Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2011, 2 (4):123-132

ISSN: 0976-8505
CODEN (USA) CSHIA5

Analytical properties of 5-methylfuran-2-carbaxaldehyde thiosemicarbazone: extractive second derivative spectrophotometric determination of Cd(II) in medicinal leaves, environmental and biological samples

***D.Nagarjuna Reddy, K.Vasudeva Reddy, T. Sreenivasulu Reddy and K. Hussain Reddy**

Department of Chemistry, Analytical division Sri Krishnadevaraya University, Anantapur, A.P., India

---

ABSTRACT

5-methylfuran-2-carbaxaldehyde thiosemicarbazone (5-MFAT)is proposed as a new sensitive and selective analytical reagent for extractive spectrophotometric determination of trace amounts of cadmium (II). 5-MFAT reacts with cadmium(II) to give a light yellow colored complex in a sodium acetate and acetic acid buffer of pH=6.0. The color reaction has been investigated in detail. This complex is easily extracted into isoamylalcohol with a 1:2 composition and has maximum absorbance at 360 nm. The molar absorptivity and Sandell's sensitivity are found to be $3.7x10^{4}$ *l* mol^{-1} cm^{-1}*, and 0.0029* μgcm^{-2} *respectively. The interference of various diverse ions has also been studied. The method has been successfully applied for the extractive second derivative spectrophotometric determination of trace amounts of Cd(II) in several standard reference materials such as medicinal leaves, leafy vegetables, biological, water and soil samples.*

Key words: Cadmium, Extractive Spectrophotometry, Medicinal Leaves, Environmental leafy vegetables, Biological Samples.

INTRODUCTION

Cadmium occurs in nature in association with zinc in minerals. Growing plants acquire and concentrate Cd(II) with in the same biochemical set up. 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 anamemia 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 for 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 reasons for cadmium accumulating in the body in the extensive use of tobacco.

Trace amounts of cadmium are important in industry [5], as a toxicant [6], and biological non-essential [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 ng-1in sea water and 2-960 ng l^{-1} in fresh water [11].

Table.1 Comparison of the present method with other reported spectrophotometric methods for determination of cadmium(II)

Reagent	**λmax(nm)**	**pH**	**Molar absorptivity**	**Ref**
1,4,8,11-Tetra1, 4, 8, 11-tetramethyl Cyclotetradecane	550	NaOH	1.1	12
P-naitrophenyldiazo Aminoazobenzene	480	0.2-.0.3	1.19	13
Polyvinyl pyrrolidinone	-	-	-	14
Phenanahraquinone monosemicarbazone (PQMS)	480	9.0	1.5	15
1,3 cyclohexanedione bisthiosemicarbazone mono-hydrochloride	515	-	1.21	16
Glyoxal dithiosemicarbazone(GDT)	427	9.0-11.0	1.3	17
1,2 Napyhaquinone-2-thiosemicarbazone 4-sulfonic acid	520	6.0-7.0	1.9	18
Bipyridyl glyoxal bis (4-phenyl-3-thiosemicarbazone)	385	9.3	4.61	19
Bie-acetyl-(2-pyridyl) hydrazone thiosemicarbazone (BPHT)	-	-	-	20
1-(2-methoxy-4-hydroxybenzylidene-4-phenyl-Thiosemicarbazone (H_2VPTS)	-	-	-	21
5-methylfurn-2-carbaxaldehyde thiosemicarbazone	360	5.0-7.0	3.6	P.M

P. M Present method.∈***:** *10^4 L mol^{-1} cm^{-1}*

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. 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 chelates 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 have introduced a new analytical reagent 5-methylfuran-2-

carbaxaldehyde thiosemicarbazone (5-MFAT) for the first time, for the extractive second derivative spectrophotometric determination of trace amounts of cadmium (II).

The proposed method when compared with other spectrophotometric methods is more sensitive and selective. It also offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and less interference. The results obtained through UV-visible spectrophotometer have been compared with those obtained through the atomic absorption spectrometer.

