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Extractive Spectrophotometric Determination of Trace Amounts of Cadmium (II) In Medicinal Leaves Environmental and Biological Samples by using 3-methylthiophene-2-carbaxaldehyde thiosemicarbazone (3-MTAT)

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ABSTRACT

A First reagent 3-mthylthiophene-2-carbaxaldehyde thiosemicarbazone (3-MTAT) is proposed as a sensitive and selective analytical reagent for extractive spectrophotometric determination of trace amount of cadmium (II). 3-MTAT reacts with cadmium(II) to give a light yellow coloured complex in a sodium acetate and acetic acid buffer solution of pH=6.0. The colour reactions have been investigated in detail. This is easily extracted into isoamylalchol with 1:2 compositions having maximum absorbanceat wavelength 360 nm. The molar absorptivity and sandell's sensitivity are found to be 4.0×10^4 *l* mol^{-1} cm^{-1}*, and 0.0029* $\mu g/cm^{-2}$ *respectively. The interfering of various diverse ions have also been studied. The method has been successfully applied for the extractive spectrophotometric determination of trace amount of cd (II) in several standard reference materials as well as medicinal leaves, environmental leafy vegetables, biological, water and soil samples.*

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

INTRODUCTION

Cadmium occurs in a nature in association with zinc minerals growing plants acquire Zn and they also take up and concentrate cd with 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 witch their bones become 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 batters 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, 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 extensive use of tobacco smoke.

Cadmium is trace elements in natural water and waste water industrial discharge, mining waste, metal plating, water pipes are important industrially[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-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 (ε x 10^4L mol-1 cm-1)	Ref
1,4,8,11-Tetra1, 4, 8, 11-tetramethyl Cyclotetradecane	550	NaOH	1.1	12
P-naitrophenyldiazo Aminoazobenzene	480	0.2-.0.3 mol^{-1} KOH	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-methylthiophene-2-carbaxaldehyde thiosemicarbazone(5-MTAT)	360	5.0-7.0	4.0	P.M

P. M Present method.

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, which comparable sensitivity and accuracy, besides having good precision. There are many organic complexing reagents [12-21] which can be 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 range of applications in the medicine and agriculture [23]. A survey of literature reveals that only a few thiosemicarbozones are employed for direct spectrophotometric determination of Cd(II), but not extractive spectrophotometric determination. Hence, the authors have introduced a new sensitive reagent 3-methylthiophene-2-carbaxaldehyde thiosemicarbazone (3-MTAT) for the first time, for the extractive 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 the addition to its simplicity instant colour 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

Experimental

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 3-methylthiophene-2-carbaxaldehyde thiosemicarbazone (3-MTAT):

3-methylthiophene-2-carbaxaldehyde thiosemicarbazone (3-MTAT) is prepared by refluxing a mixture of 3-methylthiophene-2-carbaxaldehyde (4ml, 0.0357mol, dissolved in 5ml of 10%-acetticacid-ethanol) and thiosemicarbazide (3.75grms, 0.0357mol, dissolved in 15ml of water) in 250 ml round bottom flask for 3hours. The shine light colored solid is separated out in cooling. The crystals are collected by filtration and washed several times with hot water and 50% cold methanol. Yield 80%, m.p 193-195ºC.

A 0.01 mol dm-3 stock solution is prepared by dissolving 0.208 mg of the 3-MTAT in 40% (v/v) aqueous dimethylformamode. And 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 3-MTAT 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 deprotenation of the reagent are 4.3(pK1) and 8.0 (pK2).

The working solutions were prepared by diluting the stock solution to an appropriate volume. All of 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 NH_4OH 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 stress. The samples are cleaned and dried in open air, protecting them from the mineral contamination. The dried samples are pulverized to finally 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 mater and ashed at 550ºC in a muffle furnace for 4-5 hours. The ash is dissolved 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 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 Thirupathi is made. Each filtered environmental water samples is evaporated nearly to dryness with a mixture of 10 ml 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 demonized 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 calibrated flask and made to the mark with demonized water

Preparation of soil samples: Soil samples like agriculture soil, roadside soil, and contaminated soil, the soils on air dried homogenate soil samples is weighted 100 mg accurately and taken in a 100ml flask. The sample is digested in the presence of an oxidizing agent. The content of the flask is filtered through what man No.41filter paper into a 25 ml volumetric flask and neutralized with a dilute NH_4 OH solution. It is then diluted to the mark distilled water.

