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Determination Of Cadmium (II) In Water And Plant Material With 3-Methoxy-4-Hydroxy Benzaldehyde-4-Bromo Phenyl Hydrazone(3,4–MHBBPH) And 4-Hydroxy Benzaldehyde-4-Bromophenyl Hydrazone (4-HBBPH) Using Spectrophotometry

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ABSTRACT

A facile, sensitive and selective extractive spectrophotometric methods were developed for the determination of traces of cadmium (II) in various water and plant materials using newly synthesized reagents 3-methoxy-4-hydroxy benzaldehyde- 4bromophenyl hydrazone(3,4-MHBBPH), 4-hydroxy benzaldehyde-4-bromophenyl hydrazone (4-HBBPH). Cd(II) forms red colored complex with (3, 4-MHBBPH) and yellow colored complex with (4-HBBPH)) in acetate buffer medium (pH 4.0) which increases the sensitivity and these complexes were extracted into chloroform. Under optimum conditions the maximum absorption of the chloroform extracts were measured at 503 nm, 303nm respectively. Beer's law was obeyed in the range of 0.5 to 5.0 $\mu g\ ml^{-1}$ for red colored complex and 1.0 to 10.0 $\mu g\ ml^{-1}$ for yellow colored complex. The molar absorptivity and Sandell's sensitivity of the [Cd(II)-3,4-MHBBPH] and [Cd-4-HBBPH] complex were as $0.0104\times10^4\ l\ mol^{-1}\ cm^{-1}$, $0.0048\times10^4\ l\ mol^{-1}\ cm^{-1}$and $0.067 \mu g\ cm^{-2}$, $0.102\ \mu g\ cm^{-2}$ respectively. The detection limit for [Cd (II)-3, 4-MHBBPH] and [Cd (II)-4-HBBPH] were found to be as 0.028 $\mu g\ ml^{-1}$ and 0.056 $\mu g\ ml^{-1}$. The detailed study of various interfering ions made the method more selective. The proposed methods were successfully applied for the determination of Cd(II) in water and plant materials. The performance of present methods were evaluated in terms of Student *'t'* test and variance ratio *'f'* test which indicates the significance of present method over reported method.

KEYWORDS

Cadmium (II);
3-Methoxy-4-hydroxy benzaldehyde- 4-bromophenyl hydrazone (3, 4-MHBBPH);
4-Hydroxy benzaldehyde-4-bromophenyl hydrazone (4-HBBPH);
Spectrophotometry;
Water samples and plant materials.

INTRODUCTION

Determination of trace amount of cadmium has received considerable attention in the battle against environmental pollution. Cadmium in trace amount is important for industrially, as a toxicant and as an occupational hazards. It is an extremely toxic metal and has been responsible for number of deaths. Cadmium accumulates in the organism, mainly in the liver and kidneys. The exposure to toxic elements could be mineralised by regular control of food and feed and settings maximum levels for heavy metals in these products. Commission regulation (Ec) no 466/2001 of March 2001 and polish regulation of ministry of health of 30 April 2004 established limits for cadmium in food stuff's. The limits for food of animal origin range 0.01 to 1.00 mg kg^{-1}. In view of the increasing cadmium pollution of the environment resulting from the use of fossil fuels, makes necessary for separation and determination of trace and ultra trace amounts of cadmium analysis. Several analytical techniques have been monitored for determination of cadmium(II) which includes atomic absorption spectrometry[1-3], neutron activation analysis[4], Differential pulse anodic stripping voltametry[5], Inductive coupled plasma atomic emission spectrometry[6-8] and spectrophotometry[7-20] were reviewed. A few reagents are available for the spectrophotometric determination of Cd(II) as shown in TABLE 1. The above reported reagents suffer from several disadvantages such as, poor sensitivity, selectivity, required special conditions for the formation of complexes with the reagents and few are commercial.

