

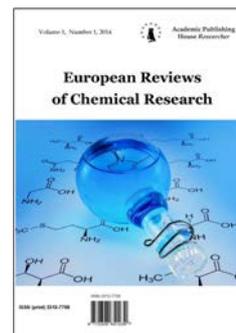
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Determination of Trace Amount of Cd (II) by using a Chromogenic reagent Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) with UV-Visible Spectrophotometry

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Abstract

Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) is used as a novel chromogenic organic reagent for the determination of Cadmium (II) with spectrophotometer. The novel chromogenic organic reagent – diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) gave yellow colored water soluble complex with Cd (II) in buffer (pH = 8.0–9.0) medium. The color complex shows maximum absorbance at $\lambda = 378$ nm. The system obeyed Beer's law in the concentration range of 0.5035–5.0535 $\mu\text{g/ml}$. The optimum Cadmium (II) concentration range for accurate determination as evaluated from Ringbom plot was 0.5035–5.0535 $\mu\text{g/ml}$. The molar absorptivity and Sandell's sensitivity were $2.94 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0036 \mu\text{g/cm}^2$ respectively. Cadmium (II) forms M:L (1:1) color complex with DMAHBH and stability constant of the complex was found to be $8.58 \cdot 10^7$. Soil samples were analyzed for the determination of Cadmium (II) present, using the proposed method. This developed method was applied for the determination of Cadmium (II) in soil and cigarette samples and good analytical results.

Keywords: chromogenic organic reagent, derivative spectrophotometry, Cadmium (II), soil, cigarette tobacco samples.

Introduction

Cadmium occurs in nature in association with zinc in minerals. Growing plants acquire and concentrate Cd(II) within the same biochemical setup. The outbreak of Cadmium (II) poisoning occurred in Japan in the form of itai itai or ouch ouch disease. Many people suffered from this disease, in which their bones became fragile. At high levels cadmium causes kidney problems, anemia and bone marrow disorders [1]. Cadmium is a lustrous, silver-white, ductile and highly malleable metal. It is soluble in acids but not in alkalis. About three-fourth of cadmium is used in Ni–Cd batteries and the remaining one fourth is used mainly pigments, coating and plating and as stabilizers for plastics [2–3]. Cadmium has been used particularly to electroplate steel and as a barrier to control nuclear fission. Naturally a very large amount of cadmium is released into the environment. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing processes, etc. Human intake of cadmium takes place mainly through diet like liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed [4]. One of the main resources for cadmium accumulating in the human body is the extensive use of tobacco. Trace amounts of cadmium are important in industry [5], as a toxicant [6], and biological nonessential [7], as an environmental pollutant [8], and an occupational hazard [9]. It is an extremely toxic metal, and the effects of acute cadmium poisoning are manifested in a variety of different symptoms including high blood pressure, kidney damage and destruction of red blood cells [10]. The reported cadmium content in the environment is 70–110 µg/l in sea water and 2–960 µg/l in fresh water [11]. For the determination of cadmium in trace amount levels, there are several frequently adopted methods using analytical techniques, such as AAS, ICP–AES, ICP–MS, X-ray fluorescence spectroscopy, spectrophotometry, spectrofluorometry and so on. Among these, the spectrophotometric method is preferred, because it is cheaper and easy to handle, and comparable in sensitivity and accuracy, besides having good precision. There are many organic complexing reagents [12–21] which are used for spectrophotometric determination of Cadmium (II). Yet they suffer from disadvantages such as low sensitivity, incomplete extraction and interferences from a large number of foreign ions (Table 1). Recently, there has been a rapid growth in the popularity of sulfur bearing ligands such as thiosemicarbazones in analytical/inorganic chemistry for determination of metal ions [22]. The metal chelate of these sulfur and nitrogen containing reagents find wide range of applications in medicine and agriculture [23]. A survey of literature reveals that only a few thiosemicarbazones are employed for direct spectrophotometric determination of Cd(II), but not extractive spectrophotometric determination. Hence the authors introduced a new chromogenic reagent – diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) for the determination of trace amount of Cd (II) in soil and tobacco samples.

Experimental

Spectrophotometric measurements were made using a Shimadzu 160 microcomputer based UV–Visible spectrophotometer (Shimadzu Corp., Japan) equipped with 1.0 cm quartz cuvette and an ELICO LI-120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water.

Reagent:

Synthesis of diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH)

DMAHBH was prepared by refluxing a mixture of diacetyl monoxime (1.0111 g, 0.01 mole) and 3-amino-4-hydroxybenzhydrazide (1.6717 g, 0.01 mole) in ethanol (15 ml) for 5 hours. On cooling the reaction mixture, a light yellowish crystalline product was separated out. The crystalline hydrazone was collected by filtration and washed several times with 20% of ethanol in water and dried in vacuum. The product was re crystallised with ethanol. Yield, 79%; m.p., 220 °C. The chemical structure DMAHBH is shown in Fig. 1.

