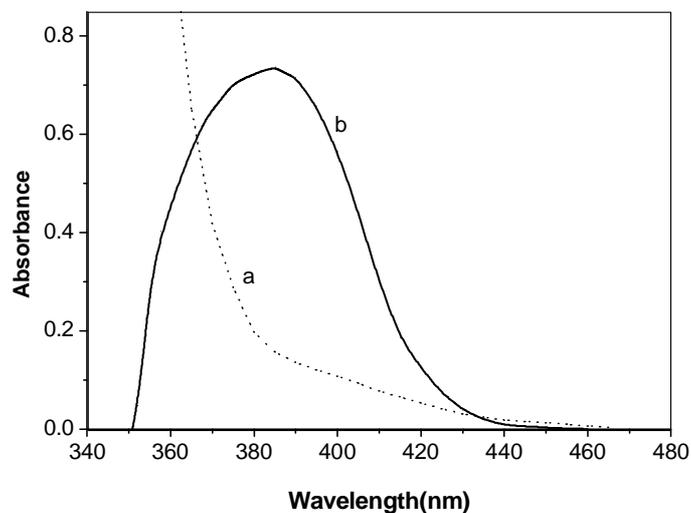
Figure 2: Absorbance spectra of (a) HMBATSC Vs Buffer blank (b) In(III) - HMBATSC Vs Reagent blank [In(III)] = 5×10^{-4}M ; [HMBATSC] = 5×10^{-3}M; pH = 6.0

From the spectrum it was observed maximum absorbance for the meal complex and negligible absorbance for the reagent blank at 385nm. Therefore 385nm was choosen as the analytical wavelength for further investigations.

The absorbance was found to be maximum and constant in pH range 5.5 to 6.5. Hence, the calibration plot was prepared by measuring the absorbance value at pH 6.0. A minimum of 10 fold excess of reagent is necessary to obtain maximum sensitivity for the colour reaction between indium (III) and HMBATSC.

The calibration graph under optimum conditions was drawn by measuring the absorbance of experimental solutions containing different amounts of metal ion and plotted against the amount of indium (III) (figure 3). The plot was linear with slope of +0.105 in the range 0.5742 μ g mL^{-1} of Indium (III) with Y intercept of 3.9×10^{-4}. The sensitivity of the proposed method has been derived from which molar absorptivity 1.05×10^{4}L mol^{-1} cm^{-1}, detection limit 0.0213 μ g mL^{-1} and detection limit 0.064 μ g mL^{-1} correlation coefficient 0.9999 and relative standard deviation 0.154 confirm the best suitability of the proposed method for the determination of indium (III).
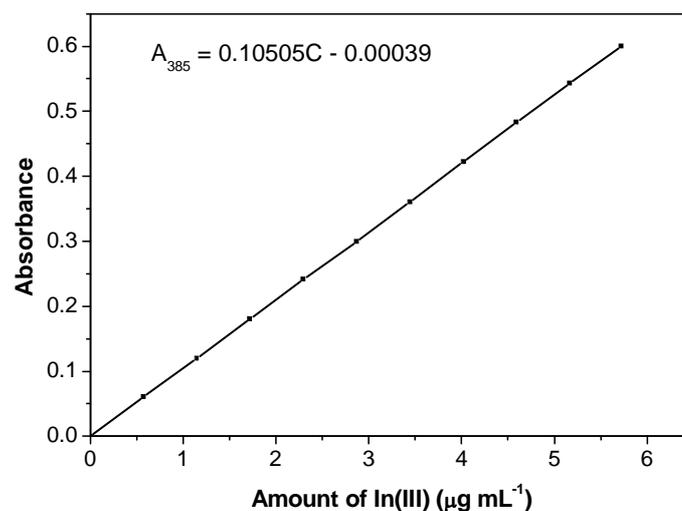
Figure 3: Calibration Plot [HMBATSC] $= 1.25 \times 10^{-2}$M ; Wavelength $= 385$nm; pH $= 6.0$

Effect of foreign ions

The effect of different anions and cations on the absorbance of experimental solutions at the optimum conditions was studied based on the procedure 3.e and their tolerance limits were evaluated and presented in the table 1. Most of the anions did not interfere even when present in more than 1000 fold excess. Majority of the remaining anions had tolerance in more than 100 fold excess. Citrate and Phosphate were tolerable in 35 fold and 90 fold excess respectively. Among the cations the tolerance limits were found to be between 45 fold to 960 fold excess.

