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DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM (II) IN PRESENCE OF MICELLAR MEDIUM IN BIOLOGICAL MATERIALS AND IN ALLOY SAMPLES USING CINNAMALDEHYDE-4-HYDROXY BENZOYLHYDRAZONE (CMHBH)

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ABSTRACT

A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Cadmium (II) using newly synthesized reagent cinnamaldehyde-4-hydroxybenzoylhydrazone (CMHBH) in neutral surfactant of TritonX-100-5% (micellar medium). Cadmium (II) forms a yellow coluored water-soluble complex with Cinnamaldehyde-4-hydroxy benzoylhydrazone in the pH range 8.0-9.0. The complex shows maximum absorbance at λmax 383 nm and in the pH range 8.0-9.0. However, at this wavelength, the reagent shows considerable absorbance. At λmax 383 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence, analytical studies are carried out at λmax 383 nm and at pH 9.0 (Phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.056-0.562 µg ml^{-1} and the optimum concentration range from ringbom plot is 0.112-0.505 µg/ml of Cadmium (II). The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be 5.6 x 10^4 L mol^{-1} cm^{-1} and 0.002-µg. cm^{-2} respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Cd (II): CMHBH] stoichiometry with stability constant 12.63 x 10^6. The standard deviation of the method in the determination of 0.224-µg ml^{-1} of Cadmium (II) is 0.0101 and the Relative standard deviation is 1.13%. First and second order derivative spectroscopic method is developed at λmax 450 nm and 470 nm respectively for the determination of Cadmium (II), which is more sensitive than the zero order method. The developed method has been employed for the determination of Cadmium (II) in biological materials (Cigarette tobacco, Radish flesh and Cabbage) and in alloy samples. The results are in good agreement with the certified values.

KEYWORDS

Determination of Cd (II), Spectrophotometry, biological materials, Cigarette tobacco, Radish flesh and Cabbage, alloy samples, CMHBH.

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al [1]. Hydrazones are important class of known analytical reagents. Due analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagent Cinnamaldehyde 4 hydroxybenzoyl hydrzone (CMHBH). In the light of the above herein we report the direct and derivative spectrophotometric methods for determination of Cd (II) using CMHBH in biological materials and alloy samples. Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. In this paper a first and second order derivative spectrophotometric method is described for the determination of Cd (II) in biological materials and alloy samples.

Cadmium is a soft, malleable, ductile, bluish-white bivalent metal. It is similar in many respects to zinc but forms more complex compounds. The oxidation state +1 can be reached by dissolving cadmium in a mixture of cadmium chloride and aluminium chloride, forming the Cd_2^{2+} cation, which is similar to the Hg_2^{2+} cation in mercury(I) chloride.[2] About three-quarters of all the cadmium is used in batteries, predominantly in rechargeable nickel-cadmium batteries, Cd was discovered in Germany in 1817 by Friedrich Stromeyer.[3].The most common oxidation state of cadmium is +2, though rare examples of +1 can be found. Cadmium burns in air to form brown amorphous cadmium oxide (CdO). The crystalline form of the same compound is dark red and changes colour when heated, similar to zinc oxide. Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride ($CdCl_2$) cadmium sulfate ($CdSO_4$) or cadmium nitrate ($Cd(NO_3)_2$).. Naturally occurring cadmium is composed of 8 isotopes ^{106}Cd, ^{108}Cd, ^{109}Cd, ^{110}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{116}Cd.

Most of cadmium which is not consumed in battery production is used mainly for cadmium pigments, coatings, plating, and as stabilizers for plastics, In some of the lowest-melting alloys, such as Wood's metal.[4] . Cadmium is used as a barrier to control neutrons in nuclear fission.[5] , in many kinds of solder.[5], and in PVC as stabilizers.[5] .

Helium-cadmium lasers are a popular source of blue-ultraviolet laser light they operate either at 325 or 422 nm and are used in fluorescence microscopes in various laboratory experiments.[6] , Cadmium selenide quantum dots emit bright luminescence under UV excitation (He-Cd laser).

Cadmium sulfide (CdS)[7] is used as a yellow pigment. Cadmium selenide can be used as red pigment, commonly called *cadmium red*. These pigments are toxic, and it is recommended to use a barrier cream on the hands to prevent absorption through the skin when working with them.[8] . The color of this luminescence can be green, yellow or red depending on the particle size. Colloidal solutions of those particles are used for imaging of biological tissues and solutions with a fluorescence microscope.[9]

Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues". Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer.[10]

Tobacco smoking is the most important single source of cadmium exposure in the general population. It has been estimated that about 10% of the cadmium content of a cigarette is inhaled through smoking. The absorption of cadmium from the lungs is much more effective than that from the gut, and as much as 50% of the cadmium inhaled via cigarette smoke may be absorbed.[11] .

