Synthesis And Spectrophotometric Study of 2-[(6-Nitro -$\bar{2}$-benzothiazolyl)azo]-4,5-diphenyl imidazole As Analytical Reagent For Determination Of Cadmium(π)

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Abstract

A sensitive ,selective and rapid spectrophotometric method was used for the determination of trace amounts of cadmium ion by using the reagent 2-[(Nitro-$\bar{2}$-benzothiazolyl)azo]-4,5-diphenyl imidazole (6-NO_2BTADI).This reagent reacts with Cd(π) in the pH rang (7.5-8.5) to from purle complex .Beer's law is obeyed in the concentration range of (1-11)μg.ml^{-1} and the stability constant was found to be $5.11\text{x}10^8 L^2.mol^{-1}$.The molar absorptivity and sandell's sensitivity values of Cd(π) complex were found to be $0.135 \text{ x } 10^3 L^2.mol^{-1}.cm^{-1}$ and $2.2 \text{ x}10^{-3}$ $\mu g.cm^{-3}$ respectively at λ_{max} 531 nm. The detection limit , relative standard deviation , relative errors and recovery values for this spectrophotometric method were found to be D.L=0.237 ;R.S.D%= 0.431 ; E_{rel}%=2.85 ;Re %=97.14 .The stoichometry of metal to reagent (M:L)were 1:2 for Cd(π)-complex by using continuous variation and mole ratio. The most important interference were due to Co^{2+}, Ni^{2+},Cr^{2+},Mg^{2+},Ca^{2+},Zn^{2+},Hg^{2+},Ba^{2+},WO_4^{2-} and suitable masking agents were used tartaric acid ,oxalic acid ,citric acid and ascorbic acid .

الخلاصة

استخدمت طريقة طيفيه وحساسة وإنتقائيه وسريعة لتقدير الكميات الضئيلة من أيون الكاديوم (π) بوساطة إستعمال الكاشف العضوي 2-[(6- نايترو - $\bar{2}$ – بنزوثيازوليل)آزو] -5,4- ثنائي فنيل أميدازول (6-NO_2BTADI) . يتفاعل هذا الكاشف مع أيون الكاديوم(π) ويكون معقد أرجواني اللون عند pH =7.5-8.5. مدى التراكيز التي ينطبق عليها قانون بير (1-11) مايكرو غرام / مليمتر وبلغت قيمة ثابت الاستقرارية $5.11 \text{ x}10^8$ لتر^2.مول$^{-1}$ وقيم معامل الامتصاص المولاري وحساسية ساندل وجدت إنها تساوي $0.135 \text{ x}10^3$ لتر^2.مول$^{-1}$.سم$^{-1}$ و $2.2 \text{ x } 10^{-3}$ مايكروغرام .سم$^{-3}$ على التوالي عند الطول الموجي الأعظم 531 نانومتر .

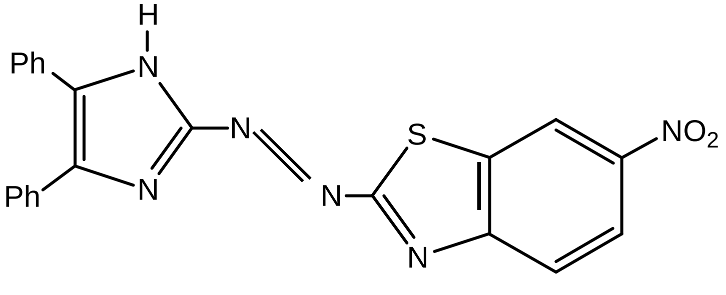
تم تحديد حد الكشف والانحراف القياسي المئوي والخطأ النسبي والاسترجاع بالمئة لهذه الطريقة الطيفية فكانت قيم D.L و R.S.D% و E_{rel}% و Re% هي 0.237 , 0.431 , 2.85 , 97.14 على التوالي .