Table 1 : Tolerance limit of foreign ions Amount of In(III) = 0.574 μg mL^{-1}, pH = 6.0

Diverse Ion	Tolerance Limit (Folds)	Diverse Ion	Tolerance Limit (Folds)
Ascorbic Acid	3050	Pb(II)	3600
Iodide	2200	Tn(I)	3560
Tartrate	1400	W(VI)	3200
Thio Urea	1300	Ce(IV)	2440
Thio sulphate	1200	Te(IV)	2220
Nitrate	1080	Cd(II)	1950
Thio Cyanate	1010	Zr(IV)	1590
Sulphate	800	Y(III)	1000
Bromide	670	Au(III)	960
Chloride	600	Ag(I)	500
Carbonate	490	U(VI)	410
EDTA	360	Th(IV)	400

Fluoride	330	Sn(II)	200
Oxalate	200	Ir(III)	190
Phosphate	90	Bi(III)	130
Citrate	30	Zn(II)	80
		Ga(III)	60
		Se(IV)	50
		Al(III)	40
		Hg(II)	40
		Pd(II)	10
		Fe(III)	10
		V(IV)	9
		Ru(III)	8
		Cr(VI)	7
		Mn(II)	7
		Mo(VI)	6
		Fe(II)	2
		Cu(II)	1
		V(V)	< 1
		Co(II)	< 1
		Ni(II)	< 1

The ratio between the In(III) and HMBATSC in coloured complex solution was established using Job's continuous variation method, molar ratio method and obtained as 2:3 (metal : ligand). The stability constant of In(III) – HMBATSC complex was calculated from Job's curve as 1.11×10^{13}.

The reagent HMBATSC acts as tridentate ligand which possesses three donor atoms S, N and O. In (III) and Al (III) were known to form dimers due to their tendency to complete their octetes. The configuration of the complex is different from perfect tetrahedron[14]. The composition of the complex, the possible geometry of indium (III) complexes and the coordination sites of the ligand suggest the following possible structure for [In(III)-HMBATSC] complex as shown in figure 4.
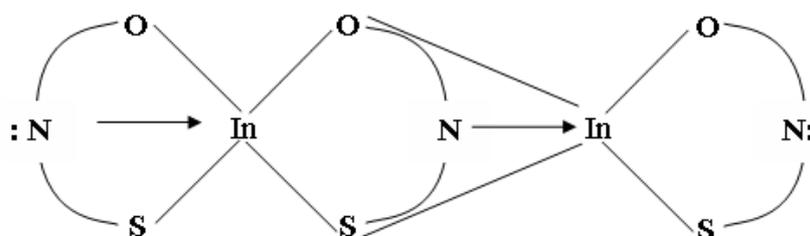

Figure 4: Structure of In (III) – HMBATSC Complex

Applications

The zero order method was applied for the determination of indium in zinc effluents [13].

The effluents were collected from the zinc smelting industry Hindustan Zinc Ltd., Visakhapatnam, India. 60ml of the effluent sample was taken and digested with 5ml of H_2O_2 (30%). The resultant solution was filtered, cooled and diluted to 25ml with distilled water. Different aliquots of the sample were taken in different 10ml volumetric flasks and the pH was adjusted to 6.0 and then treated with suitable amounts of HMBATSC. The resultant solution was diluted to 10ml with distilled water and the absorbance was measured at 385nm. From the measured absorbance the amounts of indium were computed from predetermined calibration plot. The results are presented in table 2.