The aim of the present work is to provide facile,

TABLE 1: Comparison of analytical parameters of the present methods with others spectrophotometric method for the determination of Cd (II) optimum

Reagent	λmax (nm)	Optimum pH range	Beer's law validity range ppm	M:L	Remarks	Ref.
5,7-dibrmo hydroxy qunoline	396	4.25	0.1-3.0	1:2	Many metal ions interfere and very poor sensitivity	**[9]**
1,4,8,11-tetra 1,4,8,11-tetramethyl cyclo tera decane	550	NaOH	-	-	Low sensitivity	**[10]**
2-[-5-pyridyline azo]-5 diethyl amino phenol	557	6.80	0.2-1.60	1:2	Interference of number of metal ions and poor sensitivity and selectivity	**[11]**
Ammonium pyrilidine dithio carbamate	445	7.0	-	1:3	High reagent consuming and poor selectivity	**[12]**
Fluoro-4-Fluro –phenyldiazo amino benzene	490	10.1	-	-	Less sensitivity	**[13]**
2-acetyl mercapto diazo amino azo benzene	529	8.5-10.9	-	-	Wide linear range using sodium thiosuphate as masking agent	**[14]**
p-nitro phenyl diazo amino benzene	480	0.2-0.3	-	-	Low sensitivity strong alkali medium, toxic KCN as masking agent	**[15]**
4-formyl phenyl diazoamino	525	9.5	-	-	Low sensitivity, separating interfering benzene ions with anion exchange resins.	**[16]**
o-chloro-*p*- nitro phenyl diazoamino benzene	503	7.8-8.1	-	-	Wide linear rang, many ions were interfering	**[17]**
2,6-dibromo- 4-nitro phenyl di azoamino benzene	500	8.5	-	-	Many ions interfere with color reaction	**[18]**
3-bromo –4-(4-nitro phenyl diazo amino benzene	495	8.8	-	-	Narrow linier range	**[19]**
o-hydroxy phenyl diazo amino benzene	520	9.0			Low sensitivity	**[20]**
3-methoxy- 4-hydroxy benzaldehyde –4-bromo phenyl hydrazone	503	2.0-4.0	0.5-5.0	1:1	Low reagent consumption, economical color forming reagent	present work
4-hydroxy benzaldehyde -4-bromo phenyl hydrazone	303	1:1	2.0-4.0	1.0-10.0	More stable, highly sensitive, selective and less interference	present work

sensitive and rapid extractive spectrophotometric method for the determination of trace amounts of Cd (II) in water and plant materials of significant environmental importance. Here, authors successfully synthesised new analytical reagents; 3-methoxy-4-hydroxybenzaldehyde-4-bromophenyl hydrazone (3,4-MHBBPH), 4-hydroxy benzaldehyde-4-bromophenyl hydrazone (4HBBPH) for the determination of Cd (II) in water and plant materials.

EXPERIMENTAL

Instruments

A HITACHI U 2001 Spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements. Elemental analysis was carried out as a Perkin-Elmer 240 C elemental analyser. An Elico Li-129 model pH meter with combined glass electrode was used for all pH measurements.

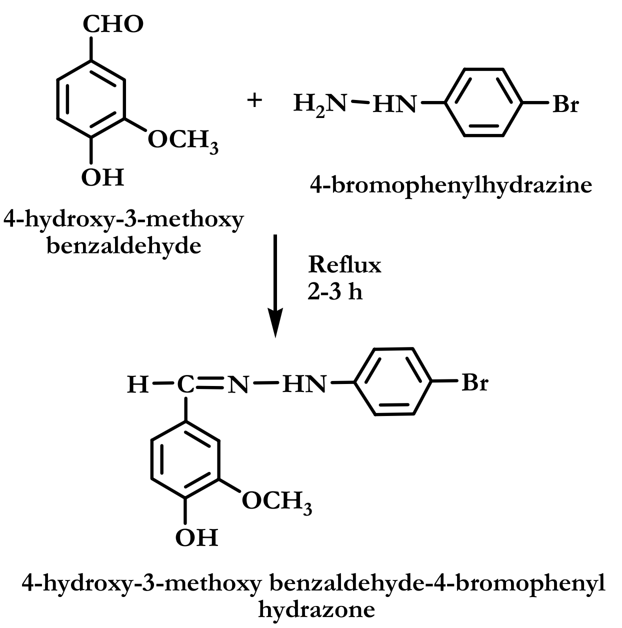
Reagents and solutions

All reagent used were of analytical reagent grade. Double distilled water was used throughout the experiment. A stock solution of Cd(II) (0.001 M) was prepared by dissolving 0.02282 mg of $CdSO_4\cdot 8H_2O$ (E-Merck, Germany) in double distilled water in 1000 ml standard flask. Cadmium(II) working standard stock solutions were prepared freshly by appropriate dilution of the standard stock solution with double distilled water. 0.01 M of 3-methoxy-4-hydroxybenzaldehyde-4-bromophenyl hydrazone, 4-hydroxy benzaldehyde-4-bromophenyl hydrazone, reagent solutions were prepared by dissolving 0.0393g and 0.03456g of reagent in 100ml of methanol. These solutions are further diluted, when ever necessary with double distilled water.

