Micro determination of Cadmium (II) and Mercury(II) with New Reagent 5-[(4- hydroxyl phenyl)azo] -4,6- di hydroxyl -2- mercapto pyrimidine as a chelating Reagent by spectrophotometric methods.

Hussain.J.Mohammed
College of Dentistry/Dept. of Basic Science/Kufa University
Maysaa A. Majeed
College of Science/Dept. of Chemistry/Al-Muthana University
Shemaa Hamza
College of Education/Dept. of Chemistry/Kerbalaa University
**Email ibrahiem_ af @ yahoo. com*

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Abstract

A simple, accurate and sensitive spectrophotometric method for the determination of cadmium (II) and mercury (II) is described. The method is based on the chelation of Cd (II) and Hg (II) ions with 5-[(4-hydroxy phenyl)azo]-4,6 dihydroxy-2- mercapto pyrimidine (HADMP) to form an intense colour soluble products, that are stable and have a maximum absorption at 573.5 nm and at 585 nm. The molar extinction coefficient (ε) 1.5×10^4 and 2.4×10^4 $L.mole^{-1}.Cm^{-1}$ for Cd (II) and Hg (II) respectively .The stability constant, relative error and standard deviations for Cd (II) and Hg (II) were, 2.02×10^8, 1.05×10^8 $L.mole^{-1}$ and (2%, 1.176%), (2%, 2%) respectively. The new reagent and the two metal complexes have been prepared in aqueous solutions and were characterized by electronic spectrum, F.T.IR and also molar conductivity. Under optimum conditions the described methods were applied satisfactorily to biological sample.

Key words **:** Spectrometrey ,cadmium,mercury,5-[(4-hydroxy phenyl)azo]-4,6-di hydroxyl -2-mercapto pyrimidine

الخلاصة

تم وصف وتطوير طريقة طيفية بسيطة ودقيقة وحساسة في تقدير الكادميوم (II) والزئبـق (II). أعتمـدت الطريقة على اساس عملية التعقيد لايون الكادميوم (II) والزئبق (II) مع الكاشف الجديـد 5-[(4-هيدروكسـي فنيـل أزو)]-4,6- ثنائي هيدروكسي -2-مركبتو بيريميدين (HADMP) وتكوين محاليل ملونة ذائبة ثابتة تمتلك أعلى قمة

امتصاص عند طول موجي 573.5 نانوميتر و585 نانوميتر ولها معاملات أمتصاص مـولاري مقـداره 1.5×10^{4} و 2.4×10^{4} لتر .مول$^{-1}$.سم$^{-1}$ للكادميوم (II) والزئبق (II) على التتالي. كانت ثوابت الاستقرار ومقدار الخطـأ النسـبي والانحراف القياسي النسبي للكادميوم (II) والخارصين (II) 2.02×10^{8} و 1.05×10^{8} لتر.مـول$^{-1}$, (2%) (2%) و(1.176%),(2%) على التوالي. تم تحضير الكاشف ومعقداته من محاليل مائية وقد تم تشخيصها بوساطة أطيـاف الاشعة مافوق البنفسجية –المرئية , ومطيافية ماتحت الحمراء وكذلك التوصلية المولارية. وباستخدام الظروف الفضلى تم تطبيق الطرق على نماذج حيوية (شعرالانسان) .

Introduction

Researchers have become widely interested in the chemistry of cadmium (II) and mercury (II) complexes that are active molecules in the biological and life sciences[1-3].Pyridyl azo , Pyrimidyl azo , azo imidazol and thiazolyl azo compounds have been synthesized and proposed as highly sensitive chromogenic reagents for the determination of several metal ions. These reagents reacted with Iron (III), Copper (II), Palladium (II) , Mercurry (II) , Cadmium (II) , Platinum (II) and Rhodium (III), and have been suitable for the analysis of trace heavy metals [4-9]. These dyes have been useful in the spectrphotometric determination due to its good selectivity and sensitivity over a wide range of pH and they are relatively easy to synthesize and purify [10-11]. Various methods for the assay of Cd (II) and Hg (II) have been reported , electro thermal atomic absorption (ETAAS)[12,13] , Cold vapor atomic absorption[14] , stripping voltammetry and pulse polaroghraphy[15,16] and inductively coupled plasma atomic emission spectrophotometry[17,18].

The work reported in this paper describe a simple, sensitive and selective spectrophotometric method for the determination of cadmium (II) and mercury (II). The method is based on the formation of the complexes of cadmium (II) and mercury (II) ions with a new reagent 5-[(4-hydroxy phenyl) azo]-4,6-dihydroxy-2-mercapto pyrimidine (HADMP).