Cigarettes are also a significant source of cadmium exposure. Although there is generally less cadmium in tobacco than in food, the lungs absorb cadmium more efficiently than the stomach.[12]

Buildup of cadmium levels in the water, air, and soil has been occurring particularly in industrial areas. Environmental exposure to cadmium has been particularly problematic in Japan where many people have consumed rice that was grown in cadmium contaminated irrigation water. This phenomenon is known under the name itai-itai disease.[13] .

Some sources of phosphate in fertilizers contain cadmium in amounts of up to 100 mg/kg[14][15], which can lead to an increase in the concentration of cadmium in soil in New Zealand[16]. Nickel-cadmium batteries are one of the most popular and most common cadmium-based products, and this soil can be mined for use in them.

The bones become soft (*osteomalacia*), lose bone mineral density (*osteoporosis*) and become weaker. This causes the pain in the joints and the back, and also increases the risk of fractures. In extreme cases of cadmium poisoning, mere body weight causes a fracture.

Research has found that cadmium toxicity may be carried into the body by zinc binding proteins; in particular, proteins that contain zinc finger protein structures. Zinc and cadmium are in the same group on the periodic table, contain the same common oxidation state (+2), and when ionized are almost the same size. Due to these similarities, cadmium can replace zinc in many biological systems, in particular, systems that contain softer ligands such as sulfur. Cadmium can bind up to ten times more strongly than zinc in certain biological systems, and is notoriously difficult to remove. In addition, cadmium can replace magnesium and calcium in certain biological systems, although these replacements are rare.

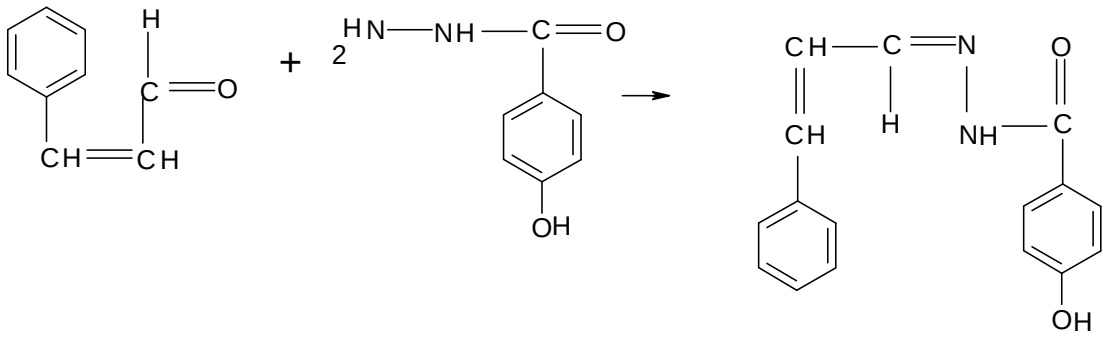
Cadmium iodide was used as a medicine to treat “enlarged joints, scrofulous glands and chilblains”.

EXPERIMENTAL

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm

REAGENTS

The reagent (CMHBH) is prepared by the Sah and Daniels[31] procedure. 1.32 ml of Cinnamaldehyde (I) and 1.52 g of 4-hydroxy benzhydrazide (II) were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{13}0_2N_2$). The resultant product is recrystallised twice from hot methanol. Pure light yellowish crystals of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CMHBH) (III) (m.p. 242-244℃.) were obtained. IR and NMR spectral studies characterized the compound. The infrared spectrum of the reagent shows bands at v 3452 (NH), 3218-3092 (OH), 1620 (C=O), 1577 (C=N). The 1H NMR (300 MHz) spectrum of the reagent was recorded in DMSO solvent. It shows signals corresponding to δ 11.57 (s, 1H, NH), 10.74 (s, 1H, OH phenolic), 8.19-8.22 (s, 1H, N-CH), 7.77 – 7.80 (d, 2H, ArH), 7.60 – 7.62 (d, 2H, ArH), 7.31 – 7.40 (m, 3H, ArH), 7.03 – 7.05 (d, 2H, ArH). The mass spectrum shows that molecular ion peak at m/z 267 (M+ 1). The structure of CMHBH was confirmed based upon above IR, NMR and mass spectral data.



I (Cinnamaldehyde) II (4-Hydroxy benzoylhydrazine) III (CMHBH)

A 0.01M solution of CMHBH in Dimethyl formamide (DMF) was employed in the present studies. The reagent (CMHBH) solution (0.01M) was prepared by dissolving suitable quantity (0.316 g) of the compound in 100 ml of dimethylformamide. The reagent solution is stable for 12 hours.