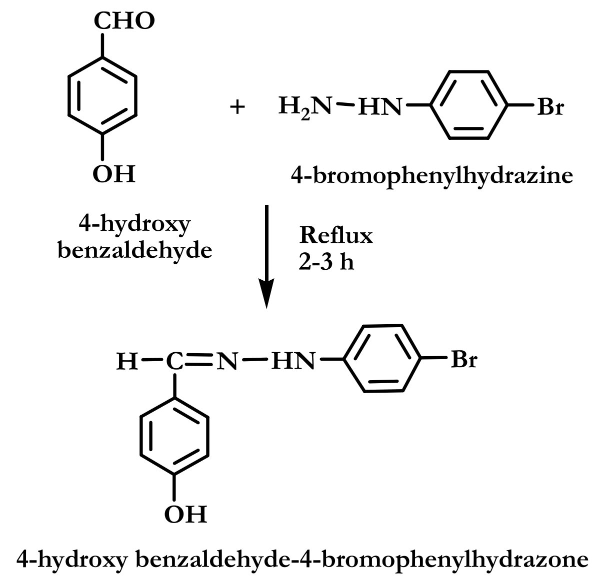
Acetate buffer was prepared by dissolving 8.2g sodium acetate in 800 ml water. It was adjusted to pH 4.0 with high purity glacial acetic acid. It was stored in clean 1 l metal free polyethylene bottle.

Synthesis of 3-methoxy-4-hydroxy benzaldehyde-4-bromo phenyl hydrazone

Equimolar solution of 3-methoxy-4-hydroxy benzaldehyde and 4-bromophenyl hydrazine in aqueous medium were refluxed for 2-3h, and the contents were cooled to room temperature for separating the formed solid product. The solid was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m.p. 147°C, 91 % yield as shown in SCHEME 1).



SCHEME 1: Synthesis of 4-hydroxy-3-methoxy benzaldehyde-4-bromophenyl hydrazone (4,3-MHBBPH)



SCHEME 1: Synthesis of 4-hydroxybenzaldehyde-4-bromophenyl hydrazone (4-HBBPH)

Synthesis of 4-hydroxy benzaldehyde-4-bromo

phenyl hydrazone.

Equimolar solution of 4-hydroxy benzaldehyde and 4-bromophenyl hydrazine in aqueous medium were refluxed for 2 - 3 h, and the contents were cooled to room temperature for separating the formed solid product. The solid was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m.p. 163 °C, 89 % yield as shown in SCHEME 1).

Elemental analysis calculated for $C_{14}N_2H_{13}OBr$ (m/z)-321.18(C=52.35%, N=8.73%, H=4.08%) was found to be C=52.04%, N=8.33%, H=4.98%. $C_{13}N_2H_{10}Br$. FAB-MS (m/z)-302.15(C=51.67%, N=9.27%, H=3.37%) was found to be C=51.32%, N=9.57%, H=3.22%. The band at 1130.01 cm^{-1} is due to the –OH group and absorption bands at 1610.34 cm^{-1}, 1530.18 cm^{-1} and 1445. 83 $cm^{-1}$are due to the C=N group of reagent. The absorption band at 590.27 cm^{-1} is due to C-Br on benzene ring.

Procedure

To an aliquot of working standard solution containing 1-100 μl is taken in to 50 ml separating funnel, 5 ml of acetate buffer solution (pH 4.0), 2 ml of reagent solution and salting out agent 0.1 M magnesium sulphate were added. The mixture was shaken with 5.0 ml portions of chloroform for 30 s and allowed to stand for few minutes. The organic phases are collected and made up to 25 ml with chloroform and absorbance were measured at 503nm, 303 nm against the corresponding reagent blank and the calibration graph was constructed.