The reactions of some impact metal ions are tested with (3-MTAT) at different pH values. The samples are prepared in 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 3-MTAT and 2.0 ml of 0.1 ml lithium chloride solution. And different metal ions. Each solution is then shaken with 10.0 ml portions of isoamylalchol for two minutes and then allowed to stand, each time. The combined organic phase of aliquot are taken in 10.0 ml standard flasks and made up to the mark with isoamylalchol. The absorbance is measured in 200 – 600 nm range against reagent blank

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 3-MTAT 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 phase are recorded at 360 nm. Against their corresponding reagent blank.

RESULTS AND DISCUSSION

Cadmium reacts with 3-methylthiphene-2-carbaxaldehyde thiosemicarbazone (3-MTAT) 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 effects, 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) - 3-MTAT Complex*:* The absorption spectra of Cd(II)- 3-MTAT complex and reagent show maximum absorbance at 360 nm and 340 nm, respectively (Fig. 1). The reagent showed 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.

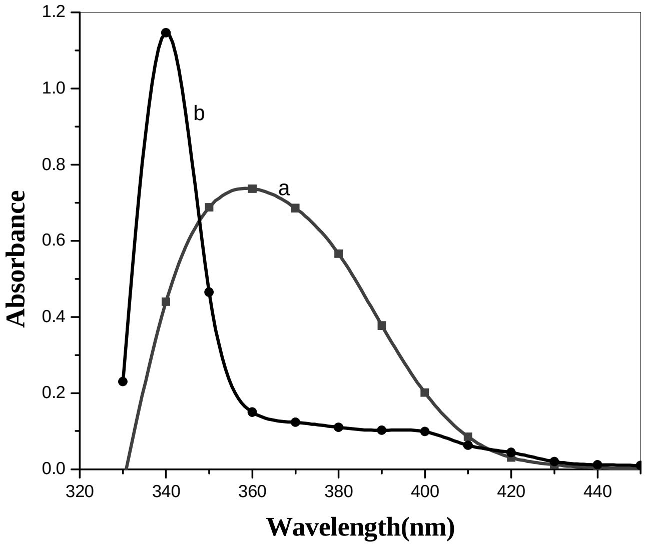

Fig. 1. Absorption spectra of (A) Cd(II)-3-MTAT complex and (B) 3-MTAT-solvent Complex. Cd(II):1.0ml of 3x10^{-4} M ;3-MTAT: 1.0 ml of 1x10^{-2}M;solvent Isoamylalchol: pH: 2.0 ml 6.0

The study of the effect of pH on the color intensity of the reaction mixture showed that the 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.

Different molar excesses of 3-MTAT are added to fixed metal ion concentration and the absorbance's are measured adopting the standard procedure. It is observed that 20 fold molar excess of reagent with respect to metal ion is necessary to get maximum absorbance. Hence, a 20 fold molar excess of reagent is used for further experimental studies.

The absorbance of the solution is measured at different time intervals to ascertain the time stability of the color complex. It is observed that the color development was instantaneous and remained constant for more than 56 hours. Physicochemical and analytical properties of cadmium (II) complex of 3-MTAT are summarized in Table-2.