تم تحديد نسبة الفلز الى الكاشف حيث وجد إنها تساوي 2:1 لمعقد الكاديوم بإستعمال طريقة التغيرات المستمره والنسبةالمولية . كما تم دراسة تأثير أيونات Co^{2+}, Ni^{2+},Cr^{2+},Mg^{2+},Ca^{2+},Zn^{2+},Hg^{2+},Ba^{2+},WO_4^{2-} والتي تتداخل عند تفاعل الكاشف ($6-NO_2BTADI$) مع ايونات الكادميوم (п) وتم حجب تأثيرها بإستخدام عوامل حجب قياسية وهي حامض التارتريك وحامض الاوكزاليك وحامض الاسكوربيك.

Introduction

The hetro cyclic azo dyes have been synthesized and proposed as highly sensitive chromogenic reagent for the determination of several metal ions(1-3).Larg number of the spectro photometric methods based on these reactions were developed and used in analytical chemistry(4,5).Avery large number of thiazolylazo reagents and its derivatives had prepared and this kind of reagents used as dyes ,in analytical chemistry used as acid-base and redox metalo chromic indicators, also then used as reagents to prepared chelate complexes(6-8). A selective and sensitive derivatives spectrophotometric methods has been developed for the determination of trace amounts of Zn(п) and Cd(п) with 2-[(5-bromo-2-pyridyl)azo]-5-diethyl amino phenol in the range of (0.06 – 0.66) and (0.02 – 1.60)$\mu g.ml^{-1}$(9).A sensitive procedure is described for the perconcentration by spectrophotometric determination of trace amounts of Cd(п) froms an intense red 1:2 complex with phenanthraquinone mono phenol thiosemicarbanzone (ppt) at pH ≥6(10).Cadmium (п) and copper(п) ions with ammonium pyrolidine dithiocarbamate(APDC) in tween 80 micell or media has been studied(11).Others using various method including ICP-MS,ion chromatograph anodic stripping analysis and electro thermal atomic absorption spectrometry have been used (12-15).

In this paper the indicator 2-[(6-Nitro – 2 – benzothiazolyl)azo]-4,5-diphenylimidazole ($6-NO_2BTADI$) was prepared according to the literature(16), which is sensitive, and selective reagent for the spectrophotometric determination of cadmium(п).The structal formula of this reagent is shown in fig(1) .



Fig(1):- structure of the reagent ($6-NO_2BTADI$)

Experimental

Materials And Physical Measurements

All chemicals were of highest purity and used as supplied by the manufactures fluka and BDH,except of 2- amino-6- nitro benzothiazole and 4,5-diphenylimidazole was prepared as described in the literature(17,18).

All solution (10^{-3})M were recorded with a shimadzu UV-1650 double beam spectrophotommeter using 1 cm quartz cells, pH measurements were carried out with aphilips pw 9421 pH meter. FT-IR spectra were recorded with FT-IR-8000 shimadzu ,single beam .Path laser by CsI discs (4000-400).Digital balance ,Sartorius BP-3015 (Germeny) and water bath Gesellschaft Fur labortecnik (Germany)were used.

Synthesis And Characterization of Azo Reagent (6-NO_2BTADI)

A diazonium solution was prepared by taking (1.8 gm, 0.01 mol) of 2–amino–6–nitro benzothiazole was dissolved in 6 ml of 12 M hydrochloric acid then 50 ml of distilled water was added. To this mixture a solution of (0.7 gm ,0.01 mol) of sodium nitrite in 30 ml of distilled water was added drop wise at (0-5) C^{o}. A (2.2 gm, 0.01 mol) from 4,5– diphenyl imidazole was dissolved in 300 ml of ethanol,then added 50 ml of 10% sodium hydroxide and 50 ml of 10 % sodium carbonate. The diazonium solution prepared was then added drop wise to this solution for coupling at (0–5)C° for three hours with stirring . The mixture was allowed to stand overnight, and the solid product was filtered off. The product was recerystallized from ethanol and then dried in an oven at 50°C for several hours. The yield was 81% of dark red crystals.

Standard Cadmium(п) Solution

A solution of cdmium (п) (1000 ppm) was prepared by dissolving (0.0237)gm of $CdCl_2$ in 1000 ml of distilled water working solution were prepared freshly appropriate dilution of the stock solution .