Procedure for the determination of Cd(II) in natural water samples

Different water samples (tap water, river water, spring water) were collected from various places in and around Tirupati, A.P., and India. The samples (150 ml) were stored at 0-5 ^{0}C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no.41 and clean solution is collected into 250 ml beaker. The contents are diluted up to the mark with double distilled water. 15 ml of this solution is further diluted to get working solution for determination of Cd(II) as described in above procedure and compared with the reported method[21] with statistical validation. The results were summarized in TABLE 3, 3a.

Procedure for the determination of Cd(II) in sea water samples

100 ml of sea water was taken from Bay of Bengal near Sullurpet, Nellore dist, A.P., India and spiked with known amounts of metal ion. The pH of the sample was adjusted to pH 4.0 with acetate buffer. The metal ion present in the sea water was analyzed from aforesaid procedure. The analytical data was presented in TABLE 3, 3a.

Procedure for the determination of Cd (II) in plant materials.

5g of finely chopped fresh plant material (Tea and Tobacco leaves) samples were placed in a 250 ml beaker and 10 ml of 1:1(v/v) mixture of concentrated sulphuric and nitric acids were added. This solution was heated until the mixture was clear. This solution was filtered and concentrated to 5 ml, cooled and diluted to 50 ml with deionized water. Then the standard procedure was applied to 1 ml of this solution.

RESULT AND DISCUSSION

Cadmium(II) reacts with 3,4-MHBBPH, 4-HBBPH to forms a 1:1 red and yellow colored complexes in buffer of pH 4.0 and complexes were extracted in to chloroform. The organic extracts shows a maximum absorption at 503 nm, 303 nm, the formation of the complexes and it's extraction into chloroform is instantaneous. The complexes were stable for more than 32 h and 24 h The conditions for effective extraction are improved by studying the effect of various factors such as, reagent concentration, choice of solvent and salting out agent, influence of diverse ions in order to enhance the sensitive and rapid extraction spectrophotometric method for the determination of cadmium(II) in μg level. The complexes formation reaction between cadmium (II) with [3,4-MHBBPH], [4-HBBPH] have been studied in detailed.

Absorption Spectra

The proposed methods involve the formation of red colored product with a λ_{max} 503 nm and a yellow

TABLE 2: Optical characteristics and precision data.

Parameters	(Cd^{2+}-3,4-MHBBPH)	(Cd^{2+-}-HBBPH)
Color	Red	yellow
λmax [nm]	503	303
Stability	36 h	24 h
Beer's law range [µg ml^{-1}]	0.5-5.0	1.0-10.0
Molar absorptivity [l mol^{-1} cm^{-1}]	0.011x104	0.098x104
Sandell's sensitivity [µg cm^{-2}]	0.067	0.102
Regression equation (Y) [b])		
Slope[a]	0.1783	0.3846
Intercept[b]	0.0184	0.0142
Correlation coefficient[r]	0.9995	0.9992
Relative Standard deviation [%][c]	0.3597	0.237
Detection Limit (µg ml^{-1})	0.028	0.056
% error	0.1274	0.0754

[a]Experiments performed under optimized conditions (see text) with 5 ml of 0.01 M $CdSO_4.8H_2O$ solution. [b] *Y=ax+b*, where x is the concentration of Cd(II) in µg ml^{-1}., [c]n=5

