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Direct and Derivative Spectrophotometric Determinaiton of Cadmium (II) Using Alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH)

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Abstract: ***An alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) is newly synthesised novel chromogenic reagent, ACINH is used for the determination of Cd (II) by a spectrophotometric method. ACINH forms a yellow coloured water soluble [Cd (II)-ACINH] complex with Cd (II) in the pH range 9.0. At λ_{max} 380 nm the complexes shows maximum absorbance and at pH range 9.0. Hence further analytical studies were carried out at λ_{max} 380 nm. Beer's law is obeyed in the range of 0.5031-5.0531 µg/ml Cd (II). The molar absorptivity and sandell's sensitivity of the complex are $2.94x10^4$ $L.mol^{-1}.cm^{-1}$ & 0.0034 µg/cm^2 respectively. Cd (II) forms metal ligand ratio as 1:1 complex with ACINH and complex shows stability constant $8.58x10^7$ was obtained by job's method. The tolerance limits of various foreign ions have also been studied. For the determination of Cd (II) newly developed derivative spectrophotometric method has been employed and good analytical results in soil samples.***

Keywords: alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH), Cadmium (II), Chromogenic, Soil, Spectrophotometery

1. Introduction

Cadmium is the harmful environment pollutant because of its harmful nature, in soils determination of Cd (II) has great importance. Bones became fragile due to itai itai or ouch ouch disease occurred in Japan caused by Cd (II) poisoning. If level of Cd (II) is high anaemia, kidney problems causes. Cd (II) is insoluble in alkali, soluble only in acid. Cadmium (II) mainly used in Ni-Cd battery, coating, pigments, electroplating and also used in plastics as stabilizers. In to the environment Cd is released due to rocks weathering, through volcanoes and forest fires released into the air. Cadmium enter to the human body through food chain, diet like mussels, mushrooms, liver, seafood and mainly more use of tobacco. Cd is a toxic metal show different symptoms in humans like red blood cells destruction, high blood pressure. Cadmium content 2-960 µg/l in fresh water and 70-110 µg/l in sea water are reported in environment. For the determination of Cadmium there are several methods are adopted using ICP-AES, AAS, ICP-MS, Spectro fluerometry and so on. Preferred method is Spectrophotometry among mention above. In present communication, for the determination of Cd in soil simples spectroscopic method was employed using an alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) as a selective and sensitive analytical regent.

Instruments

Elico digital pH meter and UV-VIS spectrometer with 1.0 cm quartz cells were used for measurements of pH measurements and absorbance respectively. For getting good results scan speed (2400) nm/min, contain instrument used having wavelength range 300-800. For the preparation of all solutions doubly distilled water was used. By dissolving requisite amount of Cd $(NO_3)_2.4H_2O$ in distilled water, 0.01M solution of Cadmium (II) was prepared and then standardized.

Reagent:

Synthesis of an alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH):

ACINH was synthesized by refluxing a mixture of equimolar mounts of alpha Amyl Cinnamaldehyde (2.022gm, 0.01M) and Isonicotinoyl hydrazide (1.3714gm, 0.01M) in hot methanol for 4 hours. Crystalline yellowish coloured product was formed and separated out by cooling the reaction mixture. By filtration crystalline hydrazone was collected, Product was washed with doubly distilled water and recrytallised with 50% ethanol (yield 78%, MP 250-252^{0}C). The structure of ACINH is shown in fig 1

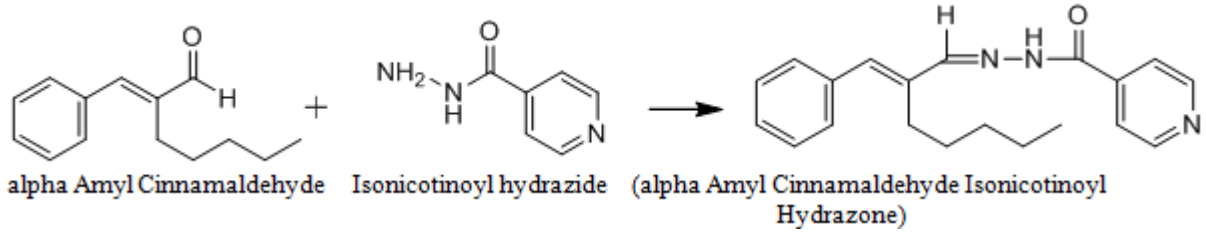

Figure 1: Alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone

Buffer solution:
By using $1x10^{-1}$ M HCl, $1x10^{-1}$ M NaOH, $1x10^{-1}$ M Na_2HPO_4 and $1x10^{-1}$ M K_2HPO_4 buffer solution were prepared. Digital pH meter was used for checking pH of these solutions.

Analytical properties of ACINH:
At different pH values few important metal ions were tested, results were summarized in table1. In standard volumetric flasks (10ml) the samples were prepared by adding 0.5 ml metal ion ($1x10^{-3}$ M), 3ml of buffer solution (pH=1.0-11), and 0.5 ml of ACINH ($1x10^{-2}$ M) solutions. By using distilled water, up to the mark the solution mixture was diluted. Against the reagent blank the absorbance was measured at wavelength range 300-800nm.