Standard Reagent Solution

In absolute ethanolic solution was prepared from the pure reagent (6-NO_2BTADI)of $(1x10^{-3}$ M) by dissolving (0.01gm) in 25 ml of absolute ethanol . The stock solution of reagent were stable for several months if stored in amber bottle .

Buffer Solution

0.01m ammonium acetate (0.77)gm of the salt was dissolved in 1litter of distilled water 0.2M acetic acid and 0.2 M ammonia solution were used for pH adjustment .

General procedure

Different volumes from ($1 x 10^{-4}$M) of ethanolic reagent solution were added to fixed amount of Cd(п) 1 ml from (4 ppm) solution .Then diluted with buffer solution (pH=8.0) to 10 ml .In to a 10 Ml calibrated flask transfer 2 ml of (4ppm). Cd(п) solution and mixed with 2 ml of ($1 x 10^{-4}$ m) ethanolic reagent solution then diluted with a buffer solution to 10 ml at pH=8.0 and after 10 minutes would be measure the absorbance at 531 nm at room temperature in a 1 cm cell against a blank solution prepared in a similar way but with out cadmium ion .These two solutions used for determination the pH, temperature and time effects but for determination calibration curve used 1ml from a set of Cd(п) solution (1-11) ppm. and mixed with 2 ml of ($1 x 10^{-4}$ M) ethanolic reagent solution also for determination the ratio of metal to ligand used mole ratio and continues variation methods with concentration (1 x 10^{-4}M) for each Cd(п) ion and ethanolic reagent solutions

Result and Discussion

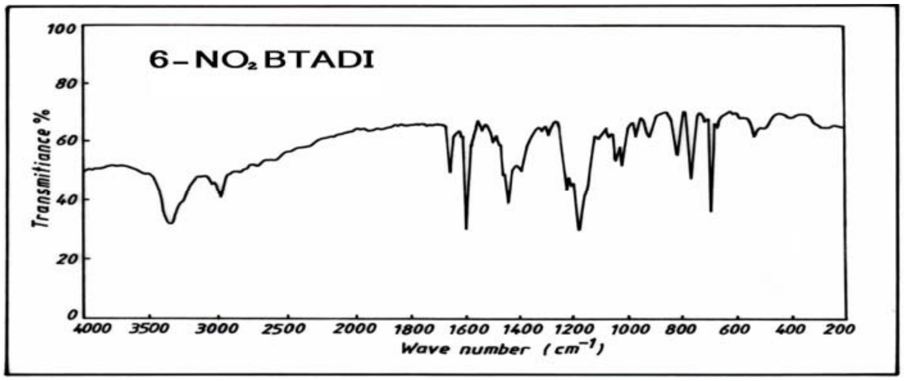
Physical properties of Reagent (6-NO2BTADI)

The reagent is a dark red crystals melting at 165 C° , which is not soluble in water .It has a good solubility in ethanol , methanol ,acetone , chloroform ,benzene ,DMF and ether .The color of the solution is red in strongly acidic solution but orange–yellowish in weakly acidic solution and purple-reddish in strongly alkaline solution(16).

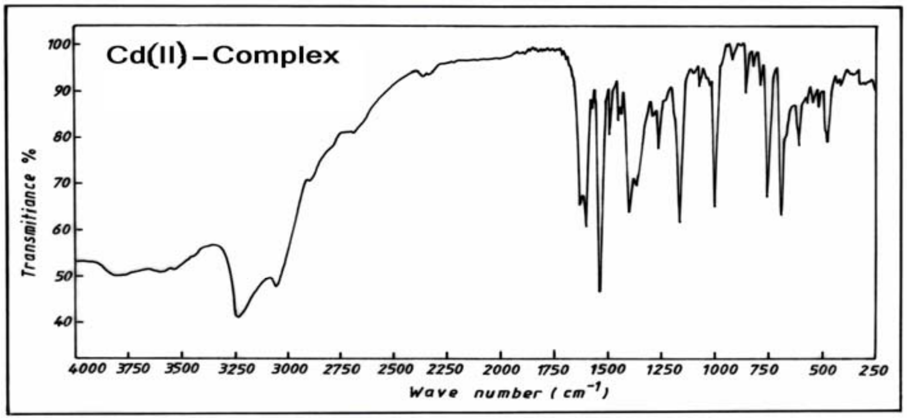
Infrared Spectra Of The Reagent And Complex