A 0.01 solution of Cadmium (II) was prepared by dissolving requisite amount of Cd $(NO_3)_2.4H_2O$ in distilled water and then standardized. The stock solution of Cadmium (II) was diluted as required.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

Buffer solutions (Phosphate)

0.2M KCl and 0.2M HCl (pH-1.0), 0.2M KCl and 0.02M HCl (pH-2.0), 0.1M Potassium Dihydrogen phosphate and 0.1M HCl (pH-3.0 and 4.0), 0.1M Potassium Dihydrogen phosphate and 0.1M Sodium hydroxide (pH-5.0 and 6.0). The pH of these solutions was checked with a digital pH meter**.**

PROCEDURE

Direct spectrophotometry

In each set of different 10ml volumetric flasks, 3.0ml of buffer solution (pH 3.0), 0.5ml of Cinnamaldehyde-4-hydroxy benzoylhydrazone ($1x10^{-3}$ M) and various volumes of ($1x10^{-5}$ M) Cadmium (II) solution were taken and made up to the mark with distilled water. The absorbance was measured at λmax 383 nm against the reagent blank. The calibration plot was prepared.

First order derivative spectrophotometry

For the above solutions, first order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees of freedom, in the wavelength range 360 – 600 nm. The First order derivative peak height was measured by the peak-zero method at λmax 450 nm. The peak height was plotted against the amount of Cadmium (II) to obtain the calibration plot.

Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}), slit width of 1 nm with nine degrees of freedom, in the wavelength range 360-600nm. The second order derivative peak height was measured by the peak-zero method at λmax 470nm. The peak height was plotted against the amount of Cadmium (II) to obtain the calibration plot.

The calibration graph follows the straight-line equation Y= ac+b; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By

substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as λmax 383 nm = 0.49165X-0.02007 for zero order data and λmax 450 nm = 0.23402X + $6.40454X10^{-4}$ for first derivative data, A λmax 470 nm = 0.57403X-0.0239 for second derivative data which gives the straight lines.

PREPARATION OF SAMPLE SOLUTIONS

Cigarette tobacco solution

The tobacco of cigarettes were dissolved in 2 ml of AR grade concentrated sulphuric acid and heated on a hot plate for 20 min. The contents were diluted with 20 ml of water and filtered. The filtrate was collected in 50 ml slandered flask with distilled water. The amount of cadmium was determined by pre determined calibration plot.

Alloys

An accurately weighed amount of steel sample (0.5g) was dissolved completely in minimum amount of aquaregia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling 5-10ml of 1:1 H_20: H_2SO_4 mixture was added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue was dissolved in 20 ml of distilled water and filtered and the filtrate was made up to 100 ml in a calibrated volumetric flask with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range.

Certified samples of bearing metal alloy samples were not available. Therefore, synthetic mixtures whose composition corresponds to bearing metal alloy were prepared. The present developed was applied to the determination of Cadmium (II) in synthetic mixtures.

Radish flesh and cabbage

The known quantity of wet radish (10g) and wet cabbage (25g) were digested in concentrated HNO_3 / HCl on hot plate till all organic matter was completely eliminated. Then the residue obtained was dissolved in water and filtered. The filtrate was collected in 50 ml slandered flask and made up to the mark with distilled water. The amount of cadmium was determined by pre-determined calibration plot.

RESULTS AND DISCUSSION

Absorption spectra of CMHBH and the Cadmium (II) complex

The absorption spectra of the solution containing Cadmium (II) complex against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 350-500 nm at pH 9.0. Typical spectra are presented in Fig-1. The spectra shows that Cadmium (II) complex has an absorption maximum at λmax 383 nm. However, at this wavelength, the reagent shows considerable absorbance. At λmax 383 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at λmax 383 nm

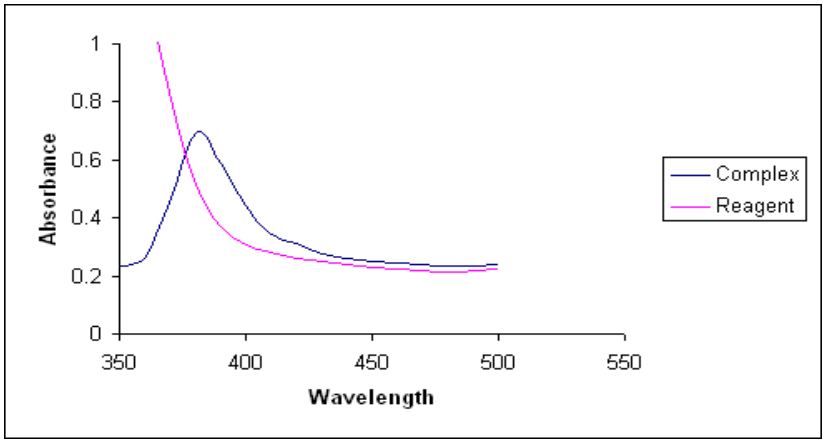


Fig- 1

Absorption spectra of

(a) CMHBH Vs Buffer blank, (b) Cd (II)-CMHBH Vs Reagent blank
Cd (II) - $2x10^{-4}$ M (0.5 ml), CMHBH- $2x10^{-3}$ M (0.5 ml),
Buffer pH-9.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml