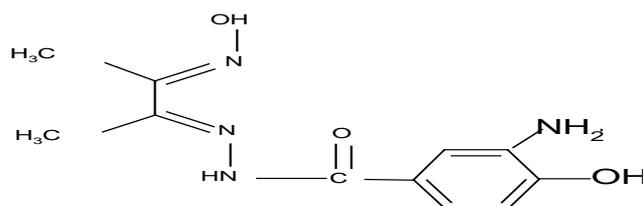


Figure 1: Structure of DMAHBH

Analytical properties of DMAHBH

The reactions of some important metal ions were tested at different pH values. The characteristics of the most important complexes are summarized in Table 1. The samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH=1.0–11), 0.5 ml of metal ion ($1 \cdot 10^{-3} M$) and 0.5 ml of DMAHBH ($1 \cdot 10^{-2} M$) solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300–800 nm range against reagent blank.

The data obtained from appropriate spectra which were derived in the presence of 10-fold molar excess of the reagent to metal ion. The pH values, which facilitate the formation of different complexes were also included.

Table 1: Characteristics of DMAHBH complexes in solution

Metal ion	λ_{\max} (nm)	pH range	Surfactant used	Colour of the complex
Os(VIII)	390	4.0	–	bright yellow
Zr(IV)	388	4.0	–	yellow
Cu(II)	412	9.0	–	bright yellow
Pb(II)	387	3.0–10.0	TritonX-100	yellow
Cd(II)	378	8.0–9.0	TritonX-100	yellow

Recommended procedure:

Determination of Cadmium (II) (zero order)

An aliquot of the solution containing 0.5035–5.0503 $\mu\text{g/ml}$ of Cadmium (II), 3 ml of buffer solution pH 1.0 to 10.0 and 0.5 ml ($1 \cdot 10^{-2} M$) of DMAHBH reagent were taken in a 10 ml standard volumetric flask and the resulting solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at $\lambda=378$ nm in a 1.0 cm quartz cuvette. The corresponding reagent blank is prepared in the same way, but without Cadmium(II) metal solution. The absorption spectra of DMAHBH and its Cd(II) complex under the optimum conditions are shown in Figure 2. The [Cd(II)–DMAHBH] complex shows the maximum absorbance at $\lambda=378$ nm, whereas the reagent blank does not absorb appreciably.

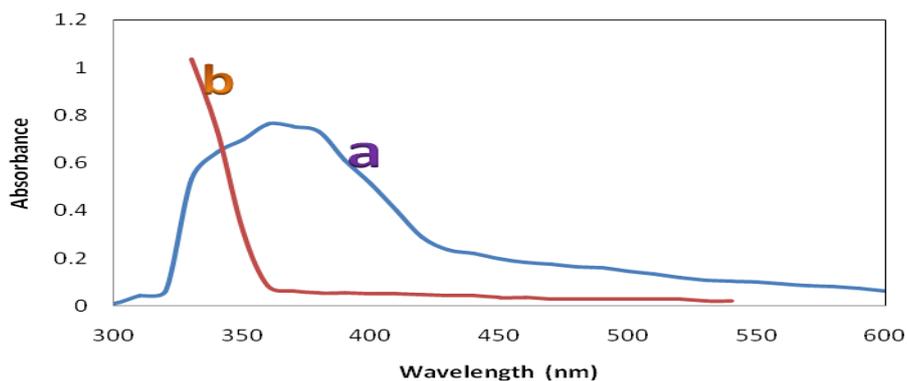


Figure 2: Absorption spectra: (a) – [Cd(II)–DMAHBH] complex Vs. reagent blank; (b) – DMAHBH Vs. buffer blank

Effect of pH on the absorbance of the [Cd(II)–DMAHBH] 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 within 8.0–9.0. Analytical studies were therefore, carried out at pH 8.0 (Fig. 3).