The most characteristic bands of the reagent (6-NO_2BTADI) and 6-NO_2BTADI-Cd(п) complex have been studied .These spectra are complicated owing to the extensive overlap of a number of bands arising dueto ν(N — H), ν(C ═ N), ν(N ═ N) and other bands originate due to imidazole and thiazole rings appeared in the region below 1650 cm^{-1},the shifts in the positions or change in shape of the Cd(п)-complex bands compared with those absorption bands dueto free reagent suggest the probable modes of bonding in the complex .Some of there main shifts along with conclusions are given below :-

The spectrum of reagent show weak band observed at 3250 cm^{-1} referred to the stretching vibration ν(N—H) of the imidazol ring does not participate in coordination (19).One weak band had been observed at 3025cm^{-1} in the free reagent spectrum which was dueto ν(C-H)aromatic. This band was stable in position in both reagent and Cd(п)-complex . Reagent spectrum shows two bands at 1635 $cm^{-1}$and 1595 cm^{-1} dueto ν(C ═ N) of imidazole and thiazole rings respectively (19).The band ν(C ═ N) of imidazol ring shifts to lower frequency 1550 cm^{-1}in the Cd(п)-complex spectrum .These shifts suggest the linkage of cadmium ion with nitrogen of imidazol ring(16,19).Two absorption bands are observed at 1500 $cm^{-1}$and 1430 cm^{-1}in the reagent spectrum , which are dueto the azo group ν(N ═ N) ,while in Cd(п)- complex spectrum these bands are shifted to a lower frequencies at 1485 cm^{-1} and 1410 cm^{-1} with decreased in intensity .This may indicates that it has been shard in coordination with cadmium ion(20,21).Another bands appeared at 1270cm^{-1} and 850 cm^{-1} in spectrum of the free reagent , which are due to to ν(C — S) of thiazole ring(22).The fixed position of these bands in chelate complex means that the sulfur atom of thiazole ring does not participate in coordination (23).The two mono substituted aromatic rings on the imidazole ring are indicated by the absorption at 695 cm^{-1} and 765 cm^{-1}.These bands shows in both reagent and Cd(п)- complex spectra(24) .Finally in the far IR spectrum of Cd(п)-complex .There are new bands appeared at 465 $cm^{-1}$and 380 cm^{-1}which are never been observed in the reagent spectrum this may at tributed to (Cd—N) and (Cd—Cl) bands respectively .The results presented above lead to suggest that the reagent behaves as a bidentate chelating agent ,coordination with cadmium ion by a nitrogen of azo group and nitrogen of imidazole ring forming one five membered chelating ring .Figs.(2 & 3) shows the spectra of free reagent (6-NO_2BTADI) and 6-NO_2BTADI- Cd(п) complex.



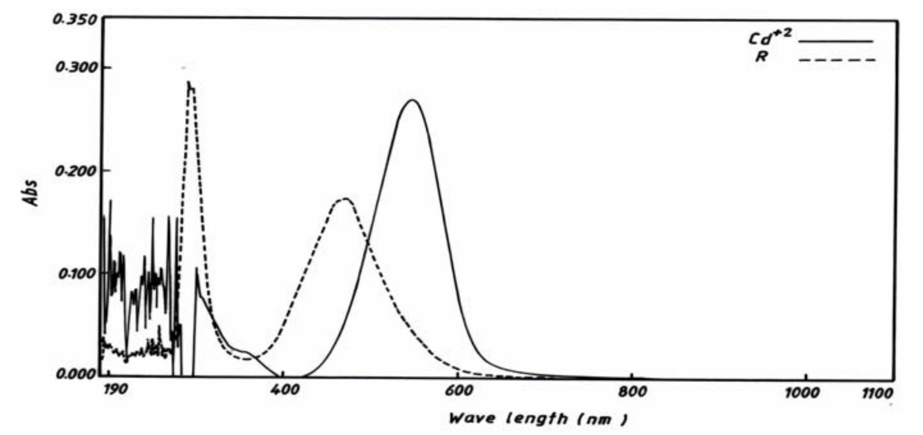
Fig(2):-FT-IR spectrum of free reagent (6-NO_2BTADI)