Effect of pH on the absorbance of the complex

The study of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was obtained in the pH range 8.0-9.0. Analytical studies were therefore, carried out at pH 9.0 Fig-2

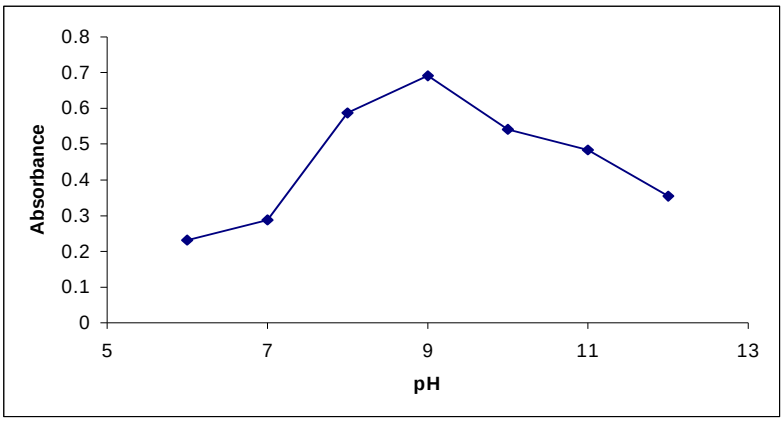


Fig-2
Effect of pH on Absorbance of Cd (II)-CMHBH
Cd (II)-$2x10^{-4}$ M (0.5 ml), CMHBH-$2x10^{-3}$ M (0.5 ml),
Buffrer pH 9.0 - (3.0 ml), Triton-X-100 (5%)-1.0 ml
λmax ---------- 383 nm

Effect of reagent (CMHBH) concentration

A 10-fold molar excess of CMHBH was necessary for complex and constant colour development. Excess of the reagent has no effect on the absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reagents.

Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex. The colour reaction between Cadmium (II) and CMHBH was found to be instantaneous at room temperature and the colour remained stable for more than 12 hours.

Applicability of Beer's law

For the possible determination of Cadmium (II) at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured. Calibration plot drawn between absorbance and amount of Cadmium (II) Fig 3 showed that Beer's law was obeyed in the concentration range 0.0562-0.562 µg ml^{-1} of Cadmium (II). The straight line obeyed the equation A λmax 383 nm =0.49165X-0.02007. The molar absorptivity and Sandall's sensitivity were $5.6x10^4$ $Lmol^{-1}cm^{-1}$ and 0.002ug/cm^2 respectively. The correlation coefficient of the calibration curve for experimental data was 0.999. The standard deviation of the method for ten determinations of 0.224-µg ml^{-1} of Cadmium (II) was 0.001.

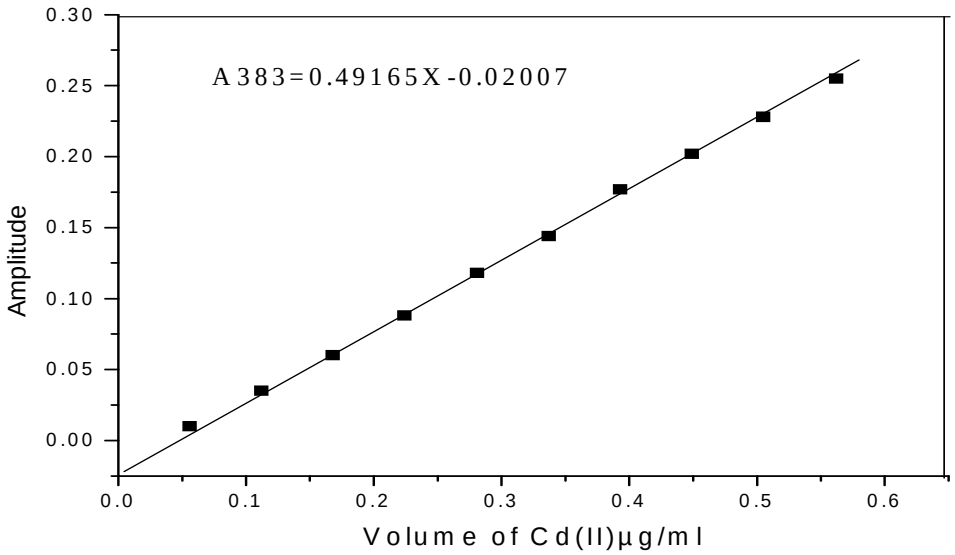


Fig - 3

Cd (II)-CHBH-Zero order Beers law

CMHBH-$1X10^{-3}$ M (0.5 ml) (Constant), Cd (II)-$1X10^{-5}$ M,
Buffer pH -9.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax ---------- 383 nm

Determination of Cadmium (II) first order derivative method: The first order derivative method has been employed for the determination of Cadmium (II) employing