MATERIALS AND METHODS

Shimadzu 160, a micro computer based UV- visible spectrophotometer equipped with 1.0cm quartz a cell is been used for all absorbance measurements. An ELICO (model LI -120 India) digital pH meter is used for pH adjustments. A Hitachi model 170-30 atomic absorption spectrophotometer is used for comparison of results

Reagents

Synthesis of 5-methylfuran-2-carbaxaldehyde thiosemicarbazone (5-MFAT)

5-methylfuran-2-carbaxaldehyde thiosemicarbazone is prepared by refluxing a mixture of 5-methylfuran-2-carbaxaldehyde (0.0357mol, dissolved in 5ml of 10%-aceticacid-ethanol) and thiosemicarbazide (0.0357mol, dissolved in 15ml of water) in 250 ml round bottom flask for 3hours. The shine light colored solid is separated out on cooling. The crystals are collected by filtration and washed several times with hot water and 50% cold methanol. Yield is 80% and its m.p is 163-165ºC.

A 0.01 M stock solution is prepared by dissolving 0.208 mg of the 5-MFAT in 40% (v/v) aqueous dimethylformamide. It is stable for at least 40 hours

A known amount of cadmium acetate is dissolved in water and then diluted to 100 ml with distilled water. The stock solution is standardized by EDTA titration [24], using xylenol orange as an indicator. Further, required dilute solutions are prepared by diluting the stock solution suitably with distilled water.

The pKa values are determined by recording the UV- visible spectra of ($1x10^{-4}$ M) solutions of 5-MFAT at various pH values and by taking arithmetic mean of the values obtained. From the four measurements at four different wavelengths (Phillips and Merritt method), the values of the deprotination of the reagent are 4.4(pK_1) and 8.0 (pK_2).

The working solutions were prepared by diluting the stock solution to an appropriate volume. All the chemicals used are of analytical grade: Quartz-processed high purity water is used throughout the experiment.

Buffer solution

1.0 M Hydrochloric acid and 1M sodium acetate (pH 0.5-3.0), 0.2 M of NaOAc-0.2 M AcOH (pH 4.0-7.0) and 2.0 M NH_4Cl-2.0 M NH4OH (7.0-10.0) buffer solutions are prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

Preparation of sample solutions

Preparation of Medicinal leaves and Leafy vegetables

The leafy vegetables and medicinal leaves analyzed are procured from the city grocery stores. The samples are cleaned and dried in open air, protecting them from the mineral contamination. The dried samples are pulverized to finely powdered particles in a mortar for the analysis of Cd (II). 10.0gm of each powered sample is taken in to a silica crucible, heated in order to oxidize the organic matter and ashed at 550ºC in a muffle furnace for 4-5 hours. The ash is dissolved in 10 ml of 2.0 M hydrochloric acid, heated and filtered through acid washed filter paper. Then the residue is washed with hot water. The filtrate and the washing are collected into a 25 ml volumetric flask and finally made up to the mark with doubly distilled water.

Preparation of water samples

A choice of three water samples in around the city of Tirupathi is made. Each filtered environmental water samples is evaporated nearly to dryness with a mixture of 10 ml of con HNO_3 and 5 ml of con H_2SO_4 in a fume cupboard and then cooled to room temperature. The residue is then heated with 10 ml of distilled water in order to dissolve the salts. The solution is cooled and neutralized with dilute NH_4 OH in the presence of 1-2 ml of 0.01% tartrate solution. The resulting solution is filtered and quantitatively transferred into a 25 ml standard flask and made up to the mark with distilled water

Preparation of soil samples

Agriculture soil, roadside soil, and contaminated soil have been selected for the determination of Cd(II). The air-dried homogenized soil samples have been weighted 100 gm each accurately and taken in a 100ml maicro-Kjeldahl flasks. The samples are digested in the presence of an oxidizing agent (65% HNO_3). The content of the flask is filtered through filter paper (Whatman No.41) into a 25 ml volumetric flask and neutralized with a dilute NH_4 OH solution. They are then diluted to the mark with distilled water.