Table1: Characteristics of ACINH

Metal ion	pH	Colour	λmax (nm)
Zr(IV)	4.0	Yellow	388
Os(III)	4.0	Bright Yellow	390
Cu(II)	9.0	Yellow	412

Determination of Cadmium (II)
In a 10 ml standard volumetric flask, 3ml of buffer solution pH (1.0-11.0), 0.5031-5.0531 µg/ml of Cadmium (II) and 0.5ml ($1x10^{-2}$M) of ACINH reagent were taken and up to mark diluted with distilled water. In a 1.0 cm quartz quevette at λ_{max} 380 nm the absorbance of the solution was recorded. The reagent blank solution is also prepared without Cd (II) metal solution in the same way. Under the optimum conditions the absorption spectra of ACINH and its complex with Cd (II) shown in figure-2. At λmax 380nm maximum absorbance showed by the complex [Cd (II)-ACINH], the reagent blank does not absorbs appreciably.

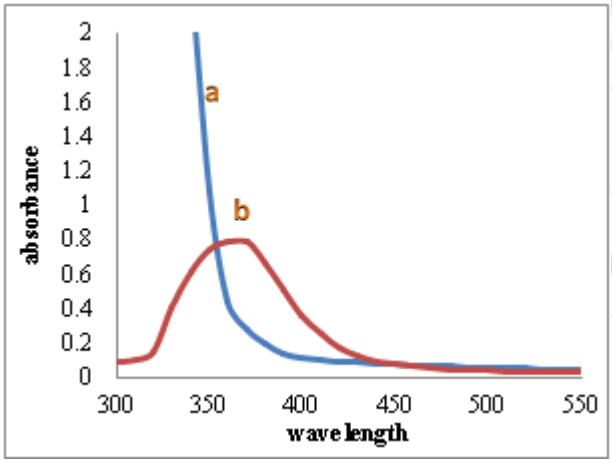

Figure2: (a) Absorption spectra of ACINH (b) Absorption spectra of [Cd (II)-ACINH]

Effect of pH:
In to a series of volumetric flasks (10ml), 1ml of ligand solution ($1x10^{-2}$M), 4.0 ml of varying buffer solution pH (1.0-12.0) and 1ml of Cd(II) solution ($1x10^{-2}$M) were taken and up to mark diluted with distilled water and at λ_{max} 380 nm the absorbance was measured against the reagent blank. Increases the absorbance up to pH 9 and then decreases, shown in figure-3. Hence pH 9 is optimized for the further studies.

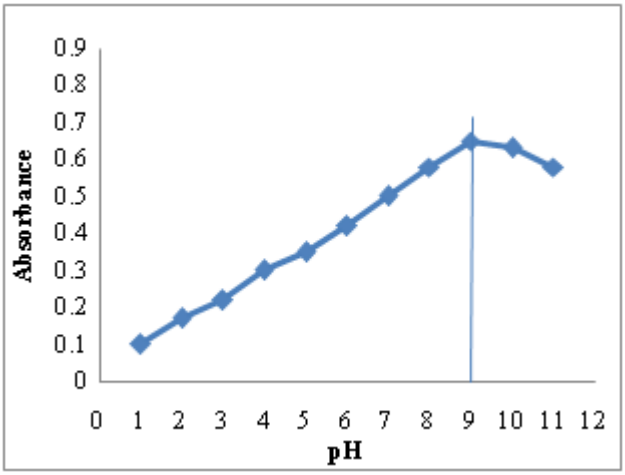

Figure 3: Effect of pH on the absorbance of [Cd (II)-ACINH]

Application of Beer's law
For the possible determination of Cd(II) at micro levels, the absorbance of the solutions contain different amounts of metal ion was measured, In figure-4 between amount of Cd(II) and absorbance, a calibration plot was drawn, shown that in the concentration range 0.5031-5.0531 µg/ml of Cd(II) Beers law was obeyed. The Sandalls's sensitivity is 0.0034 µg/ml and molar absorptivity is $2.89x10^4$ $L.mol^{-1}cm^{-1}$.

