Direct spectrophotometric determination of Pb (II) in alloy, biological and water samples using 5-bromo-2-hydroxyl -3-methoxybenzaldehyde-4-hydroxy benzoichydrazone

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ABSTRACT

A rapid, simple, sensitive and selective direct spectrophotometric method has been developed for the determination of lead (II) in various real samples. 5-Bromo-2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone reacts with Pb(II) forming green coloured soluble complex [Pb(II)-5-BHMBHBH] in basic buffer solution. The maximum absorbance was observed in the pH range 7.0-9.0. Pb(II)-5-BHMBHBH complex solution shows λ_{max} at 415 nm. The method obeys Beer's law in the range 1.036-16.50µg /ml. The molar absorptivity is 1.125×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0184mg/cm^2. The standard deviation of the method for ten determinations of 4.144 µg/ml of Pb(II) is 0.00420. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9999. The effect of various diverse ions is studied. The formula of the complex is 1:1 and its stability constant is 5.93×10^6. The method developed has been applied for the determination of lead (II) in alloy samples, biological samples such as human hair, tea leaves and polluted ground water samples.

Keywords: Pb(II), Spectrophotometry, 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone(5-BHMBHBH).
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INTRODUCTION

Lead was known since ancient times. The name originated from the Anglo-Sanon word "Lead; Latin; Plumbum". Lead is a relatively abundant metal in nature, occurring in lead minerals. In the atmosphere it is relatively more abundant than other heavy metals. It is one of the metals extensively used in lead storage batteries. Tetraethyl lead is used as antinocking agent in automobile combustion fuels cause air pollution. Even trace amounts of lead (II) in environmental samples leads to environmental pollution. Lead is considered as one of the environmentally hazardous elements because, along with cadmium, mercury, copper, zinc and chromium, it poses a particularly high risk of disturbing the chemical balance in the ecosystem.

Lead is cumulative poison[1] that enters the body from lead water pipes, and lead based paints. Lead pollution is a serious danger to the environment and human health[2-3]. Lead intake causes many fatal diseases including disfunction of renal, blood and neurological systems. Lead (II) easily deposits in blood, kidney, reproductive system, nervous system and brain and cause lead poisoning[4-8]. Even low levels of lead in children cause brain and neuro-developmental deseases[9-11]. Hence the determination of trace amounts of lead is important for environmental monitoring and this demands sensitive and accurate determination of lead.

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Several methods developed for the analysis of Pb(II) include methods based on atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma mass spectrometry, anodic stripping voltammetry and reversed – phase high performance liquid chromatography coupled with UV-Vis or fluorescence detection[12-17]. Though these methods are sensitive and accurate, they are time consuming, expensive and require sophisticated equipment. Hence, the development of simple inexpensive, rapid, highly sensitive and selective methods for estimation of Pb(II) is a necessity.

Spectrophotometry is a relatively sensitive method for lead (II) as it is of low cost, simple and within the reach of even ordinary laboratories, which is based on reaction between lead and chromogenic reagents. For this reason there is an ongoing search for new chromogenic reagents for direct and rapid spectrophotometric estimation lead at trace levels, especially in aqueous solution. Many spectrophotometric methods are reported for the determination of lead [18-31]. These methods suffer from interference due to diverse metal ions[32] or involve extraction, preconcentration [33] or involve the use of surfractants[34].

Singh etal. have reviewed[35] the potentialities of hydrazones as analytical spectrophotometric reagents. However, 4-hydroxybenzoichydrazones are very scarcely employed[36]. Hence, the author has undertaken the study of the colour reaction between Pb(II) and 5-BHMBHBH, in order to develop and accurate, sensitive and rapid direct spectrophotometric method for the determination of Pb(II).

EXPERIMENTAL SECTION

The chromogenic reagent,5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxy benzoic hydrazone was synthesized in the laboratory by condensing 5 - Bromo-2- hydroxy-3-methoxybenzaldehyde and p-hydroxybenzoichydrazide. A 0.01M DMF solution of the reagent is used in the studies.

0.01M stock solution of Pb(II) was prepared by dissolving requisite amount of $Pb(NO_3)_2$ in distilled water and standardized volumetrically[37]. The working solutions were prepared by diluting the stock solutions with distilled water.

Buffer solution of pH 8.0 was prepared by mixing 0.2M ammonia and 0.2M NH_4Cl solutions in suitable proportion and the pH was adjusted by a pH meter.

The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively.