General procedure

Known aliquots of 10.0 ml of the solution containing constant volume of 2.0 ml of buffer solution (pH 6.0), 1.0 ml of $1x10^{-2}$ M APMT and 2.0 ml of 0.1 ml lithium chloride solution and varying amounts of cadmium(II) from 0.224 μg cm^{-3} to 2.24 μg cm^{-3} are prepared. Each solution is then shaken with two 10.0 ml portions of isoamylalchol for two minutes and then allowed to stand, each time. The combined each organic phase of each aliquot are taken in a 25 ml standard flasks and made up to the mark with isoamylalchol. The absorbances of all the organic phases are recorded at 360 nm. against their corresponding reagent blank.

RESULTS AND DISCUSSION

Cadmium reacts with 5-methylfuran-2-carbaxaldehyde thiosemicarbazone (5-MFAT) in sodium acetate- acetic acid buffer solution (pH 6.0) and gives a 1:2 light yellow colored complex, which can be easily extracted into isoamylalchol. The complex has a maximum absorbance at 360 nm. The optimum reaction conditions for the quantitative determination of the metal-ligand complex are established through a number of preliminary studies, such as the effect of the pH, choice of the solvent, reagent concentration, salting-out agent and diverse ions, in order to develop a rapid, selective and sensitive extractive spectrophotometric method for the determination of cadmium (II) at micro gram levels.

Absorption Spectra of the Reagent and Cd (II) – 5-MFAT Complex:

The absorption spectra of Cd(II)-5-MFAT complex and the reagent show maximum absorbance at 360 nm and 340 nm respectively (Fig. 1). The reagent showed a minimum absorbance at the wavelength of maximum absorbance of the complex. Hence, all the spectral measurements of the complex have been carried out at 360 nm.

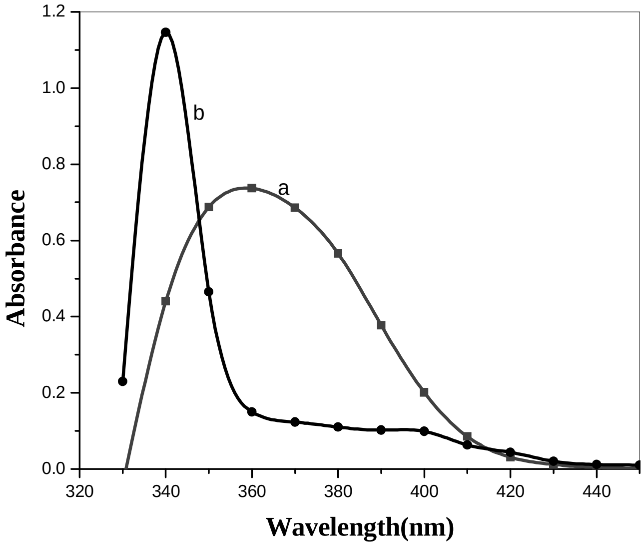

Fig. 1. Absorption spectra of (A) Cd(II)-5-MFAT complex and (B) 5-MFAT-solvent Complex. Cd(II):1.0ml of $3x10^{-4}$ M ;5-MFAT: 1.0 ml of $1x10^{-2}$M;solvent Isoamylalchol: pH: 2.0 ml 6.0

The study of the effect of pH on the color intensity of the reaction mixture showed that constant and maximum color is obtained in the pH range 5.0-7.0. The complex has maximum absorbance in buffer solution of pH (6.0). The analytical studies were therefore, carried out at pH 6.0.