Table 2: Analysis of effluents samples

Sample	Indium found (μg mL^{-1})		Relative error (%)
	Proposed method*	AAS Method (n=2)	
1	0.220	0.225	-2.22
2	0.280	0.273	2.56
3	0.350	0.342	2.34

* Average of five determinations.

Second order derivative method

In order to improve the sensitivity and selectivity of the direct spectrophotometric method proposed, the absorbance data was derivatized twice and plotted against the wavelength which gave the 2nd order derivative curve.

Derivative Curve

0.72 to 8.2μg mL^{-1} In(III) were treated with suitable amounts of HMBATSC in Buffer solutions of pH 6.0 and made up to 10ml with distilled water. The 2nd derivative curve was recorded in wavelength region 350-550nm. Figure 5 shows the corresponding derivative curve. In the second derivative curve one small trough at 405nm and huge crust at 425nm was observed with zero amplitude at 409nm. Determination of Indium was carried out by measuring the derivative amplitude for all the crust and trough as noticed above for the derivative spectra.
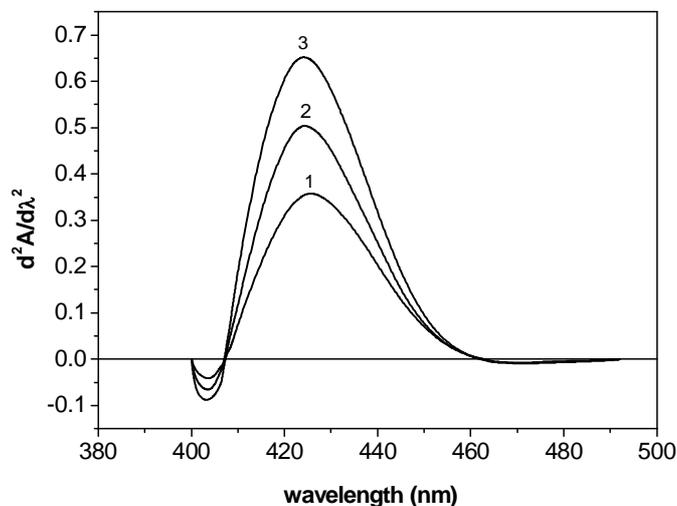
Figure 5: Second derivative spectra of [In(III) – HMBATSC] Vs reagent blank [In(III)] (μ g mL^{-1}) = (1) 0.574; (2) 1.148; (3) 2.296

Determination of In(III)

Calibration plot drawn between the amount of In(III) and measured derivative amplitude are shown in figure 6. The determinable range for indium (III) by 2nd order derivative method is 0.072–6.884 μ g mL^{-1} (412nm). The analytical and statistical results of the zero order and derivative methods are presented in table 3. The results show that the derivative method is more sensitive and possess larger determinable ranges than the zero order method.
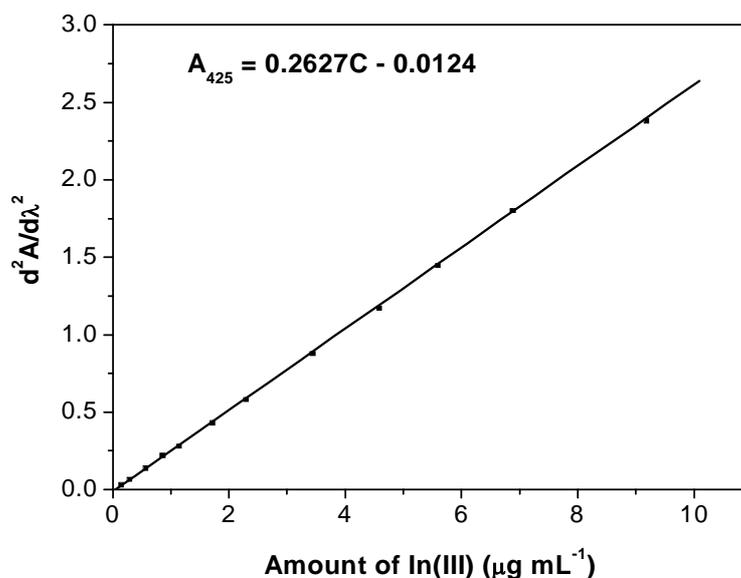