Experimental

Appartus

All spectral and absorbance measurements were carried out on a Shimadzu UV-visible 1700 double beam spectrometer using 1 cm glass cells. Vibration spectra were recorded on test scan Shimadzu 8000 series. A digital pH meter was used. Electric molar conductivity measurements were carried out at room temperature using an Alpha digital conductivity.

Reagents

All the chemicals used were of analytical reagent (AR) grads. Distilled water was used throughout the present study.

5-[4-hydroxy phenylazo]-4,6-dihydroxy-2-mercaptopyrimidine(1×10^{-3}) M. 0.066 g of reagent was dissolved in 250 ml of ethanol. Working of (HADMP) 5×10^{-5} M solution was prepared by simple dilution of the appropriate volume of the (HADMP) solution with ethanol.

Standard Cd (II) solution (1 mg.ml^{-1}).

This solution was prepared by dissolving 0.407 g at $CdCl_2.2\frac{1}{2}H_2O$ in 200 ml distilled water, working standard of Cd (II) solutions were prepared by simple dilution of the appropriate volume with distilled water.

Standard Hg (II) solution (1 mg.ml^{-1})

This solution was prepared by dissolving 0.268 g of $HgCl_2$ in 200 ml distilled water, working standard Hg (II) solution were prepared by simple dilution of the appropriate volume of the standard Hg (II) solution (1000) ppm with distilled water.

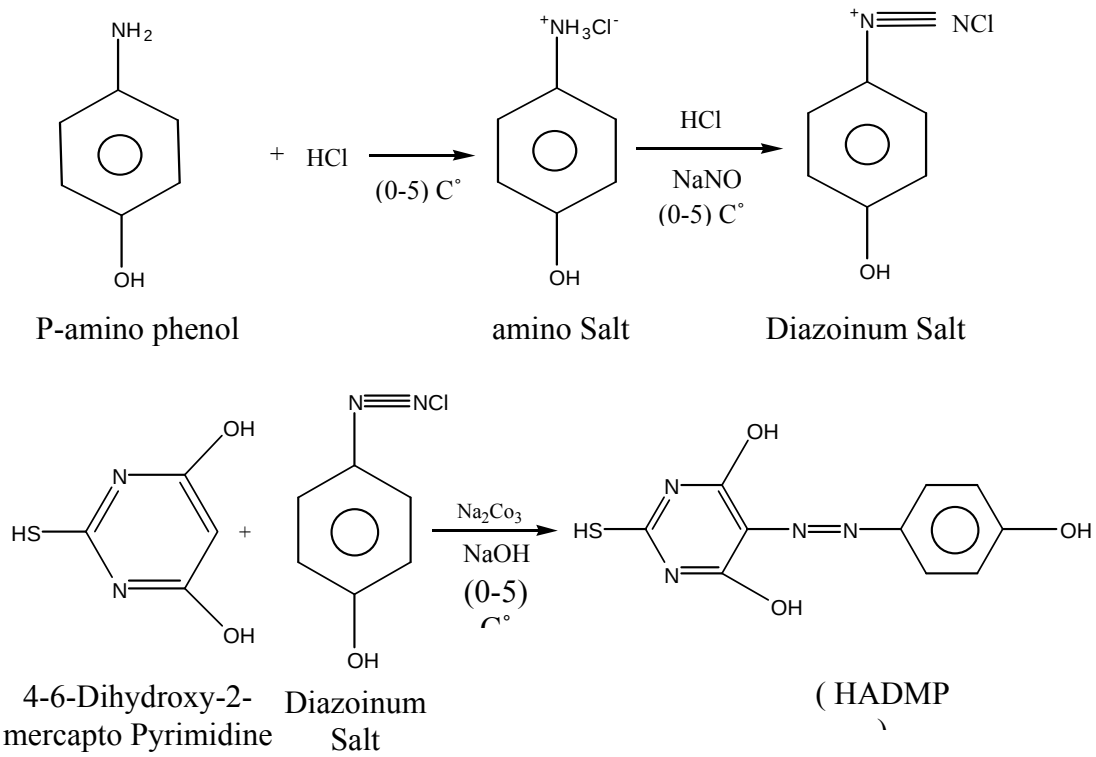
Masking reagents and foreign ions solutions (1 mg.ml^{-1}).

These solutions were prepared by dissolving an amount of the compound in distilled water and completing the volume in a volumetric flask with distilled water.

Preparation of reagent (HADMP) [7]

The reagent was prepared by coupling of 4,6-dihydroxy-2-mercapto pyrimidine (1.5 g was dissolve in 150 ml of ethanol and 50 ml of NaOH at (0-5)C°) with diazonium solution (2.0 g of 4-amino phenol in 5 ml of concentrated HCl and 10 ml of distilled water and adding 8ml of 10% $NaNO_2$ solution drop wise at (0-5)C°.