Table.2. Physico - Chemical analytical characteristics of Cd (II) Complex of 5-MFAT

Characteristic property	Cd(II)-5-MFAT
Absorbance Maximum (λmaxnm)	360
pHrange(Optimum)	5-7
Mole of reagent required per mole of metal ion for full Color development	10
Beers law validity range(μg ml^{-1})	0.2248-2.2482
Molar absorptivity (ε) ($L.Mol^{-1}cm^{-1}$)	3.75×10^4
Specific absorptivity ($ml.g^{-1}.cm^{-1}$)	0.333
Sandall's sensitivity (μgcm^{-2})	0.0029
Composition of the Complex	1:2
Stability constant of the complex	2.96×10^{10}
Relative standard deviation (RSD %)	0.6268
Angular coefficient (m)	0.389
Y-Intercept (b)	-0.0016

Different molar excesses of 5-MFAT are added to fixed metal ion concentrations and the absorbances were measured adopting the standard procedure. It is observed that a 20 fold molar excess of reagent with respect to metal is necessary to get maximum absorbance. Hence, a 20 fold molar excess the of reagent was used in all experimental studies.

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the color complex. It is absorbed that the color development was instantaneous and remained constant for more than 56 hours. Physicochemical and analytical properties of cadmium (II) complex of 5-MFAT are summarized in (Table 2).

Effect of salting-out agent

Various salting out agents such as magnesium sulphate, magnesium nitrate, lithium acetate, lithium sulphate, lithium nitrate, lithium chloride, and ammonium sulphate are tried experimentally to study the effect on the extraction of the complex into the organic phase in a single step. It is observed that the presence of 2.0 ml of 0.1 M of lithium chloride facilitates maximum extraction. Hence, cadmium (II) was quantitatively extracted into organic phase with lithium chloride as a salting-out agent and with a 20 fold molar excess of reagent. The aqueous phase was titrated with EDTA using xylenol orange as indicator, which confirmed the absence of cadmium(II) in it.

Adherence of the Cd (II) – 5-MFAT Complex System to Beers law:

For the possible determination of cadmium (II) at micro levels, the absorbance of the solution containing different amounts of the metal ion is measured at 360 nm. The linear plot between the absorbance and the amount of cadmium (II) is drawn and the straight line obtained fits the equation $A_{360} = 0.38958C-0.00167$. Further Beers law is obeyed in the range of 0.2248 – 2.2482µgml^{-1}. The molar absorptivity and Sandell's sensitivity are found to be 3.7×10^4 L.mol^{-1}cm^{-1} and 0.0029 µgcm^{-2} respectively. The standard deviation of the method for ten determinations of 1.12 µg ml^{-1} is ± 0.0021.

To assess the precision and accuracy of the method, estimations were carried out for a set of five determinations of cadmium (II), under optimum conditions. The results show that standard deviation of the method is not more than 0.0021 and relative standard deviation is less than 0.62%. These results indicate that this method has good precision, besides being accurate.

Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded in (Fig.2) 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 350 – 450 nm. The derivative amplitude was measured at wavelengths 373 nm and 395 nm and plotted against amount of Cd(II) to obtain the calibration plots.

The calibration graph follows the straight line equation Y = a. C + b; where the C is Concentration of the solution, Y is measured absorbance or peak or valley height and a & b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as $A_{360} = 0.38958C-0.00167$ for zero order method, $A_{373} = 0.00029C + 0.00033$ and $A_{395} = 0.00019C + 0.00003$ for second derivative method.