Fig(3):-FT-IR spectrum of 6-NO_2BTADI- Cd(п)- complex

Electronic Spectra of Reagent (6-NO_2BTADI)

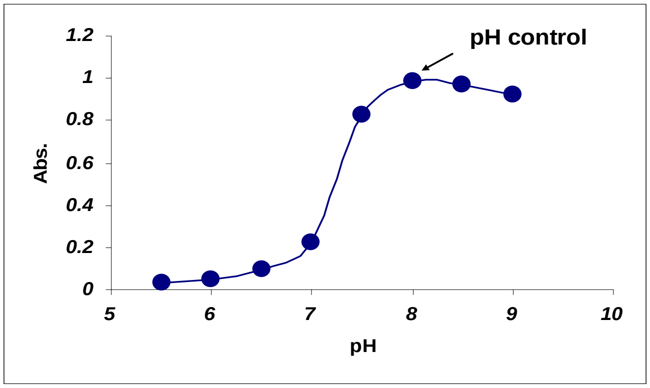
The absorption spectra of the reagent and cadmium(п)-complex are shown in fig.(4) under optimum conditions .The wavelength for the maximum absorption (λ_{max}) of the reagent was found at 471 nm, and the λ_{max} of the complex was found at 531 nm , hence the wavelength difference ($\Delta\lambda_{max}$) is 60 nm .Cadmium(п)-complex is diamagnetic due to the electronic configuration $d^{10}(t_2{}^6g\ e^4g)$ gave magnetic susceptibility (μ_{eff}=0.0 B.M) because of location of this complex in second round (low spin) and do not show any d—d transition bands. There were three absorption bands appear at the free reagent (6-NO_2BTADI) spectrum .The bands 258 nm(38759 cm^{-1}) and 298nm(33557 cm^{-1}) referring to the π—π^* transition while the band 471 nm(21231cm^{-1}) is due to the color of the ligand (25).



Fig(4):-Absorption spectra of reagent (6-NO_2BTADI) and 6-NO_2BTADI –Cd(п) complex

Effect of pH

The effect of pH on the absorbance value of the complex was studied over the range (5.5 - 9.0) .Fig(5) shows the relation ship between absorbance of complex and pH .The absorbance of the Cd(п)-complex system is maximum and constant in the pH range (7.0–8.5) and a pH of 8.0 was adopted at pH>8.5 decrease in absorbance may be due to the hydrolysis of Cd(п)–complex and also which pH< 6.5 a decrease in absorbance occur due to form azolium cation result from the reaction hydrogen ions and the ion pair of electron which found in the nitrogen atoms for imidazole and thiazole rings.



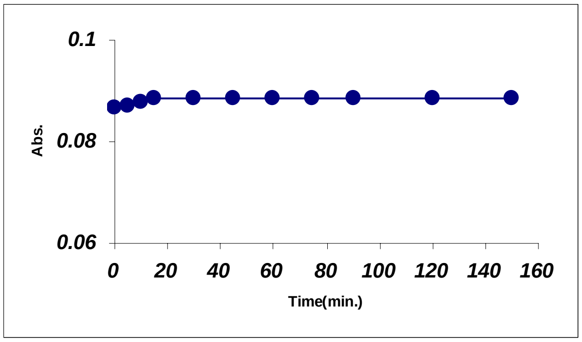
Fig(5):-Effect of pH on the absorbance of Cadmium complex ;Reagent Conc.=2 x 10^{-4}M,Cadmium(п) Conc.=2 x 10^{-4}M

Effect of Reagent Concentration

2 ml of 1 x 10^{-4} M reagent was found enough to develop the color its full intensity and give minimum blank value and was considered to be optimum for the concentration range 5 μg/ml of Cd(п) .