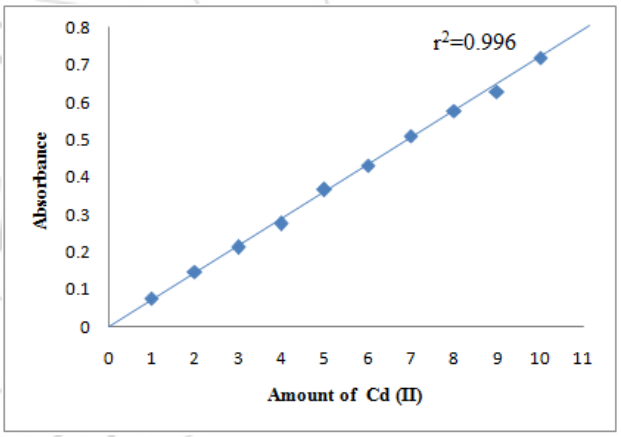

Figure 4: Beer's law spectrum of [Cd (II)-ACINH]

2. Results and Discussion

An alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) reagent blends of a carbonyl compound and hydrazide. The reagent solution is stable in buffer medium more than one day. Natural water soluble complex was given by ligand when coordinates to the metal ions. [Cd (II)-ACINH] yellow coloured water soluble complex was formed when Cd (II) react with ACINH in basic medium. At pH 9 instantaneous colour reaction occurred between Cd (II) and ACINH even at room temperature. The absorbance of the yellow coloured complex remains constant for three hours. At pH 9 the maximum colour intensity is observed. For full colour development a 10 fold molar excess of reagent is adequate. For the absorbance there is no effect in order of addition of reagent, buffer and metal ion solutions. Complex stoichiometry was found to be 1:1 (M:L) by molar ratio method and Job's continuous variation method.

Stability constant is $8.56x10^7$. The most important analytical and physic-chemical characteristics of [Cd (II)-ACINH] are summarized in table-2.

Table 2: Analytical and Physico-chemical characteristics of [Cd (II)-ACINH] complex

Characteristics	Results
λ_{max} (nm)	380
Colour	yellow
pH range (optimum)	9.0
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	$2.94x10^4$
Sandell's sensitivity ($\mu g/cm^2$)	0.0034
Mole of reagent required per mole of metal ion for full colour development	10-folds
Beer's law validity range (µg/ml)	0.5031–5.0531
Stability constant of the complex (Job's method)	$8.58x10^7$
Relative standard deviation (%)	0.1
Regression coefficient	0.996
Composition of complex (M:L) obtained in Job's and mole ratio method	1 : 1

In figure-5 the first order derivative spectral graph was shown, at λmax 435 nm derivative amplitude was measured. The first order was found to be proportional to the amount of Cadmium (II) respectively.

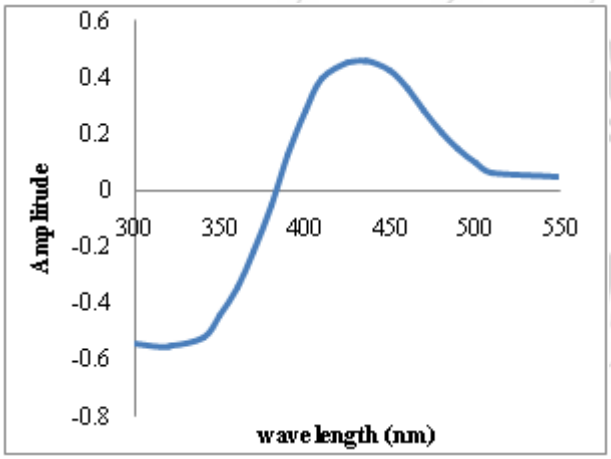

Figure 5: First derivative spectra of [Cd (II)-ACINH] Vs reagent

Interference

To decrease the interference very useful technique is derivative spectrophotometery, which is increase the tolerance limit value of foreign ions of metal ions having overlapping spectra. To the determination of Cadmium (II) the recommended spectrophotometrtric procedures have been employed. In the determination of Cadmium (II) the effect of various diverse ions was studied to find out the tolerance limit of foreign ions in the present method. The foreign ion causing an error of ±2% is observed in amplitude or absorbance which is the limitations of tolerance of foreign ions. In table-3 the results are shown.

Table 3: Tolerance limits of foreign ions in the determination of 1.5888 µg/ml of Cd (II)

Ion added	Tolerance limit (µg/ml)
Chlorides	345
Tartarate	521
Iodide	469
Phosphate	41
Ascorbic acid	90
Citrate	655
Bromide	242
Tetra borate	135
Nitrate	57
Acetate	163
Zn(II)	6.4
Ru(III)	5.4
Hg(II)	1.7
V(V)	11.1
Co(II)	6.5
Se(IV)	30
Ba(II)	10
Pb(II)	2
Ag(II)	12
U(VI)	63
Zr(IV)	24
Bi(III)	5
Pd(II)	4
Sn(II)	38

Applications:

Determination of Cd (II) in soil samples:

Preparation of soil sample:

Soil samples like contaminated, agricultural, roadside soil were taken. The soils were air dried and in a 100ml flask, 100mg of accurately weighing homogenate soil samples were taken. By using oxidising agent the samples were digested. Using no 41 filter paper the content of the flask was filtered in to a volumetric flask (25ml) and by using dilute NH_4OH, solution was neutralised and up to mark diluted with distilled water. Results are shown in Table-4.

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

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

*Notes: Average of three determinations

3. Conclusion

An alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) is a newly synthesized reagent. To determine various metal ions like Cd (II) in various soil samples by spectropotometically using an alpha Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) as mentioned in applications.

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