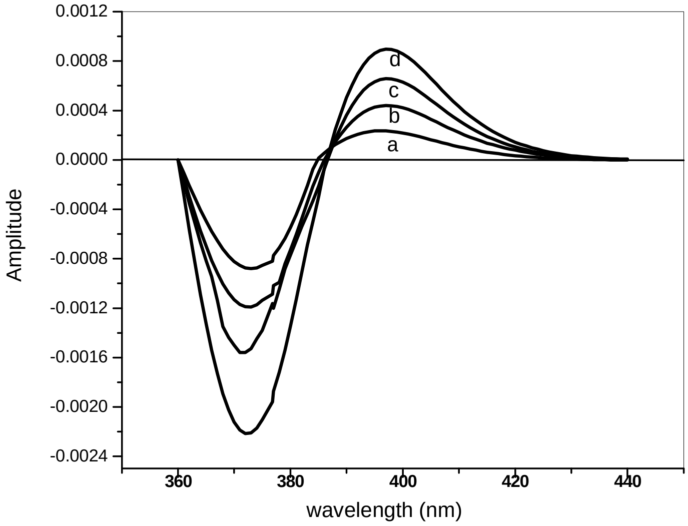

Fig.2 Second derivative spectra of Cd(II)-5MFAT complex ; Cd(II), µg/ml; a. 0.45; b.0.9; c. 1.35; d. 1.80;5-MFAT: 1.0 ml of 1x10^{-2}M;solvent Isoamylalchol: pH: 2.0 ml 6.0.

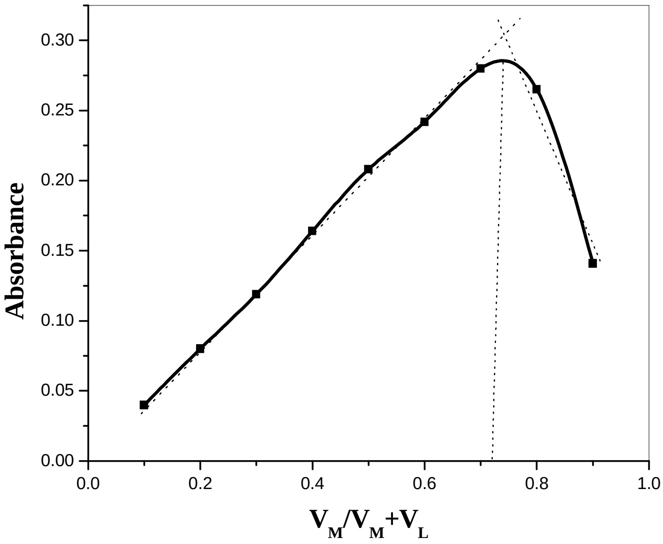

Fig. 3. Job's method of continuous variation Cd(II)-5-MFAT. Cd(II) and 5-MFAT 5x10-4M; solvent: isoamylalchol; pH: 2.0 ml of 6.0

Composition and stability constant of the complex

Job's method of continuous variation and molar-ratio methods were applied to ascertain the stoichiometric composition of the complex. It is found that 5-MFAT forms 1:2 complex with cadmium (II) as shown (in Fig.3). The stability constant was determined by Job's method as 2.94x10^{10} .

Effect of foreign ions on the extraction of the Cd(II)-5-MFAT complex

The effect of foreign ions is studied by measuring the absorbance of the reaction mixture containing 1.12 µgml^{-1} of cadmium (II) in the presence of different amounts of foreign ions. An error of ±2% in the absorbance value caused by foreign ions is considered as a tolerable limit.

The effect of various ions was studied. All the anions and the cations Pb(II), Cd(II), Te(IV), U(VI), Th(IV), W(VI), Ce(IV), Ti(IV), Zn(II) and Al(III), do not interfere even when present in more than 100 fold excess. Cr(III), Zr(IV), Mn(II), Ru(III), Pd(II), Mo(VI) and Pt(IV) are tolerable when present between 50-90 fold excess. Cu(II) and Fe(II), interfere when present in more than 10-fold excess, Ni(II) and V(V) interfere when present in more than 5- fold excess. However, in the presence of 1860 µg of EDTA, Cu(II) and Ni(II) do not interfere even in 100 fold excess. Fe(II) is tolerable up to 90 fold excess in the presence 1270 µg of iodide. In the presence of 950 µg of phosphate, V(V) is tolerable up to 100 fold excess.