Figure 6: Calibration plot for Indium (III) [HMBATSC] = 1.25×10^{-2}M; pH = 6.0

Table 3: Analytical Characteristics of [In(III) – HMBATSC]

S. No.	Parameter	Direct Method	Second Derivative Method	Third Derivative Method	
				412nm	440nm
	Wavelength	385nm	425nm	412nm	440nm
1	Beer's Law rang (μg mL^{-1})	0.574 – 5.740	0.144 – 9.185	0.072 – 6.884	0.072 – 8.252
2	Molar absorptivity, ε (L mol^{-1} cm^{-1})	1.05×10^{4}	-	-	-
3	Sandell's sensitivity (μg cm^{-2})	1.0109×10^{-2}	-	-	-
4	Angular coefficient (m)	0.1050	0.263	0.293	0.362
5	Y-intercept (b)	3.9×10^{-4}	-0.013	0.0094	0.0295
6	Correlation coefficient (r)	0.9999	0.9997	0.9995	0.9997
7	Determination limit	0.064	0.058	0.042	0.059
8	Detection limit (μg mL^{-1})	0.0213	0.019	0.011	0.019
9	Composition (M:L)	2 : 3	-	-	-
10	Stability constant	1.11×10^{13}	-	-	-

Effect of diverse ions

When compared to the zero order method, the tolerance limits of large number of ions which were very low in the zero order method were found to be much higher in the derivative methods. This shows the greater selectivity of the derivative methods when compared to zero order method. The results obtained in these studies are presented in table 4.

Table 4: Tolerance limits of foreign ions

Foreign ion	Direct method 385nm (Folds)	Derivation second order 425nm (Folds)	Third order	
			412nm (Folds)	440nm (Folds)
Pd (II)	10	22	36	43
Fe(III)	10	34	47	33
V(IV)	09	16	15	18
Ru(III)	08	12	Interfere	16
Cr(VI)	07	11	12	09
Mn(II)	07	09	10	14
Mo(VI)	06	09	15	13
Fe(II)	02	05	07	08

Cu(II)	01	03	05	05
V(V)	< 1	02	01	Interfere
Co(II)	< 1	02	04	09
Ni(II)	< 1	03	03	12

Applications

Some synthetic alloy samples were prepared by mixing In(III) along with other metals in different proportions. The solutions of the synthetic alloys were prepared according to the prescribed procedure and the amount of Indium was determined by the proposed derivative method. To ascertain the acceptability of the results, the synthetic samples were analyzed by atomic absorption spectrophotometric method for In(III) and the results obtained were compared with those obtained by the proposed method which were found to be in good agreement, and the results are presented in the table 5.

Table 5: Analysis of synthetic alloy samples

S. No.	Sample and description	Percentage of Indium		Relative error (%)
		AAS (n=2)	Present method (n=6)	
1.	Ga(32%) – In(9%) Tl(5%) – Zn(4%) SiO$_2$ (50%)	9.00	8.98	+0.22
2.	Ga(25%) – In(20.5%) Tl(35%) – Pb(1.5%) SiO$_2$ (18%)	20.04	20.11	-0.35

Conclusions

The proposed methods for the spectrophotometric determination of indium(III) in zinc effluents and in synthetic mixtures were rapid simple selective and sensitive statistical analysis of the results indicates that the methods yield good values, it was clear that second order derivative method was more sensitive than the zero order method. The results obtained in zero order method and second order derivative spectrophotometric methods for In(III)-HMBATSC complex were compared and presented in table 3. From the results it was clear that the second order derivative method that more sensitive than zero order method.

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