Effect of Time

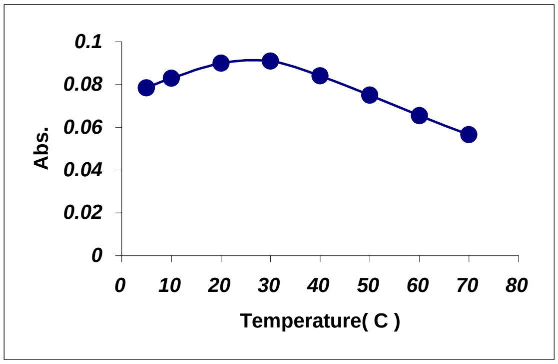
It was found that the absorbance of the Cd(п)-complex chromogenic system reaches a maximum value with 15 min. at room temperature and remains stable for about 24 hours .The stability of the chromogenic system with the time is shown in fig.(6).



Fig(6):-Effect of time on the absorbance of cadmium complex ; Cd(п)ion =4 μg.ml^{-1}

Effect of Temperature

The effect of temperature on the absorbance of the Cd(п)- complex was studied ,fig(7) show this effect .The study was performed at temperature at the range (10-70)C^o, and the maximum absorption was obtained at 20 C^o and 30 C^o ,at temperature higher than 30 C^o the absorbance gradually decreased with increasing temperature until it reaches 70 C^o, which may be due to the dissociation of the complex .



Fig(7):-Effect of temperature on the absorbance of cadmium complex ; Cd(п)ion =4 μg.ml^{-1}

Composition of The Complex

The composition of the Cd(п)-complex was determined by job's method of continuous variation(26) and molar ratio(27).Both methods were showed the mole ratio of Cd(п) complex is 1:2 (M:L) figs.(8 & 9).The stability constant (β) was found to be 5.11x10^8.L^2.mol^{-2} (log β=8.71) by spectra photometrically method.

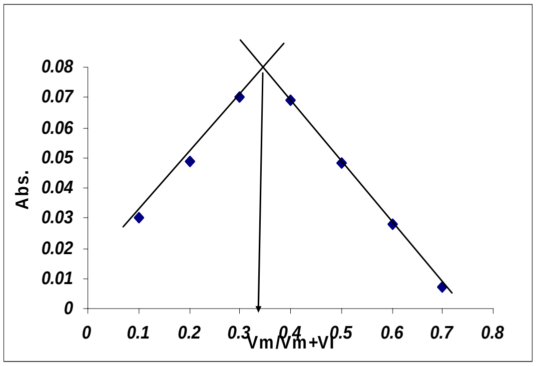
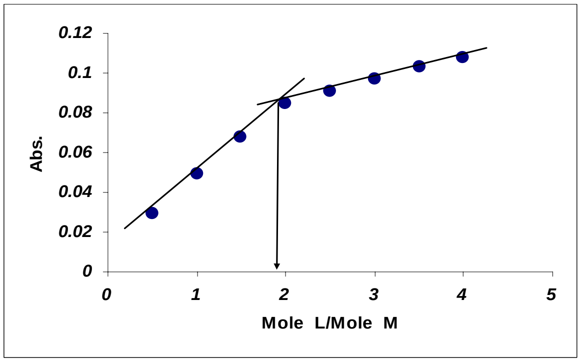


Fig (8):-Continuous variation method for Cd(п)- complex at optimum conditions



Fig(9):- Molar ratio method for Cd(п) -complex at optimum conditions

On the basis of the IR, and analytical data the structure of the Cd(п)-complex can be suggested as follows (fig.10).

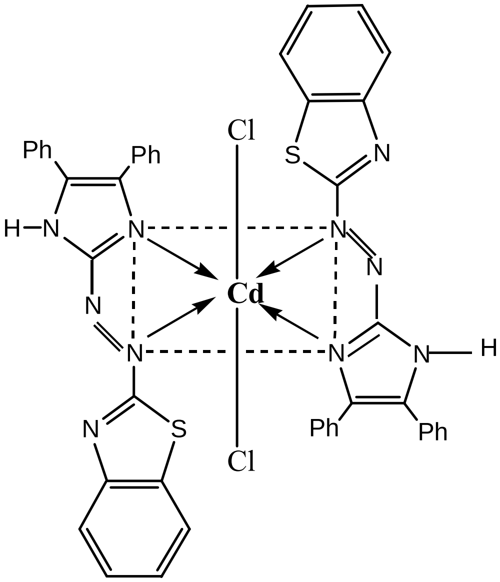


Fig.(10):- The suggested structural formula of Cd(п)-complex .