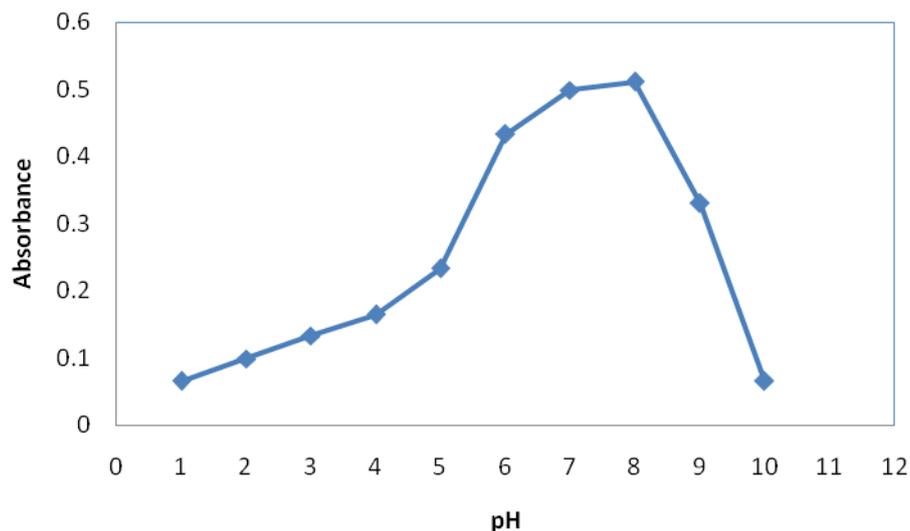


Figure 3: The dependence of absorbance of the [Cd(II)–DMAHBH] complex on the pH value

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) presented in Figure 4 showed that Beer's law was obeyed in the concentration range $0.5035\text{--}5.0535\ \mu\text{g}\cdot\text{ml}^{-1}$ of Cadmium (II). The molar absorptivity and Sandall's sensitivity were $2.94\cdot 10^4\ \text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $0.0036\ \mu\text{g}/\text{cm}^2$ respectively. The correlation coefficient of the calibration curve for experimental data was 0.996.

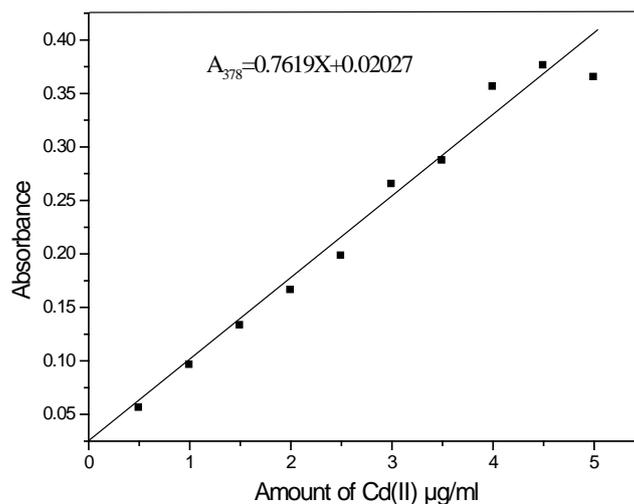


Figure 4: Absorbance Vs Amount of Cd(II) ($\mu\text{g/ml}$):
 $[\text{DMAHBH}] = 1 \cdot 10^{-2} \mu\text{g/ml}$
 $\text{pH} = 8.0$
Wavelength = 378 nm

Results and discussion

Determination of Cadmium (II) using DMAHBH

Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) reagent is a blend of a carbonyl compound and hydrazide. The reagent solution is stable for more than 24 hours in the presence of buffer medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

Cadmium (II) reacts with DMAHBH in basic medium to give yellow coloured water-soluble $[\text{Cd(II)}\text{-DMAHBH}]$ complex. The colour reaction between Cadmium (II) and DMAHBH was instantaneous even at room temperature in the pH range 8.0 to 10.0. The absorbance of the yellow coloured complex remains constant for three hours. The maximum colour intensity is observed at pH 8.0. A 10-fold molar excess of reagent is adequate for full colour development. The order of addition of buffer solution, metal ion and the reagent has no adverse effect on the absorbance. The complex formation reaction between Cadmium (II) and DMAHBH has been studied in detail based on the composition of the $[\text{Cd(II)}\text{-DMAHBH}]$ complex as determined by using the Job's and molar ratio methods. The most important physico-chemical and analytical characteristics of $[\text{Cd(II)}\text{-DMAHBH}]$ complex are summarized in Table 2.

Table 2: Physico-chemical and analytical characteristics of $[\text{Cd(II)}\text{-DMAHBH}]$ complex

Characteristics	Results
λ_{max} (nm)	378
Colour	yellow
pH range (optimum)	8.0–9.0
Molar absorptivity ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	$2.94 \cdot 10^4$
Sandell's sensitivity ($\mu\text{g}\cdot\text{cm}^{-2}$)	0.0036
Mole of reagent required per mole of metal ion for full colour development	10-folds
Beer's law validity range ($\mu\text{g/ml}$)	0.5035–5.0535

Optimum concentration range ($\mu\text{g/ml}$)	0.5035–5.0535
Stability constant of the complex (Jobs method)	$8.58 \cdot 10^7$
Relative standard deviation (%)	0.1
Regression coefficient	0.996
Composition of complex (M:L) obtained in Job's and mole ratio method	1 : 1

The first order derivative spectral graph was shown in Figure 5. This shows the derivative amplitudes measured at $\lambda=430$ nm. The first order was found to be proportional to the amount of Cadmium (II) respectively.