CMHBH in trace quantities. The second derivative spectra Fig-4 (a) showed maximum amplitude at λmax 450 nm. The derivative amplitudes at λmax 440 nm were proportional to the concentration of Cadmium (II). The straight line obeyed the equation A λmax 450 nm =0.23402X + 6.40454X10$^{-4.}$

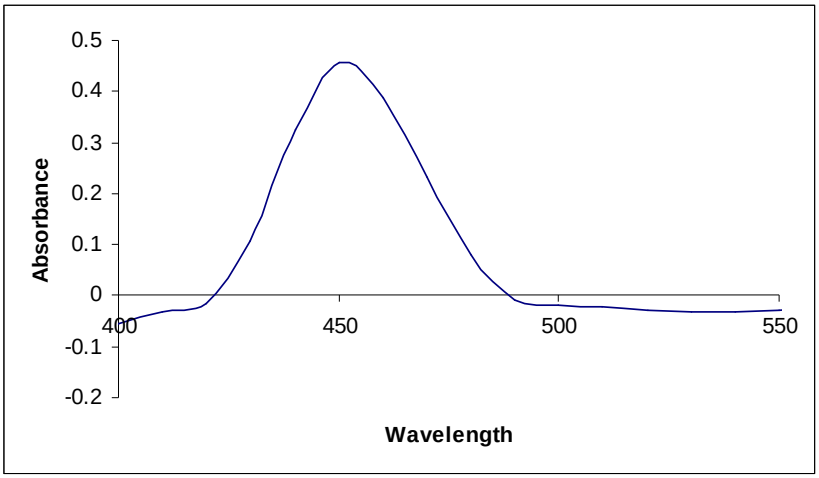


Fig - 4

(a) Cd (II)-CMHBH- Fist order derivative spectra

CMHBH-2 X 10^{-3} M (0.5 ml), Cd (II)-2 X10^{-4} M (0.5 ml), Buffer-3.0 ml (pH-9.0), Triton X100 (5%) 1.0 ml
λ max 450 nm

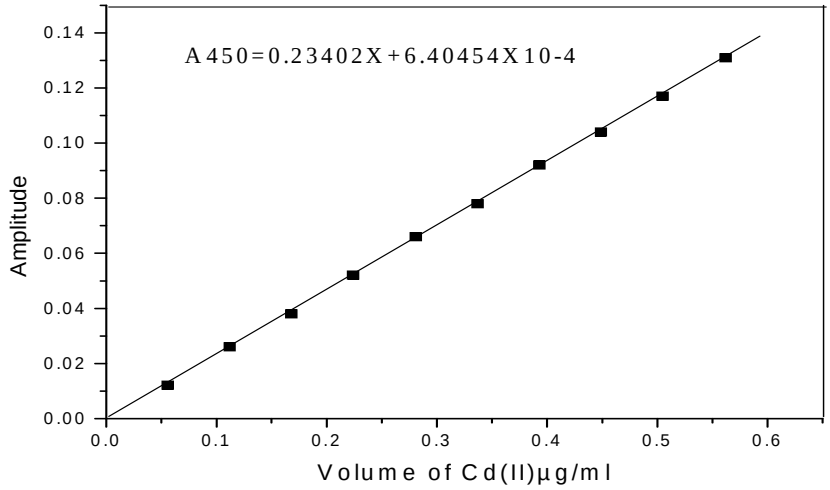


Fig – 4
(b): Cd (II)-CMHBH- First order Beers law

CMHBH-1X10^{-3} M (0.5 ml) (Constant), Cd (II) -1X10^{-5} M,Buffer pH-3.0 (9.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax ---------- 450 nm

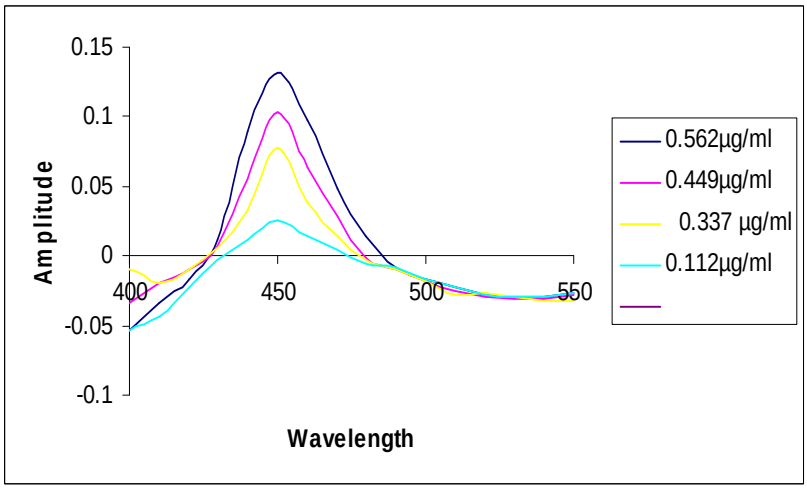


Fig - 4

(c) Cd (II)-CMHBH- Beers law first order derivative spectra

CMHBH-1X10^{-3} M (0.5ml) (Constant), Cd (II)-1X10^{-5} M,Buffer pH --3.0 (9.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax----------450 nm

Determination of Cadmium (II) by second order derivative method

The second order derivative method has been employed for the determination of Cadmium (II) using CMHBH in trace quantities. The second derivative spectra Fig-5 (a) showed maximum amplitude at λmax 470 nm. The derivative amplitudes at λmax 470 nm were proportional to the concentration of Cadmium (II). The straight line obeyed the equation λmax 470 nm = 0.57403X-0.0239.