The mixture was allowed to stand over night. The precipitate was filterted off, and recrystallized from ethanol. Schemes (1)



Scheme (1): Preparation of reagent (HADMP)

Preparation of complexes

$[Cd(HADMP)_2].H_2O$: The complex was prepared by mixing stoichiometric amounts of $CdCl_2$and ligand (HADMP) in a 1:2 ratio in aqueous solutions. The mixture was stirred at room temperature for five min. The pH of solution was adjusted to 6 , then the solution left at room temperature 24 hrs , the precipitate was filterate off , and washed with distilled water and dried at 50 C°.

$[Hg(HADMP)_2].H_2O$: The same procedure as described for $[Cd(HADMP)_2].H_2O$ was used for the preparation of this complex. Only the pH of the solution was adjusted to 7.

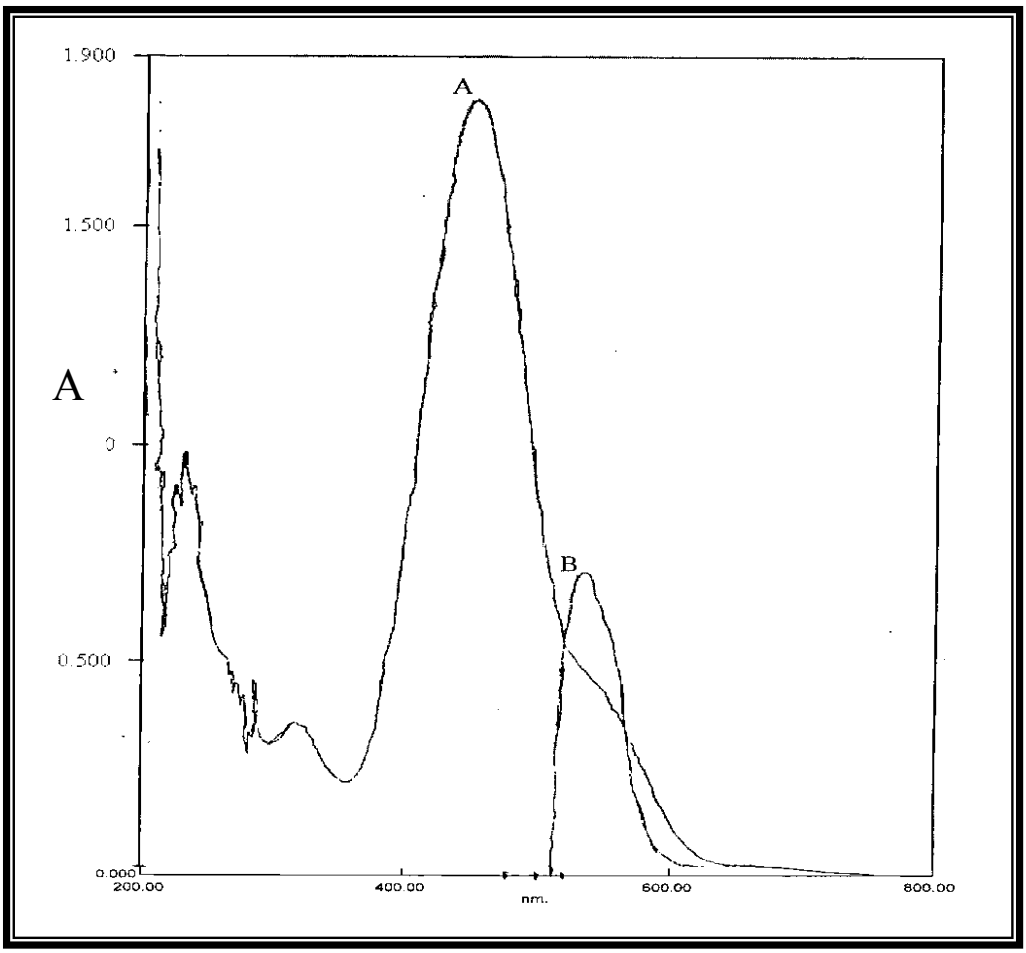
Procedure of analytical study

In to a series of five calibrated flask , transfer increasing volumes of Cd (II) and Hg (II) working solution 20 µg.ml^{-1} to cover the range of the calibration curve , add 3.0 ml and 2.5 ml of 5×10^{-5} M of HADMP solution and pH was adjusted to 6 and 7 by 0.05 M of HCl and 0.05Mof NaOH. The complexes formed were solubilizied in water and diluted up to five ml with distilled water. Allow the reaction mixture to stand for five min. at room

temperature. Measure the absorbance at 573.5 nm for Cd (II) complex and at 585.0 for Hg (II) complex against a reagent blank prepared in the same way but containing no Cd (II) and Hg (II) respectively. The color of the complexes were stable for 24 hrs.