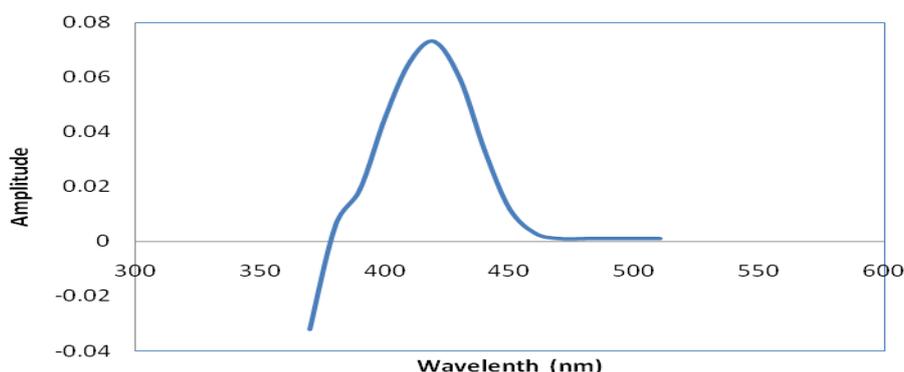


Figure 5: First derivative spectra of [Cd (II)–DMAHBH] Vs reagent

Effect of foreign ions:

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 of metal ions having overlapping spectra. The recommended procedures have been employed for the spectrophotometric determination of Cadmium (II). The effect of various diverse ions in the determination of Cadmium (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of an foreign ion was taken as the amount of foreign ions required to cause an error of $\pm 2\%$ in the absorbance or amplitude. The results are presented in Table 3.

Table 3: Tolerance limit of foreign ions in the determination of 1.5888 $\mu\text{g/ml}$ of Cadmium (II)

Ion added	Tolerance limit ($\mu\text{g/ml}$)
Ascorbic acid	91
Acetate	165
Bromide	243
Phosphate	43
Chlorides	344
Citrate	654
Iodide	468
Nitrate	56
Tetra borate	136
Tartarate	523
Ba(II)	09
Co(II)	6.3
Cu(II) ^a	5.1
Hg(II)	1.9

Fe(III) ^b	1.65
Bi(III)	4.1
Ru(III)	5.1
Pd(II)	3.86
Zn(II)	6.6
Pb(II)	1.08
Ag(II)	10.4
Se(IV)	32
Sn(II)	36
V(V)	11.3
U(VI)	65
Zr(IV)	26

Notes: (a) – masked by fluoride, 132 µg/ml; (b) – masked by thiourea, 513 µg/ml

Applications

Determination of Cadmium (II) in soil samples:

Preparation of soil samples

Soil samples like agricultural soil, roadside soil and contaminated soil were taken. The soils were air dried and homogenate soil samples weighing 100 mg accurately taken and placed in a 100 ml flask. The samples were digested in the presence of an oxidizing agent. The content of the flask was filtered through No. 41 filter paper into a 25 ml volumetric flask and neutralized with a dilute NH₄OH solution. It was diluted to the mark distilled water. The calibrated results are presented in Table 4.

Table 4: Determination of Cadmium (II) in soil samples*

Sample name	Cd(II) found µg/g
Industrial sample	0.26±0.3
Agriculture soil	0.57±0.5
Road side soil	1.1±0.2

*Notes: Average of the best three determinations among five determinations

Preparation of cigarette tobacco solution

The tobacco from cigarettes was 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 a 50 ml flask made up using distilled water. The amount of Cadmium (II) was determined by pre-estimated calibration plot. The calibrated results are presented in Table 5.

Table 5: Determination of Cadmium (II) in cigarette samples*

Commercial sample	Stock solution (ml)	Sample taken (ml)	Zero order
Cigarette (Tobacco) Sample-1	50	2 3 4	2.7
Cigarette (Tobacco) Sample-2	50	2 3 4	2.51

*Notes: Average of the best three determinations among five determinations

Conclusion

In basic buffer medium, the diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) reacts with Cadmium (II) and imparts yellow coloration of the water soluble [Cd(II)–DMAHBH] complex. The color reaction between Cadmium (II) and DMAHBH is instantaneous

and the absorbance of the colored compound remains to be constant for three hours. The addition of other constituents (buffer, metal ion and reagent) has no adverse effect on the absorbance of the complex. DMAHBH has been proven a sensitive and selective chromogenic organic reagent for the determination of Cadmium (II). Molar absorptivity of the colour complex makes up $2.94 \cdot 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$. The proposed method was especially sensitive and selective with respect to metals, which commonly seriously interfere with the determination of Copper and Iron performed by literature methods. The proposed method can be successfully applied the determination of Cadmium (II) in soil and cigarette samples. This method was favorably compared with previously reported spectrophotometric methods.

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