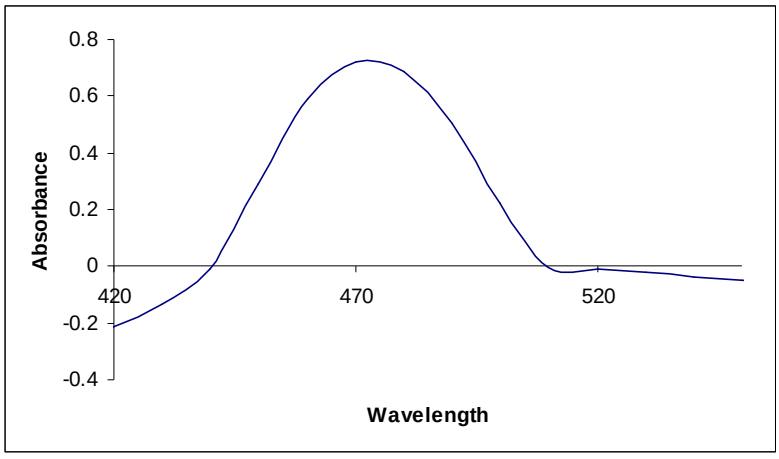


Fig-5

(a) Cd (II)-CMHBH- Second order derivative spectra

CMHBH-2X10^{-3} M (0.5 ml), Cd (II) -2X10^{-4} M (0.5 ml), Buffer pH --3.0 (9.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax----------470 nm

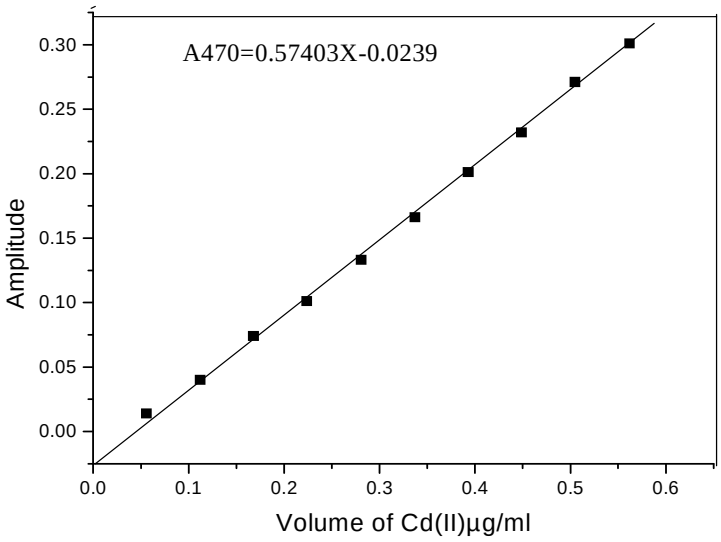


Fig - 5 (b)

Cd (II)-CMHBH- Second order Beers law

CMHBH-1X10^{-3} M (0.5 ml) (Constant), Cd (II) -1X10^{-5} M,Buffer pH-3.0 (9.0 ml), Triton-X-100 (5%)-1.0 ml (Constant) , λmax ---------- 470 nm

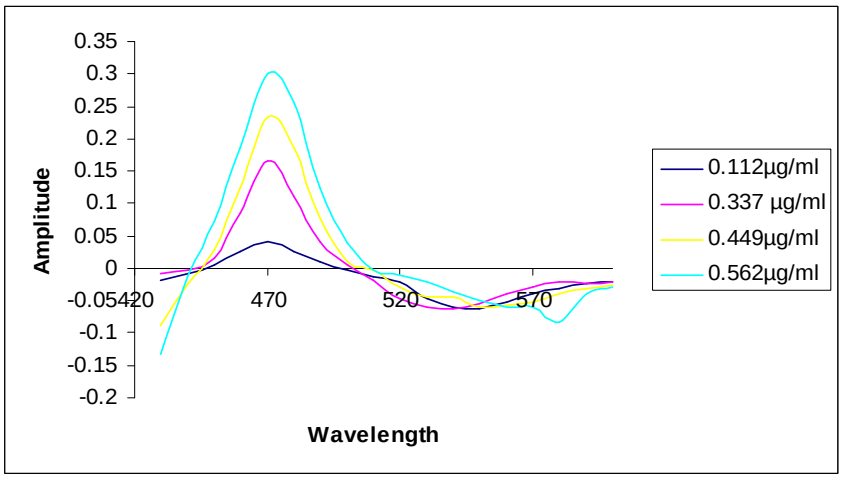


Fig - 5

(c) Cd (II)-CMHBH- Beers's law second order derivative spectra

CMHBH-1X10^{-3} M (0.5 ml) (Constant), Cd (II)-1X10^{-5} M,Buffer pH --3.0 (9.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax----------470 nm

Composition and stability of the complex

The stoichiometry of the complex was determined by Job's method and molar ratio method and found to be 1:1 (M: L). The stability constant was determined by Job's method as12.63×10^{6}.