Result and Discussion

The results of this investigation indicated that the reactions of Cd (II) and Hg (II) with HADMP yields highly soluble coloured complexes which can be utilized as a suitable assay procedure for determination of Cd (II) and Hg (II). The colored complexes have a maximum absorption at 573.5 nm for Cd (II) and at 585nm for Hg (II) , the blank at these wave length shows zero absorbance Fig 1,2.



wavelength

Fig (1): Spectrophotometric spectra of (A) L-HADMP reagent and (B)Cd (II) – HADMP complex.

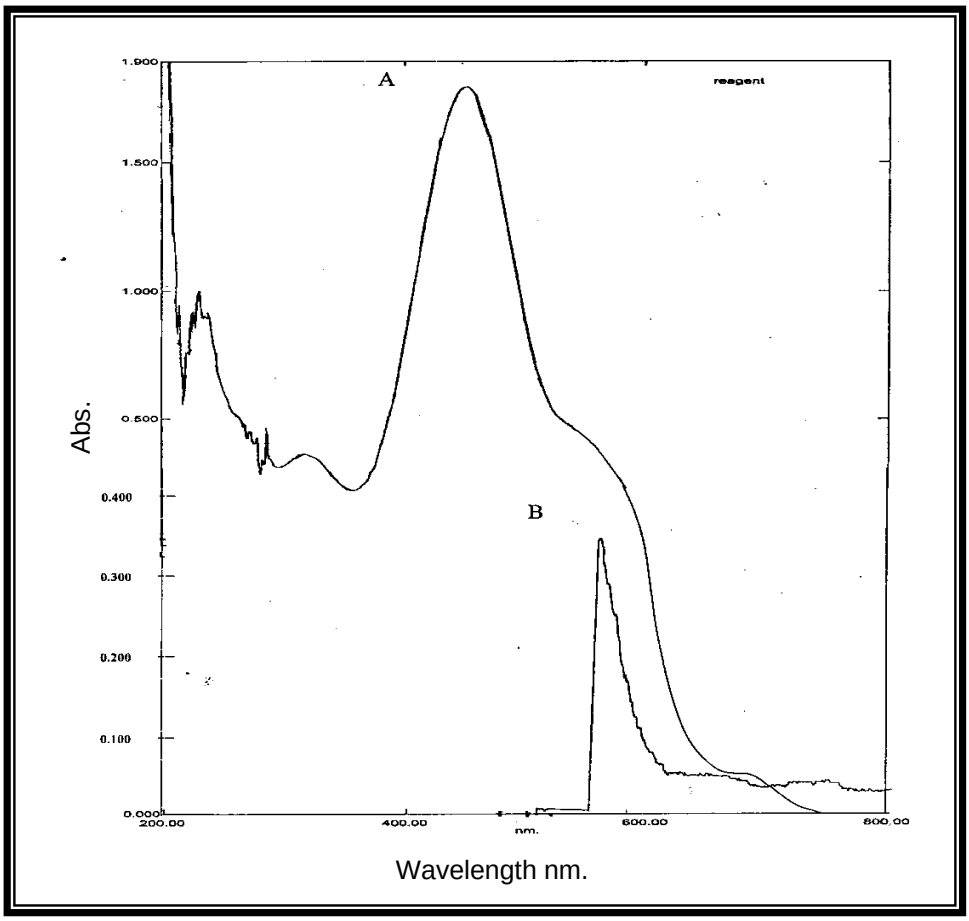


Fig (2): Spectrophotometric spectra of(A) L-HADMP reagent and(B) Hg (II) – HADMP complex.

The effect of various parameters on the absorption intensity of the formed products was studied and the reactions conditions were optimized.

Effect of reagent concentration

Various concentrations of 5-[4-hydroxy phenyl azo]-4,6-dihydroxy-2-mercapto pyrmidine solutions were added to a fixed amount of Cd (II) and Hg (II) , 3 ml and 2.5 ml of 5×10^{-5} M of reagents were found enough to develop the color to its full intensity and give a minimum blank value and were considered to be optimum for the concentration range (0.1- 3.5) $\mu g.ml^{-1}$ and (0.1-3.0) $\mu g.ml^{-1}$ of Cd (II) and Hg (II) , respectively.

Effect of pH

The pH of metal complex solution was adjusted using dilute solution of (0.05) M HCl and (0.05) M NaOH, and the effect on absorbance was studied. The absorbance of complexes was maximum

and constant at the pH range given in Table 1.and Fig 3. The bands appearing in the range 280-435 nm are attributed to $\pi \longrightarrow \pi^*$ transition. The other bands observed in the region of 573.5 nm for Cd (II) and 585 nm for Hg (II) are attributed to $n \longrightarrow \pi^*$ electronic transition[19,20].