TABLE 3: Determination of Cd (II) in water and plant materials

Sample	Cadmium added µg ml^{-1}	Proposed method		(Cd^{2+}-3,MHBBPH)		Reported method[21]	
		found[a] µg ml^{-1}	Recovery (%)[a]	t-test	F-test	found[a] µg ml^{-1}	Recovery (%)[a]
Synthetic mixture	0.5	0.49	98.0±0.05	0.03	-1.26	0.45	90.0±0.02
	1.0	1.99	99.0±0.97	0.02	3.51	0.95	95.0±0.47
	1.5	1.49	99.4±0.08	0.45	2.62	1.45	96.6±0.05
Lake water	-	0.29	-			0.25	-
	0.6	1.89	98.0±0.05	0.38	6.59	0.85	91.6±0.09
	1.2	1.49	99.2±0.11	0.25	3.14	0.85	95.8±0.05
River water upper stream	-	0.69	-			0.65	-
	1.4	2.09	98.3±0.03	0.16	2.01	2.05	97.1±0.09
	2.8	3.49	98.0±0.05	0.18	1.22	3.45	98.2±0.12
Lower stream	-	1.49				1.46	
	3.0	4.49	99.3 ± 0.08	0.45	0.92	4.46	98.3 ± 0.05
	6.0	7.49	99.6 ± 0.05	0.08	0.83	7.46	98.6 ± 0.17
Sea water upper level	-	1.99	-			1.95	-
	4.0	5.99	99.7±0.05	0.76	0.94	5.95	98.7±0.06
	8.0	9.99	99.8±0.03	0.24	0.43	9.95	99.3±0.07
lower level	-	0.99	-			0.95	-
	2.0	2.99	99.5 ±0.07	0.92	1.98	2.95	97.5±0.07
	4.0	4.99	99.7±0.09	0.42	0.94	4.95	98.7±0.05
Tobacco (5g)	3.0	2.99	99.6± 0.03	0.16	0.91	2.95	98.6±0.09
	6.0	5.99	99.8± 0.03	1.00	0.59	5.95	99.1±0.03
	9.0	8.98	99.7 ± 0.09	0.95	0.32	8.94	99.3 ± 0.08
tea leaves (5g)	2.0	1.98	99.0 ± 0.09	1.00	1.40	1.95	97.5 0.09
	4.0	3.98	99.5± 0.07	0.82	1.28	3.93	98.2 ± 0.06
	6.0	5.91	98.5 ± 0.03	0.06	0.85	5.85	97.5 ± 0.12

[a]n=5, [b]Collected around Tirupati area, [c]Collected form bay of Bengal.

TABLE 3a: Determination of Cd (II) in water and plant materials

Sample	Cadmium added µg ml^{-1}	Proposed method		(Cd^{2+}-4-HBBPH)		Reported method[21]	
		Found[a] µg ml^{-1}	Recovery (%)[a]	t-test	F-test	Found[a] µg ml^{-1}	Recovery (%)[a]
Synthetic mixture	0.5	0.48	96.0±0.91	0.18	-3.20	0.45	90.0±0.02
	1.0	0.98	98.0±0.05	0.00	2.53	0.95	95.0±0.47
	1.5	1.48	98.6±0.08	0.50	1.94	1.45	96.6±0.05
Lake water[b]	-	0.28	-			0.25	-
	0.6	1.88	96.6±0.05	0.38	4.81	0.85	91.6±0.09
	1.2	1.48	98.3±0.05	0.99	2.46	0.85	95.8±0.05
River water[b] upper stream	-	0.68	-			0.65	-
	1.4	2.08	98.5±0.06	0.58	1.29	2.05	97.1±0.09
	2.8	3.48	99.2±0.05	0.07	0.85	3.45	98.2±0.12
Lower stream	-	1.48				1.46	
	3.0	4.48	99.0 ± 0.09	0.42	0.60	4.46	98.3 ± 0.05
	6.0	7.48	99.5 ± 0.07	0.22	0.69	7.46	98.6 ± 0.17
Sea water[c] upper level	-	1.98	-			1.95	-
	4.0	5.98	99.5±0.08	0.70	0.77	5.95	98.7±0.06
	8.0	9.98	99.3±0.05	0.58	-3.90	9.95	99.3±0.07
lower level	-	0.98	-			0.95	-
	2.0	2.98	99.0 ±0.09	0.92	1.41	2.95	97.5±0.07
	4.0	4.98	99.5±0.09	0.64	0.77	4.95	98.7±0.05
Tobacco (5g)	3.0	2.95	99.0± 0.18	0.28	0.25	2.95	98.6±0.09
	6.0	5.96	99.3± 0.05	0.52	0.94	5.95	99.1±0.03
	9.0	8.92	99.1 ± 0.06	0.66	-0.29	8.94	99.3 ± 0.08
tea leaves (5g)	2.0	1.96	98.0 ± 0.18	0.28	0.35	1.95	97.5 ± 0.09
	4.0	3.95	98.7± 0.06	1.00	0.44	3.93	98.2 ± 0.06
	6.0	5.89	98.1 ± 0.04	0.23	0.44	5.85	97.5 ± 0.12

colored product with a λ_{max} 303 nm. The reagent blanks has negligible absorption at these wave lengths. The absorption spectrum of the products was shown in figure 1 (available in SUPPLEMENTARY INFORMATION).