Effect of diverse ions

The tolerance limits (µg ml^{-1}) of various diverse ions in the present method are given in Table1

Tolerance limit was set as the amount of foreign ion that caused an error in the absorbance by ± 2%. The effect of several diverse ions on the determination of Cadmium (II) was examined under the optimum conditions.

The extent of interference by various anions and cations was determined by measuring the absorbance of solutions containing a constant amount of Cadmium (II) and varying amounts of diverse ions.

Table – 1

Tolerance limit of foreign ions in the determination of 0.562 µg/ml of Cd (II)

Ion Added	Tolerance Limit (µg/ml) (Zero order) 383 nm	Tolerance Limit (µg/ml) (D1) 450 nm	Tolerance Limit (µg/ml) (D2) 470 nm
Iodide	508	761.4	899.2
Sulphate	576	576	576
Ascorbic acid	35	56	56
Urea	120	240	240
Thiocyanide	697	697	697
Bromide	239	239	239
Thiourea	456	533	533
Nitrate	37	112	112
Tetra borate	98	246	491
Acetate	118	177	177
Phosphate	38	38	38
Chlorides	213	248	248
Tartarate	500	750	750
Citrate	567	567	567
Flourude	76	76	76
Oxalate	264	264	264
Thiosulphate	224	359	359
U^{+6}	47.61	47.61	47.61
Sn^{+2}	60	60	60
La^{+3}	13.39	13.39	13.39
Ba^{+2}	13.7	13.7	13.7
Na^{+}	23	42	42
Hg^{+2}	20	20	20
Pb^{+2}	21	21	21
W^{+6}	55.15	55.15	55.15
Zr^{+4}	45.61	45.61	45.61
Zn^{+2}	2	3	3
Bi^{+3}	7	7	7
Ti^{+4}	38.30	38.30	38.30
Ni^{+2}	1.76	1.76	1.76
Ce^{+4}	280	2.80	2.80
Fe^{+3} **	2.23	2.23	2.23
Cu^{+2} *	1.90	1.90	1.90
Ru^{+3}	2	3	3
Pd^{+2}	1.06	1.06	1.06
Ag^{+}	2.15	2.15	2.15
Pt^{+4}	1.76	1.76	1.76
Sr^{2}	26.28	26.28	26.28
Se^{+4}	23.66	23.66	23.66
V^{+5}	1.52	1.52	1.76
Co^{2+}	11.78	11.78	11.78

*Masked by Fluoride 76 µg/ml,** Masked by Thiourea 446 µg/ml

The effect of various diverse ions in the determination of 0.562µg/ml Cadmium (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ± 2% in the absorbance or amplitude. The results are given in Table 1. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess, such as iodide, thiosulphate, thiocyanide, bromide, sodium (I), bismuth (III), tungsten (VI) and zirconium (IV). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as iron (III) and copper (II) is decreased by adding masking agents thiourea and Fluoride respectively.

APPLICATIONS

Zero order method The method proposed in the present studies was applied for the determination of Cadmium (II) in biological materials (Cigarette tobacco, Radish flesh and Cabbage) and in alloy samples. The results are in good agreement with the certified values.

Cigarette tobacco solution

A known aliquot of the sample solution was taken in 25 ml slandered flask containing buffer solution of pH 9.0 and CMHBH reagent solution ($1x10^{-3}$) solution and made up to the mark with distilled water. Absorbance of the solution was measured at 383 nm against the reagent blank. The absorbance values were referred to the pre determined calibration plot to compute the amount of cadmium.

Table – 2

Determination of Cadmium (II) in commercial samples

Commercial sample	Stock solution (ml)	Sample taken (ml)	Amount of Cadmium (II) (µg/ml) Cadmium (II) found (µg/ml)* Zero Order	D1	D2
Cigarette (Tobacco) Sample-1	50	2	2.4	2.32	2.36
		3			
		4			
Cigarette (Tobacco) Sample-2	50	2	2.53	2.28	2.30
		3			
		4			

*Mean of three determinations

Application to alloys

Certified samples of bearing metal alloy samples were not available. Therefore, synthetic mixtures whose composition corresponds to bearing metal alloy were prepared. The present developed was applied to the determination of Cadmium (II) in synthetic mixtures.