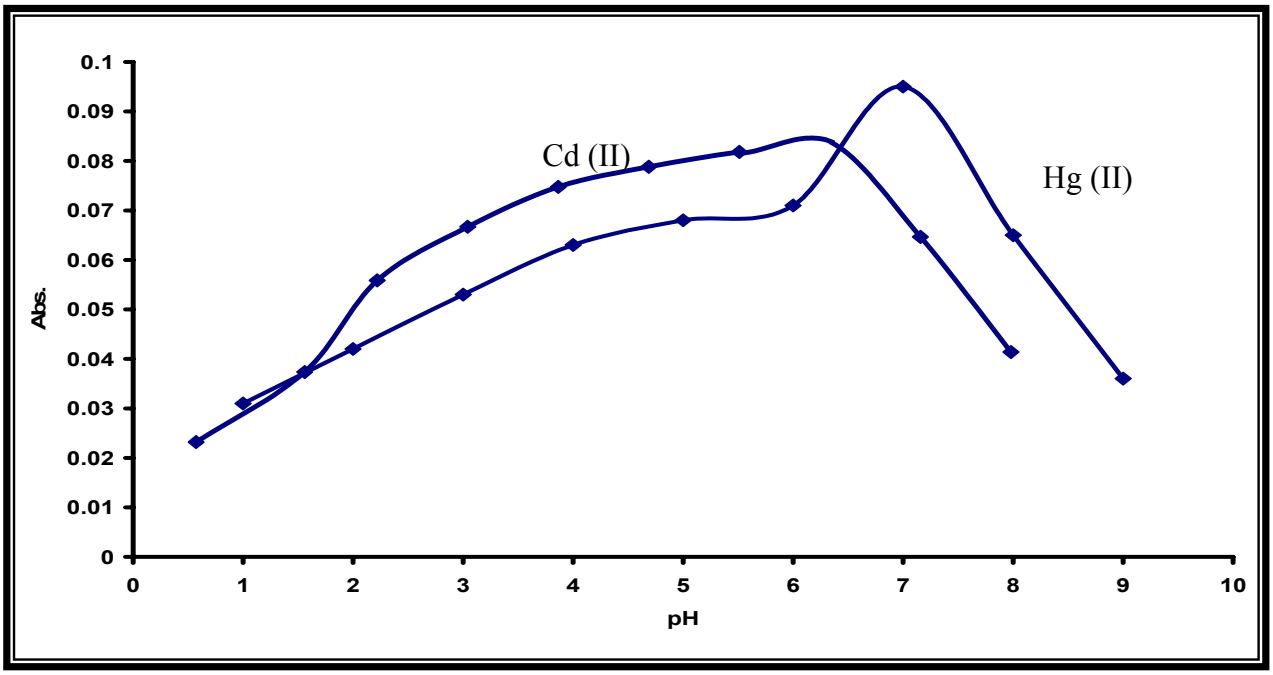


Fig (3): Effect of pH on absorbance of HADMP and its metal chelates

Effect of order of addition

To obtain optimum results, the order of addition of reagents should be followed as given under the procedure; other wise a loss in color intensity and stability were observed.

Effect of temperature

The effect of temperature on the color intensity of the products was studied. In practice, the same absorbance was obtained when the color was developed at room temperature (25-30) C°, but when the volumetric flask were placed in water-bath at (5-10) C° or in a water-bath at (50-60) C° a loss in color intensity and stability were observed, therefore it is recommended that the color reaction should be carried out at room temperature for both complexes. Fig (4).