Analytical parameters

Beer's law range, molar absorptivity and Sandell's sensitivity and other parameters were given in TABLE 1. The precision and accuracy of the proposed methods were studied by analysing the solution containing known amount of cited reagents with in the Beer's law limit. The lower values of relative standard deviation (%) and percentage of error indicated the high accuracy of the proposed method and the results were shown in (TABLE 2). It reveals that the good correlation between the two methods indicate that the present method is more sensitive than the reported method in literature.

Physico chemical properties of 3, 4-MHBBPH

3,4-MHBBPH being a green colored solid, easily soluble in methanol and slightly soluble in 40% DMF methanol. The spectra of 3,4-MHBBPH in different pH are shown in figure 5 (available in SUPPLEMENTARY INFORMATION). It can be seen that 3, 4-MHBBPH in acidic medium (pH < 2) in phosphate buffer with an absorption peak at 480 nm, corresponding to less protonized ligand possessing orange. It changes to red in weak acidic up to pH 4.0 in acetate buffer with absorption peak at 503 nm, corresponding to strong protonized form (H_2L^+). In borax buffer pH 6.0, its appears light red at absorption peak of 400 nm corresponding to feasible protoniza-tion of the ligand.

At phosphate buffer, dark yellow, instability and maximum absorption at 390 nm, corresponding to the protonation appears and disappears. According to the absorbance of the reagent at 503 nm. The dissociation constant of 3, 4-MHBBPH was measured to be 1.01 $\times 10^{-12}$ by potentiometric titration.

Physico chemical properties of 4-HBBPH

4-HBBPH being a colorless solid, easily soluble in 40 % DMF and slightly soluble in methanol. The spectra of 4-HBBPH in different pH are shown in figure 5a (available in SUPPLEMENTARY INFORMATION). It can be that 4-HBBPH in acidic medium (pH < 2) in phosphate buffer with an absorption peak at 300 nm, corresponding to less protonized ligand possessing greenish yellow. It changes to intense yellow in weak acidic up to pH 4 in acetate buffer with absorption peak at 303 nm, corresponding to strong protonized form(H_2L^+). In borax buffer pH 6.0, its appears light yellow at absorption peak of 290 nm corresponding to feasible protonization of the ligand.

At phosphate buffer, dark yellow, instability and maximum absorption at 390 nm, corresponding to the protonation appears and disappears. According to the absorbance of the reagent at 303 nm. The dissociation constant of 4-HBBPH was measured to be 1.02 $\times 10^{12}$ by potentiometric titration.

Effect of the reagent concentration

In the present study the effect of reagents concentration on the formation of color complexes were studied in the range of 0.5-4 ml, the experimental observations were found that 2 ml of 0.1 M reagents were necessary for the formation of maximum color intensity.

Hence 2 ml of 0.1 M reagent solutions (3, 4-MHBBPH, 4-HBBPH) were selected for the further studies as it gives good results.

Stoichiometry of the complexes

On the basis of the Job's method of continuous variation as modified by Vosburg and Cooper for the two phase system, the composition of the extracted species is found to be [Cd^{2+}: 3,4-MHBBPH], [Cd^2-4-HBBPH] =1:1 The molar ratio of the methods have further confirmed this stoichiometry of the complex was shown in figures 2, 2(a) and 3, 3(a) (available in SUPPLEMENTARY INFORMATION).

Effect of solvent

Extraction for Cd (II)-3, 4-MHBBPH, Cd (II)-4-HBBPH complexs is tested in various organic solvents such as toluene, benzene, xylene, n-butanol, amylalcohol, dimethyl formaldehyde, CCl4, chlorobenzene, cyclohexane and chloroform. Among the various solvent studies chloroform was selected as the suitable solvent for the extraction of [Cd (II)-3, 4-MHBBPH] and [Cd(II)-4-4HBBPH] complexs, because of its maximum absorbance and greater extraction ability due to polarity.

Ringbom plot for (Cd (II)-3, 4-MHBBPH) complex

Ringbom plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log C of Cd(II) and (1-*T*) (Where *T* is the transmittance). The plot was straight line with a linear segment intermediate absorbance values (0.15to1.5) and concentration values (1.5 to 4.0 μg ml^{-1}). The slop of the Ringbom plot from figure 4 (available in SUPPLEMENTARY INFORMATION) is 0.145. Hence, the ratio between the relative error in concentration and photometric error 0.15 for concentration of 0.15 for 1.0 % photometric error.