PROCEDURE
To 5 ml of buffer solution (pH 8.0), 0.5 ml of 5-BHMBHBH (1 x 10^{-2}M) in DMF,1.5 ml of DMF taken in each of a set of 10 ml volumetric flasks, varying amounts of Pb(II) were added and diluted to 10 ml in a volumetric flask with distilled water. The absorbance of these solutions was measured at 415 nm. A straight line is obtained which corresponded to the equation $A_{415} = 0.05616C + 0.00125$.(C is the amount of lead in µg/ml).

RESULTS AND DISCUSSION

The reagent 5-bromo-2-hydroxy-3-methoxy benzaldehyde-4-hydroxy benzoichydrazone (5-BHMBHBH) was used for the spectrophotometric method for determination of lead (II). Lead(II) reacts with 5-BHMBHBH to form yellow coloured complex in the pH range 7.0-9.0. The absorption spectra of 5-BHMBHBH and its lead (II) complex under the optimum conditions were shown in Figure1. The lead (II)-5-BHMBHBH complex shows maximum absorbance at 415 nm, where the reagent has negligible absorbance . The colour formation is instantaneous. It is stable for 48 hours. The analytical measurements were made at pH 8.0. A five fold molar excess of the reagent is sufficient to produce maximum absorbance. The formula of the complex was ascertained from jobs and molar ratio methods as 1:1. The stability constant of the complex is 5.93×10^6. The analytical characteristics of the complex are given in table-1.

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Table 1. Analytical characteristics of [Pb(II) – 5-BHMBHBH]

Parameter	Direct method (415 nm)
Beer's law range (μg/m l^{-1})	1.125 – 16.5 μg /ml
Molar absorptivity (L mol^{-1}cm^{-1})	1.125×10^4 L mol^{-1}cm^{-1}
Sandell's sensitivity (μg/c m^2)	0.0184μg/c m^2
Correlation coefficient (γ)	0.9999
Standard deviation	0.00420
Y- intercept(b)	0.00125
Detection limit(μg/m l^{-1})	0.224
Composition (Metal :Ligand)	1:1
Stability constant(β)	5.93×10^6

Table -2 Tolerance limits of foreign ions

Amount of Pb (II)   =   4.144 µg/ml   *pH   =   8.0*

Ion	Tolerance limit µg/ml	Ion	Tolerance limit µg/ml
Tartarate	880	Mg(II)	200
Citrate	820	Hg (II)	80
Fluoride	1200	Al (III)	120
Iodide	410	W (VI)	116
Sulphite	180	Cd (II)	100
Bromide	120	Mn (II)	50
Phosphate	Interferes	Zn (II)	45
Nitrate	890	Ce (IV)	32
Carbonate	180	Co (II)	24
Thiocyanate	410	Sn(II)	12
Chloride	80	Se (IV)	30
Thiourea	100	Te (IV)	26
Thiosulphate	100	Tl (III)	18
Oxalate	Interferes	Ni(II)	12
Ascorbic acid	1200	Cr (VI)	8
EDTA	Interferes	Fe (III)	100[a]
U(VI)	16	V (V)	85
Ca(II)	120	Zr (IV)	85
Sr(II)	120	Mo (VI)	40
Ba(II)	120	Ti (IV)	24
Cu(II)	80	Th(IV)	16

[a]Masked with fluoride or tartarate

Table -3 Determination of Pb (II) in alloy sample

Sample	Composition (%)		Error (%)
	Certified	Found *	
BCS-364[a]	9.25	9.21	-0.43
Gun metal[b]	1.13	1.14	0.88

*Average of seven determinations.
% Composition
a) Cu 80.00; Sn 9.35; Pb 9.25; Ni 0.28; Sb 0.18; Zn 0.13; As 0.065; P 0.056; Al 0.002;Si 0.003;
b) Zn 1.37 ; Sn 9.22 ; Cu 87.95 ; Pb 1.13 ; Fe 0.01 ; P 0.07 ; Ni 31.0 ;

Table -4 Determination of Pb(II) in the Human hair and Tea leaves

Sample	Amounnt of Pb(II) (µg/g)		Relative error (%)
	Present method*	AAS method	
Human hair	6.00	6.04	-0.6
Tea leaves	0.90	0.89	+1.1

* Average of five determinations.