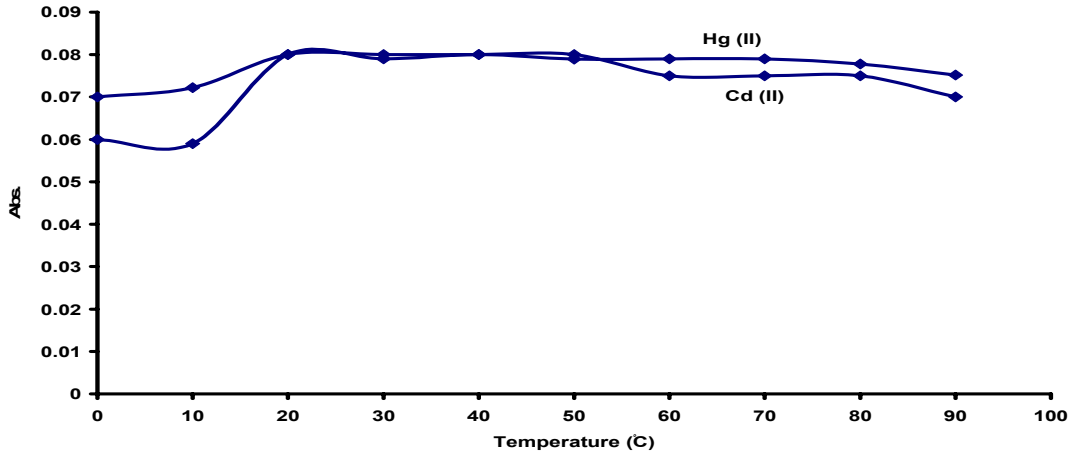


Fig (4) Effect of temperature on absorbance of HADMP and its metal chelates

Calibration graph

Employing the conditions described under procedure, a linear calibration graph of Cd (II) and Hg (II) are obtained, that Beer's law is obeyed over the concentration range of (0.1-3.5 ppm) and (0.1-3 ppm) with correlation coefficient (0.9750), (0.9819 and an intercept of (0.0245), (0.0154) respectively. The molar absorptivity and Sandell's sensitivity are given in Table 1.

Table 1: Analytical data of metal-HADMP complexes

Parameter	Cd (II)	Hg (II)
Absorption maximum (nm)	573.5	585.0
pH range	5.0-7.0	6.5-7.0
Beer's law range (µg/ml)	0.1-3.5	0.1-3.0
Molar absorptivity ($L.mole^{-1}.cm^{-1}$)	1.5×10^{4}	2.5×10^{4}
Sandell's sensitivity ($\mu g.cm^{-1}$)	7×10^{-3}	8×10^{-3}
Stability constant ($L^{2}.mole^{-2}$)	2.02×10^{8}	1.05×10^{8}