Calibration graph And Sensitivity

The calibration graph for Cd(п)-complex was obtained by following the proposed procedure under the optimum conditions (Fig.11).The result indicated that beer's law was obeyed over the concentration range (1-11)ppm. for Cd(п)-complex with a correlation coefficient (r)= 0.999. The molar absorptivity (Є) of the complex was found to be 1.36 x 10^3 L.mol^{-1}.cm^{-1} at λ_{max} 531 nm and the scanled sensitivity was 2.2 x 10^{-3} μg.cm^{-1}.

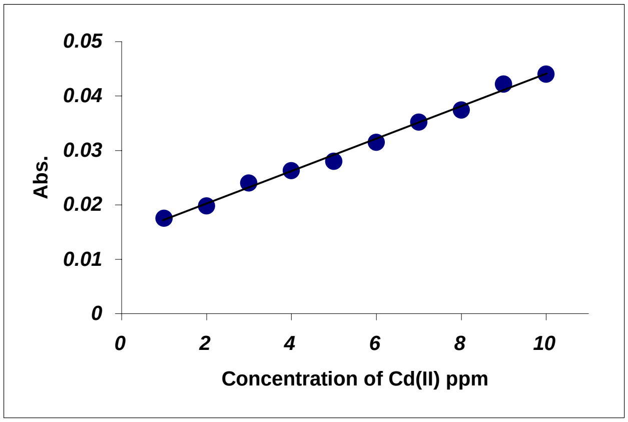


Fig.(11):- Calibration curve of Cd(п)- complex .

Precision And Accuracy

The precision of the present analytical method was evaluated by determing different concentrations of Cd(п) each analyzed. The relative standard deviation(R.S.D%) was 0.431 $\mu g.ml^{-1}$ of Cd(п)-complex. The recovery (Re%) and relative errors (Ere%) for the complex solution were found to be 97.14 and 2.85 respectively. The detection limit was found to be 0.237 $\mu g.ml^{-1}$of Cd(п) .These results indicating that this method is highly precise and suitable for the determination of Cd(п) spectrophotometrically .

Interferences

The selectivity of Cd(п)-complex system is tested by carrying out of determination of $\mu g.ml^{-1}$in the presence of foreign ions .These ions Co(п), Ni(п), Cr(п), Mg(п), Ca(п), Zn(п), Hg(п), Ba(п), WO_4^{2-},which also reacts with the reagent (6-NO_2BTADI)during its reaction with Cd(п).Above cations were masked by using suitable masking agent .The results obtained are summarized in table (1) .

Table (1):- Effect of interference

Foreign ion	Form added	Amount added /μg	Interference
Co(п)	$Co(NO_3)_2.6H_2O$	2	+ 4.7
Ni(п)	$NiCl_2.6H_2O$	2	+5.6
Cr(ш)	$CrCl_3.\ 6H_2O$	2	+8.4
Mg(п)	$Mg(NO_3)_2.6H_2O$	2	-2.8
Ca(п)	$Ca(NO_3)_2.4H_2O$	2	-6.6
Zn(п)	$ZnCl_2$	2	+2.3
Hg(п)	$HgCl_2$	2	+1.4
Ba(п)	$Ba(NO_3)_2$	2	-5.2
WO_4^{-2}	$Na_2WO_4.2H_2O$	2	-9.6

Effect of Masking Agents

The effect of masking agent (29) was studied to increase the selectivity of Cd(п)-complex ,this effect is shown in table (2).The results shown in table(2) indicate that analytical application

Table (2):-Effect of masking agent

Masking agent	Cd(п) μg.ml^{-1}	Absorbance
Complex with out any addition	4	0.082
Tartaric acid	4	0.071
Oxalic acid	4	0.080
Citric acid	4	0.082
Ascorbic acid	4	0.078

Conclusion

The proposed method is more simple speed and sensitive compare to determination of cadmium ion .The method has very high selectivity thus ,the proposed method can be used routinely for the determination of cadmium in alloys and other samples of different matrixes. The cadmium(п)-complex under conditions is stable to more than 24 hours .

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