Table.3. Determination of trace amount of Cd (II) in Medicinal Leaves & Leafy Vegetables

Sample name	**Cd (II) found µg g-I**			
	AAS	**Proposed method[a]**	**S.D**	**RSD (%)**
Vepaku (Azadirachta indica) [b]	0.334	0.352	0.00429	1.22
Rampala (Kalanchoe lanceolata) [b]	0.122	0.121	0.00118	0.98
Gaddi chamanthi (Tridax Procumbent) [b]	0.156	0.155	0.00204	1.32
Papatahommi (Pavetta indica) [c]	0.320	0.319	0.00443	1.39
Tellagorrak (Sidda cord folia) [c]	0.122	0.123	0.00119	0.97
Bangi (Tagetes erecta willd) [b]	0.123	0.121	0.00121	0.99
Thotakura (Amaranths Gangeticus) [c]	0.125	0.123	0.00192	1.56
Chukkaku (Rumex vesicarius) [b]	0.100	0.099	0.00198	1.98
Tutikura (Ipomoea Reptams) [b]	0.329	0.342	0.0042	1.23
Cauliflower green (Brassica Deraceavar, botnties) [c]	0.180	0.178	0.00312	1.7
Khesari (Latyrus sativus) [b]	0.531	0.545	0.011	2.02
Kappatega (Taliacora Acuminate) [c]	0.351	0.362	0.0076	2.12

a. *Average of the five determinations.*
b. *Collected at Tirumala forest, A.P, India.*
c. *Collected at Talakona forest A.P, India.*

Table.4. Determination of trace amount of Cd (II) in Biological Samples

Sample name	**Volume of sample**	**Cd (II) found µg g-I**			
		AAS	**Average**	**Proposed method[a]**	**Average**
Cigarate Tobacco-1[b]	4	19.74	19.96±0.38	19.98	19.97±0.33
	6	20.34		20.30	
	8	19.82		19.65	
Cigarate Tobacco-2[b]	4	21.55	21.75±0.41	21.55	22.06±1.44
	6	22.16		23.50	
	8	21.55		21.14	
Raddish [c]	4	1.75	1.81±0.13	1.81	1.84±0.13
	6	1.75		1.75	
	8	1.94		1.97	

a Mean of three determinations
b Dried samples
c Wet sample

Applications

The proposed extractive spectrophotometric method was applied for the determination of cadmium (II) in medicinal leaves, leafy vegetables, biological, soil and water samples.

A known aliquot of the above sample solution is taken into a 25 ml separating funnel and the cadmium content is determined as described in the general procedure. . The results are checked with parallel determinations by direct atomic absorption spectrometry. The data obtained in the analyses of medicinal leaves, leafy vegetables, biological, water and soil samples are given in (tables 3, 4, 5, & 6) respectively.

Table.5. Determination of trace amount of Cd (II) in Water Samples

Sample name	Cd (II) found µg g-I			
	AAS	**Proposed method[a]**	**S.D**	**RSD(%)**
River water (Swarnamukhi)	1.92	2.01	0.012	0.609
Waste water (Tiruchanoor)	2.3	2.51	0.1322	0.728
Sea water (Marina beach)	1.9	0.91	0.1322	0.725

a Average of the five determinations

Table.6. Determination of trace amount of Cd (II) in Soil samples

Sample name	Cd (II) found µg g-I
Agriculturesoil (Thiruchanuru)	0.28 ± 0.4
Road side Soil (Tirupathi)	0.58 ± 0.5
Industrial Soil (Sri kalahasthi)	1.3 ± 0.6

a Average of the five determinations

CONCLUSION

The literature available indicates that a few thiosemicarbozones have been used for the direct spectrophotometric determination of Cd(II), but not for extractive spectrophotometric determination of it. Hence, the authors have introduced a new reagent, APMT for the extractive spectrophotometric determination of cadmium(II). The selectivity of the reagent is improved by using masking agents to suppress the interference of metal ions like Cu(II), Ni(II), Fe(II), and V(V).

Finally, this method has been successfully applied for the determination of Cd(II) in medicinal, leafy vegetables, water and soil samples.

Acknowledgements

The authors thank Mr. G. Ramachandra Reddy, Mr. A. Babul Reddy and Mr. P. Hari babu for their immense help in carrying out my research investigations. I would also like to acknowledge UGC-SAP Government of India, New Delhi for providing financial assistance in the form of Junior Research fellowship.