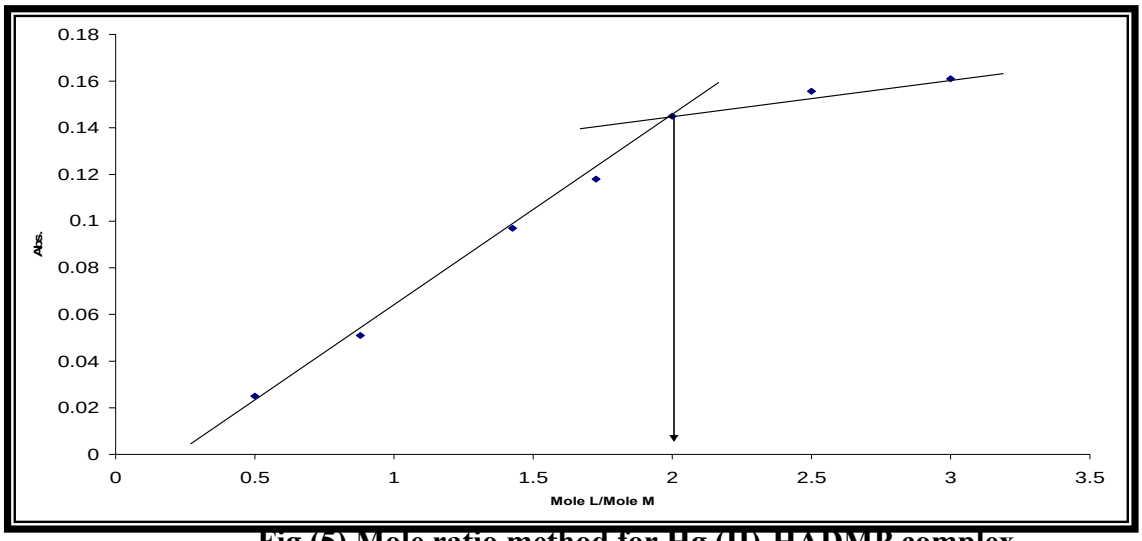


Fig (5) Mole ratio method for Hg (II)-HADMP complex

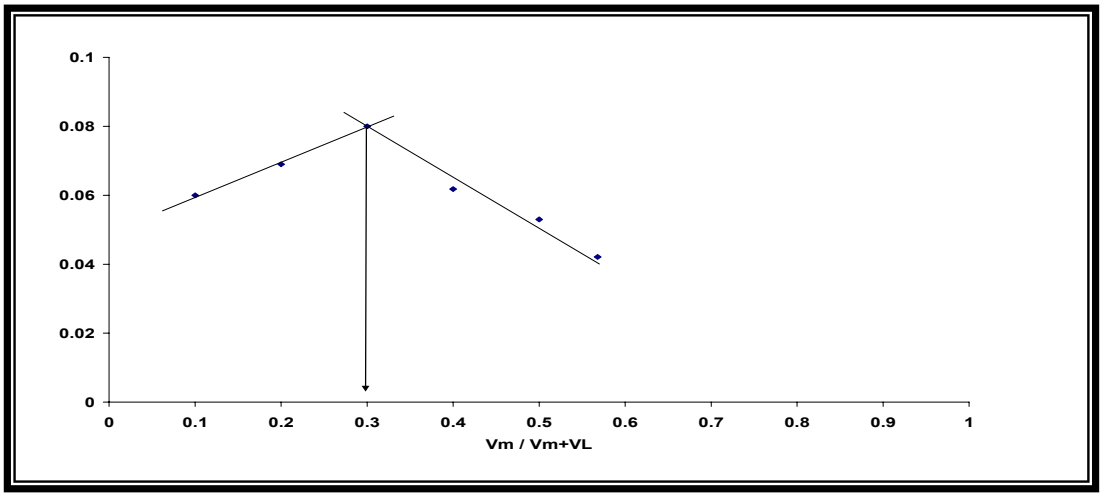


Fig (6) Job's method for Cd (II)-HADMP complex

Accuracy and Precision

To determine the accuracy and precision of the method, Cd (II) and Hg (II) were determined at three different concentrations. The results shown in Table 2 shows a satisfactory precision and accuracy of the proposed method.

Table 2: Accuracy and precision of proposed method

Amount taken (ppm)		E%		R.S.D.%	
Cd (II)	Hg (II)	Cd (II)	Hg (II)	Cd (II)	Hg (II)
1.00	1.00	+2.0	+2.0	1.176	2.000
1.50	1.50	+1.5	-1.20	1.05	1.340
2.0	2.0	+0.80	-1.50	0.95	1.250

* For five determinations

Conductivity measurement

The solubility of the complexes in acetone and ethanol permitted the measurement of the molar conductivity of 10^{-3} M solution at 25 °C and, by comparison, the electrolytic nature for both complexes. The low values of molar conductance data listed in Table 3 indicate that the complexes are non electrolytes.

Table 3: Conductivity values of complexes

Complex	Molar conductivity S.mole^{-1}.cm^2	
	In Acetone	In Ethanol
$Cd(HADMP)_2.H_2O$	21.60	7.40
$Hg(HADMP)_2.H_2O$	21.40	8.0

Interferences

The effect of diverse ions on the determination of these metal ions was studies. To test of diverse ions were determined by the general procedure, in the presence of respective foreign ions.

Table 4: Effect of foreign ions

Ions	Amount added µg	Interferences with Cd^{+2} E%	Interferences with Hg^{+2} E%
Ag^{+}	100	-10.90	30.60
Co^{+2}	100	-3.60	21.50
Cu^{+2}	100	-14.00	30.60
Pd^{+2}	100	-45.00	72.70
Pt^{+2}	100	-39.00	7.90
Hg^{+2}	100	17.00	——
Zn^{+2}	100	-24.30	19.30
Ni^{+2}	100	-1.20	25.0
Cd^{+2}	100	——	27.20
Sr^{+2}	100	-3.60	23.80
Mn^{+2}	100	-12.00	25.0
Fe^{+3}	100	-3.60	6.80
Rh^{+3}	100	1.20	28.40
Th^{+4}	100	-19.20	27.20
Cl^{-}	100	46.0	10.22
NO_3^{-}	100	59.0	37.5
NO_2^{-}	100	28.0	30.6
SO_4^{-2}	100	29.0	19.30
CO_3^{-2}	100	2.40	3.40

In the experiment, a certain amount of standard cadmium (II) or mercury (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. The results are listed in Table 4. It is found that large amount $C_2O_4^{-2}$, CN^-, EDTA and tartaric acid do not interfere in the determination of Cd (II) and Hg (II). It is found that Co^{+2}, Ni^{+2}, Fe^{+3}, and Mn^{+2} do not interfere where as Zn^{+2}, Ag^+, Pd^{+2} and Sr^{+2} interfere seriously, there interferences are masked by addition of 1 ml of 0.01 M of $C_2O_4^{-2}$.

Composition of complexes and infrared studied

The composition of the complexes was studied by molar ratio and Job's methods[21]. A break at 1:2 (M:L) suggested the formations of $M(HADMP)_2$ where M = Cd (II) and Hg (II) respectively, Fig 5, 6.

The I.R. bands of the (HADMP) and its cadmium (II) and mercury (II) complexes with their probable assignment are given in Table (5). The two bands due to ν(S-H) and thioamide moiety present in the ligand appeared in the spectra of the complexes. However, the ν(N=N) stretching band in the free ligand is observed at 1560 cm^{-1}. This band is shifted to lower with low intensity at 1535 cm^{-1} and 1525 cm^{-1} frequency values upon complexation suggesting chelation via the (M-N)[22,23].