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3.0 ml of buffer of pH 9.0, 76 µg of fluoride (to mask Cu) and 0.5 ml of ($1x10^{-3}$ M) CMHBH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λmax 383 nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Cadmium present. The results are presented in table 3

Table – 3

Determination of Cadmium (II) in synthetic alloy sample

Sample	Amount of Cadmium (II)) (µg/ml)						
		Amount found*					
	Certified	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Bearing metal alloy	(a) 90.65	90.22	0.47	90.31	0.37	90.44	0.23
	(b) 95.75	95.41	0.35	95.54	0.21	95.63	0.12

*Mean of five determinations

(a) Cd 90.65 %; Ni 1.35 %; Ag 4.5 %. (b) Cd 95.75 %; Ni 2.25 %; Ag 2.0 %.

Table – 4

Determination of Cadmium (II) in Biological materials.

Biological sample	Stock solution (ml)	Sample taken (ml)	Amount of Cadmium (II) (µg/ml) Cadmium (II) found (µg/ml)* Zero Order	D1	D2
Radish flesh	50	2 3 4	1.88	0.82	0.86
Cabbage	50	4 6 8	0.72	0.75	0.77

*Average of three determinations

Cadmium is detected in drinking water at relatively low concentration. The world health organization uses a maximum guideline of 0.005 µg/ml in drinking water. In humans acute exposure to cadmium leads to nausea, vomiting and muscular cramps. Renal toxicity such as proteinuria is the most common symptom of chronic exposure to cadmium. Cadmium is effectively removed from raw water by destabilization and aggregation of pre-existing solids that contain Cd or by adsorption onto amorphous iron or aluminium oxides. This can be used for the analysis of cadmium in a wide variety of waters, including surface, ground and seawaters. Minimum detectable limit is 0.5 mg/L

Physico-chemical and analytical characteristics of Cd (II)-CMHBH complex

The results obtained in zero order and derivative spectrophotometric methods for Cadmium (II)-CMHBH complex were compared and presented in Table 5. From this it was noticed that in derivative spectra the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

Table – 5

Physico-chemical and analytical characteristics of Cd (II)-CMHBH complex

Characteristics	Results
λ_{max}	383 nm
pH range	8.0-10
Optimum pH range	8.0-9.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)
Molar absorptivity ($L.mol^{-1}cm^{-1}$)	5.6×10^4
Sandal's sensitivity ($\mu g/cm^2$)	0.002
Beer's law validity range (µg/ml)	0.0562-0.562
Optimum concentration range (µg/ml)	0.112-0.505
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1
Stability constant of the complex	12.63×10^6
Standard deviation in the determination of 0.224 µg/ml of Cd (II) for ten determinations.	0.001
Relative standard deviation (%)	1.136
Regression coefficient	0.9997
Detection limit (µg/ml)	0.003
Determination limit (µg/ml)	0.009

Table – 6

Comparison of spectrophotometric methods for the determination of Cadmium (II)

Reagent	λmax (nm)	pH	Molar absorptivity (L mol^{-1} cm^{-1})	Extraction/ Heating	Beer's law Range	Reference
1-Antipyrinal diazo amino 2,4 dinitrobenzene (in presence of Triton X-100)	540	10.2-12	15.2×10^4	$CHCl_3$	0-15 µg/25ml	17
4-formyl benzene diazoamino azobenzene (in presence of Triton X-100)	525	9.5	13.3×10^4	$CHCl_3$	0-10 µg/25ml	18
P-acetyl benzene diazoamino azobenzene (in presence of Triton X-100, SDBS)	505	7.8	15.7×10^4	$CHCl_3$	0-12 µg/25ml	19
3-Bromo-4- (4-nitrophenyl diazoamino) azobenzene (in presence of Triton X-100)	495	Alkali medium	15.6×10^4	$CHCl_3$	0-8.0 µg/25ml	20
3-Bromo-4- (2 Bromo -4- nitro phenyl diazoamino) azobenzene (in presence of Triton X-100	504	Alkali medium	15.0×10^4	$CHCl_3$	0-10.0 µg/25ml	21
P-chloro benzene diazoamino azobenzene (in presence of Triton X-100)	490	10.0	11.1×10^4	$CHCl_3$	0-15.0 µg/25ml	22
2-hydroxy-5-sulphobenzene diazoaminoazobenzene	520	NH_4OH	18.8×10^4	$CHCl_3$	0-1.0 µg/25ml	23
2-Pyridine diazoamino azobenzene (in presence of Triton X-100)	530	Ammonia buffer	19.2×10^4	$CHCl_3$-	0-1.0 µg/25ml	24
Cinnamaldehyde isonicotinoyl hydrazone.	380	8.5	3.3×10^4	Ethanol	0.224-4.496	
Cinnamaldehyde 4hydroxybenzoyhydrazone (in presence of Triton X-100-5 %) (CMHBH)	383	9.0	5.6×10^4	Carbinol	0.0562.562	Present method

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