REFERENCES

[1] Lee.S.D.,; Biochemical effects of Environmental Pollutants, Ann Arbor Scince Publishers Inc., Ann arbor, Mich. **(1977)**

[2] Salim.R., ; Al-subu.M.M.,; Sahrhage .E.;*Sci. Health* A, **(1992),** 27. (3), 603.

[3] Cheung. C.W.;. Porter.J.F.; . Mckay G.; *J Chem. Technol. Biotechnol*.(**2000).** 75, 963.

[4] Hirano.Y.; Nakajima .J.; Oguna.K.; Terui .Y.; *J. Anal. Sci*. **(2001)**, 17, 1073.

[5] Clayton G.D.; and Clayton.F.A.; (Ed) , "patty s Industrial Hygiene and Toxicology", 3rd ed., John wiley and sons, New York,(**1981),** 1563.

[6] Hammond P.B.; and Robert, Beliles. In: P.; Klassen.C.D.; Amdur.O.M.; Doull.J.;(Eds), "Metals in Casarett and Doull s Toxicology", 3rd ed., Macmillan and New york,**(1986),** 428.

[7] Friberg.L.; Piscator.M.; Norbberg.G.F.; and Kjellstrom .T.; (Ed), "Cadmium in the Environment" , 2nd ed., CRC Press, Inc., Cleveland **(1974).**

[8] Taylor D.M.; and Willams .D.R.; the Royal society of Chemistry Cambridge **(1995**), 22.

[9] Key M.M.; Hensche.A.F.; Butter. J.; Ligo.R.N.; and Tabershaed I.R..; (Ed), " Occupational diseases-A Guide to their Recognition" U.S. Department of Health, Education and Welfare, Us Govermet Printing Washington, D.C., June **(1977),** 265.

[10] Ghazy.S.E.; Sep. Sci. Technol, **(1995),** 30(6), 933.

[11] Reimann.C and Caritat.P.; "Chemical Elements in the environment Springer, Berlin, **(1998)**, 80.

[12] Szczepaniak. W.; Juskowisk.B.; Ciszewska.W.; *Anal. Chim.Acta*, **(1984)**, 156, 245.

[13] Hsu C.G.; Hu. C.S.; Jing, J.H.; *Talanta* **(1980)**, 27, 676.

[14] Chavanne.P.; Gerorimi.C.L.; Emploi du, 'cadion' en chimie analytique; *Anal. Chem. Acta* **, (1958),** 19, 377.

[15] Kmail.F.; Sinha,.P.P.; Sindhwani.S.K.; *J. Inst. Chem. (India)*. **(1982),** 54, 119.

[16] Roman Ceba.M.; Munoz Leyva. Berzas Nevado J.A.; *J.J., An. Quim.*,(**1980)** 76, 465.

[17] Hoshi.S.; Yotsuyangi.T. and Amoura,K,; *Bunseki Kagaku*; **(1977),** 26, 592.

[18] Vajagand.V.; Jaredic.M.; *Chem. Anal. (Warsaw),* **(1975)**, 20, 1125.

[19] Baustista Rabriguez. J.M.; and CanoPavon.J.M, *Talanta*, **(1980)**, 27, 923.

[20] DePablos, Fernando, Gomez Afriza, Jose L.; Pino Francisco. *Mikrochim. Acta*,(**1985),** 411-420.

[21] El-Asmy.A.A.; Moussa.M.N.H.; EI-shafie. A.A.; *Bull. Soc. Chim. Fr.* **(1987)**, 2, 247-249.

[22] Casas.J.S.; Garcia-Tasende.M.S.; Sordo.J.: A structural review, *Coord. Chem. Rev*. **(2000),** 2, 197.

[23] Hall. I.H.; Lackey.C.B.; Kistler.T.D.; Durham.R.W.; Jouad.E.M.; Khan.M.; Die Pharma, **(2000),** 55, 937.

[24] Vogel, A.I.;A Text book of Quantitative Inorganic Analysis, 4th edition, Longman, Green, London,**(1978)**.