Table 5: Selected I.R. bands of HADMP and it Cd (II) and Hg (II) complexes

Compound	Thioamide I	Thioamide II	Thioamide III	νC=N	νN=N	νO-H	νC-N aromat	νM-N	νM-O
HADMP	1546 m	1265 m	970 s	1645 s	1560 m	3380 m	3105 w	—	—
$Cd[HADMP]_2.H_2O$	—	1345 s	978 m	1625 s	1535 m	3415 w	3115 w	510 w	430 w
$Hg[HADMP]_2.H_2O$	—	1360 s	960 m	1615 s	1525 m	3425 w	3080 w	530 w	425 w

s = strong, m = medium, w = weak

The I.R. spectrum of the ligand revealed a sharp band at 15 cm^{-1} due to ν(C=N) of the nitrogen pyrimidine. This band is shifted to lower (20-30 cm^{-1}) frequencies in the complex indication to that it has been affected upon chelation to the metal ion[24]. The bonding of oxygen to the metal ion is

provided by the occurrence of bands at 425-430 cm^{-1} as the result of ν(M-O) [25].

On the basis of the I.R. and a stoichiometric data the structure of complex can be suggested as follows Fig 7.

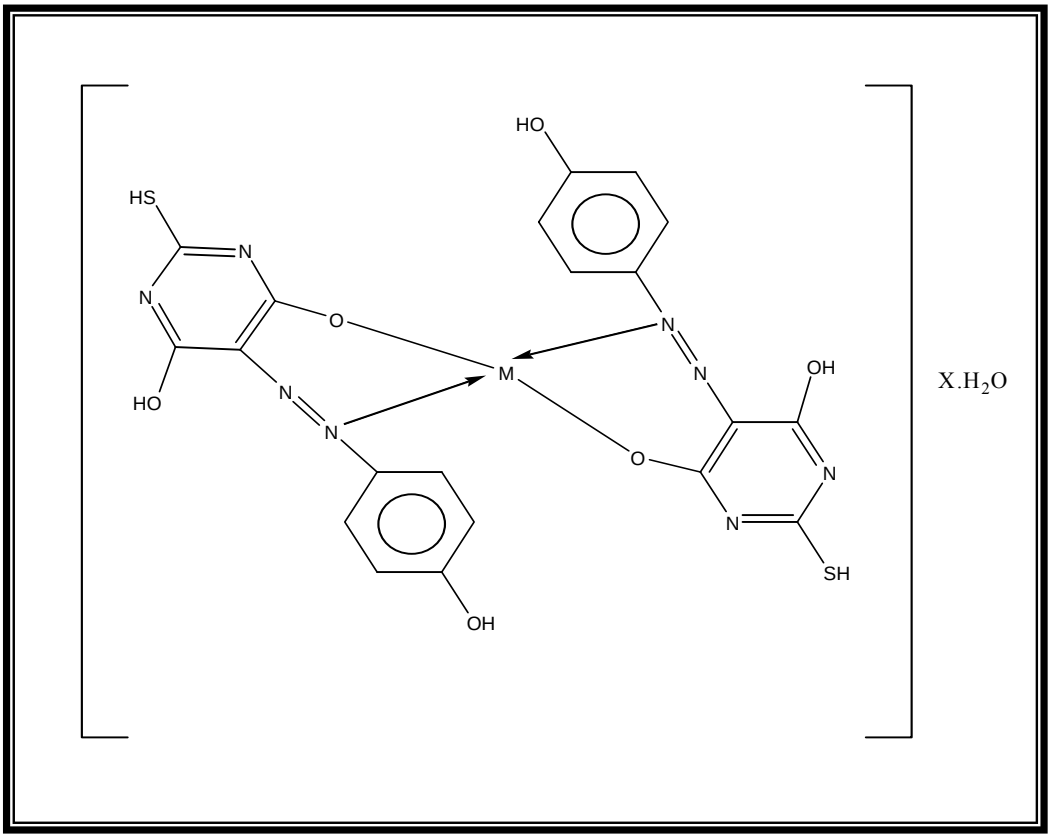


Fig (7) Suggested structures of complexes

Applications

Determination of cadmium and mercury in human hair[26]

A 5.0 g human hair was placed in a 50 ml round-bottom flask and digested with 15 ml concentrated nitric acid for 3 hrs heating. The solution was cooled neutralized with NaOH and filtered. The filtrate was made up to 25 ml in a volumetric flask with double distilled water. 1 ml of the solution was analyzed by standard addition method. The results are given in Table 6.

Table 6: Determination of Cd (II) and Hg (II) in human hair

Sample Human hair	$Mg.g^{-1}$ Certified value	$\mu g.g^{-1}$ Amount found (R.S.D.%)*
Cd (II)	0.20	0.23 (0.65)
Hg (II)	4.40	4.60 (0.80)

***for five determinations**

Conclusion

This method using HADMP was successfully applied for determination of cadmium (II) and mercury (II) because of the sensitivity and selectivity of the method, its application can be determination of those ions environmental and industrial samples.

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