Ringbom Plot for (Cd(II)-4-HBBPH) complex

Ringbom plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log C of Cu (II) and (1-*T*) (Where *T* is the transmittance). The plot was straight line with a linear segment intermediate absorbance values (0.3 to 0.8) and concentration values 2.5 to7.5 μg ml^{-1}). The slop of the Ringbom plot from figure 4a (available in SUPPLEMENTARY INFORMATION) is 0.10. Hence, the ratio between the relative error in concentration and photometric error 2.5 for concentration of 0.3 for 0.12% photometric error.

Effect of salting out agents

Various salting out agents such as lithium nitrate, thorium sulphate, magnesium sulphate lithium chloride, and ammonium chloride and ammonium sul-

TABLE 4: Tolerance limits of foreign ions on the determination of 50 μg l^{-1} Cd (II) ion.

Tolerance limit (μg l^{-1})	Foreign ions	
	[Cd^{2+}-3,4-MHBBPH]	**[Cd^{2+}-4-HBBPH]**
5000	Na^+	K^+,Mn^{2+},Na^+
1000[a]	Ca^{2+},Sr^{2+}, Ba $^{2+}$ Br^{2+},Mn^{2+}	Cr^{3+},Zn^{2+},Co^{2+}
500[b]	SiO_3^{2-},$CO^{2-}{}_3$,K^+,$Cr^{3+}$$Zn^{2+}$	Sn^{2+}, Sio_3^{2-}, CO_3 $^{2-}$
200[c]	$Pb^{2+}$$Cu^{2+}$,$Sn^{2+}$	Al^{3+}
100	Co^{2+}, Fe^{3+}, Pb^{2+}	Fe^{3+}, Pb^{2+}
50	50 Ni^{2+},Co^{2+},I^-,CN^-	Co^{2+},Cu^{2+},Ni I^-,CN^{-a}

[a] Can be masked up to 10.00 μg l^{-1} by the addition of 2ml of EDTA, thiosulfate, cyanide.
[b] Can be masked up to 500 μg l^{-1} by the addition of 2ml of 2%citrate solution.
[c] Can be masked up to 50 μg l^{-1} by the addition of 1% thiocyanate.

phate were used for the enhancement of the metal complex extraction into the organic phase in a single step. It is observed that the presence of 1.0 ml of 0. 1 M magnesium sulphate solution ensure the complete extraction .The aqueous phases is tested for the complete extraction of cadmium(II) by using chloroform, disclosing that there is no cadmium (II) content in the aqueous phase. It is established that 1.0 ml of 0.1 M magnesium sulphate as salting out agent and a ten-fold molar excess of the reagent quantitatively extracts cadmium (II) in to organic phase.

Effect of foreign species

Several anions and cations were studied in detail as summarized in TABLE 4 the tolerance limits of interfering ions in the determination of 50 μg l^{-1} Cd (II). The tolerance limit was taken as the amount causing an error of ± 2 % at the peak height. The results are shown in TABLE 4.

Applications of the extractive spectrophotometric method for the determination of cadmium (II) with reported method

The proposed extractive spectrophotometric method for the determination of Cd (II) has been employed for water and plant materials were presented in TABLES 3, 3a. The obtained results were compared with reported methods in terms of Student't' test and *'f'*-test. The analytical data summarised in TABLES 3, 3a suggest that the percentage recovery of Cd(II) from water and plant materials range from 96.0% to 99.7% which is more reliable and sensitive than the reported method[21].

CONCLUSION

The proposed extractive spectrophotometric method is simple, highly sensitive and selective for the determination of Cd (II) in water and plant materials. The limit of detection of the proposed methods is superior when compared to reported method[21]. The methods have additional advantage over reported method owing to it's.

i Complexing reagent employed in the present method i.e. 3-methoxy-4-hydroxy benzaldehyde-4-bromophenyl hydrazone, 4-hydroxy benzaldehyde-4-bromophenyl hydrazone was economical and easy to prepare in an ordinary laboratories.
ii. Proposed methods were highly sensitive due to the stabilization of colored complexs for more than 36 h, 24 h formed by interactions of the metal ion with newly synthesized reagent.
iii. Low reagent consumption, elimination of the analytical error, less interference and statistical analysis which made the method to be more sensitive and selective.

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