Table -5 Determination of Pb(II) in the Water samples

Sample	Amounnt of Pb(II) (µg/ml)		Relative error (%)
	Present method*	AAS method	
Ground water	1.02	1.01	+0.9
Tap water	1.19	1.20	-0.8
Polluted water	2.49	2.50	-0.4

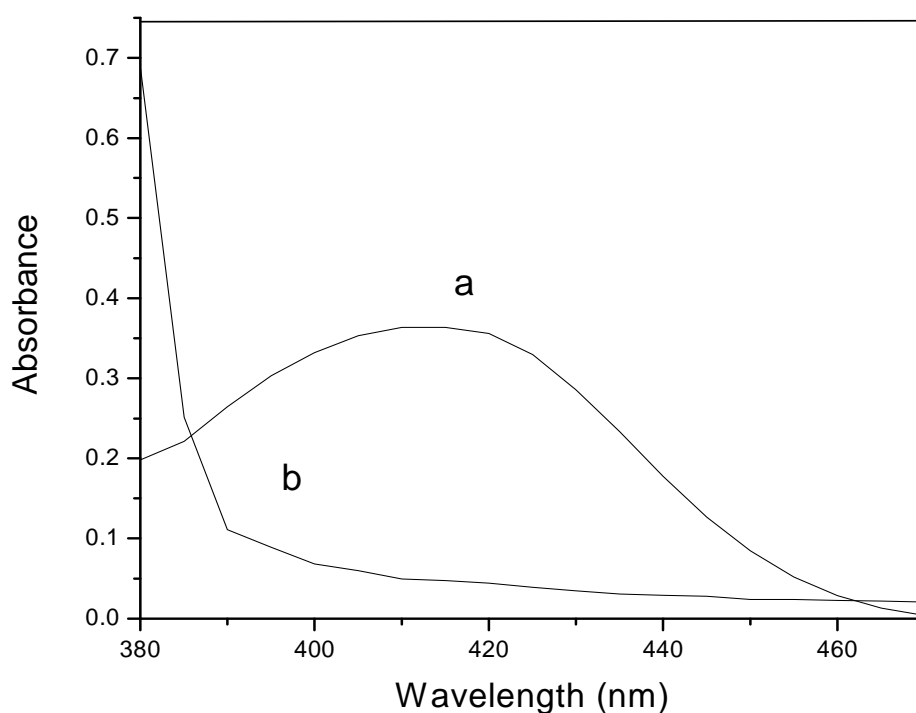** Average of five determinations.*

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Fig.1 Absorption spectra of a) 5-BHMBHBH Vs buffer blank b) [Pb (II)] – 5-BHMBHBH Vs reagent blank [Pb (II)] = 3.0×10^{-5} M: [5-BHMBHBH] = 1.0×10^{-3} M pH = 8.0

Effect of foreign ions:
The effect of foreign ions and cations on the determination of Pb(II) under optimal conditions were studied table-2. The data indicate that many metal ions and anions do not interfere in the determination of Pb(II). 50 fold excess of Fe(III) is masked by fluoride or tartarate. Hence the method is selective for the determination of Pb(II).

Applications
The developed spectrophotometric method for the determination of lead (II) was applied successfully for its determination in alloy samples, biological samples such as human hair, tea leaves and polluted ground water samples.

a) Determination of Pb(II) in Alloy sample:
The alloy sample was brought into solution by the following procedure.

1gm of the alloy sample was dissolved in a mixture of 2ml of concentrated hydrochloric acid and 10ml of concentrated nitric acid. The solution was evaporated to a small volume. 5ml of 1:1 sulfuric acid was added and the solution was evaporated to dryness. The residue left over was extracted with 15ml of water and the solution was diluted to 100ml with double distilled water. This serves as the stock solution. The stock solution was appropriately diluted and analyzed by the general procedure. The results are given in table-3.

b) Determination of Pb(II) in Biological samples :
The biological sample-human hair is brought into solution by the following procedure.

A 0.1 gm sample was taken in a beaker and dissolved in concentrated nitric acid (5ml) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100mL with water in a calibrated flask. A known aliquot of sample was analysed by the general procedure. The results are present in table-4.

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c) Determination of Pb(II) in Water samples :
The water samples were collected from different parts of anantapur district. (A.P. India) and treated as follows.

1 litre of the water sample was taken in a 2 litre beaker and evoparated slowly 225 ml. 5 ml of H_2O_2 were added and evaporated to dryness in a china dish. filtered. It was then dissolved in 20 ml of water and transferred quantitatively into a 100 ml volumetric flask and made up to the mark with distilled water. An aliquot the sample was analysed by the following procedure. The results are present in table-5.

CONCLUSION

The proposed method is simple, accurate, sensitive, do not involve extraction or heating and also do not use surfactants. The method can be easily applied for the determination of lead(II) in alloy samples, biological samples such as human hair, tea leaves and polluted ground water samples. The results compare well with standard values.

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