Table-2. Physico - Chemical analytical characteristics of Cd (II) Complex of 3-MTAT

S.No	Charctistric property	Cd(II)- 3-MTAT
1.	Absorbance Maximum (λmax nm)	360
2.	pH range (Optimum)	5-7
3.	Mole of reagent required per mole of metal ion for full Color development	10
4.	Beers law validity range (µg/ ml)	0.2248-2.2482
5.	Molarabsorptivity (ε) (L. Mol $^{-1}$ cm^{-1})	4.0x10^{4}
6.	Specific absorptivity (ml.g^{-1}.cm^{-1})	0.333
7.	Sandall's sensitivity (µg/ cm^{-2})	0.0029
8.	Composition of the Complex	1:2
9.	Stability constant of the complex	2.96x10^{10}
10.	Relative Slandered deviation (RSD %)	0.6268
11.	Angular coefficient (m)	0.389
12.	Y-Intercept (b)	-0.0016

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 of metal complexes extraction 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) is quantitatively extracted into organic phase with lithium chloride as a salting-out agent and a 20 fold molar excess of reagent. The aqueous phase is tested with EDTA titration using xylenol orange. This conforms the absence of cadmium(II) in it.

Adherence of the Cd (II) - 3-MTAT 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 the equation A_{360} = 0.38958C-0.00167. Further Beers law is obeyed in the range of 0.2248 – 2.2482µg/ ml. the molar absorptivity and sandell's sensitivity are found to be 4.0 x10^{4} L.mol^{-1}cm^{-1}. And 0.0029 µg/cm^{2} respectively the standard deviation of the method for ten determinations of 1.12 µg /ml is ± 0.0021.

To assess the precision and accuracy of the method, estimations are 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 the method has good precision, besides being accurate.

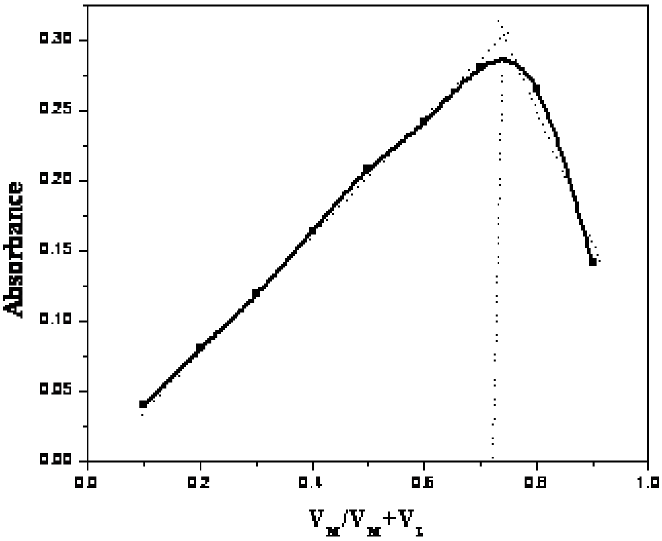

Fig. 2. Job's method of continuous variation Cd(II)-3-MTAT. Cd(II) and 3-MTAT 5x10-4M; solvent: isoamylalchol; pH: 2.0 ml of 6.0

Table-3. Effect of foreign ions

Diverse ions (µg/ml)	**Tolerance limit**	**Diverse ions (µg/ml)**	**Tolerance limit**
EDTA	1860	Pb(II)	1025
Ascorbic acid	1760	Cd(II)	880
Iodide	1270	Te(IV)	750
Citrate	1215	U(VI)	480
Phosphate	950	Th(IV)	280
Tartrate	900	W(VI)	250
Oxalate	880	Ce(IV)	210
Bromide	800	Ti(IV)	200
Urea	760	Zn(II)	150
Nitrate	720	Cu(II)	12,130[a]
Sulphate	680	Al(III)	110
Bromate	640	Ni(II)	6,107[a]
Acetate	600	Fe(II)	11, 112[b]
Thiosulphate	560	V(v)	5.8, 110[c]
Thio urea	380	Cr(III)	88
Chloride	355	Zr (IV)	80
Fluoride	200	Mn (II)	74
		Ru (III)	65
		Pd (II)	60
		Mo(VI)	59

Amount of Cadmium(II) = 1.12 µg /ml
In the presence of a) 1860 µg of EDTA
b) 1270 µg of Iodide
c) 950 µg of phosphate.

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

Effect of foreign ions on the extraction of the Cd(II)-APMT complex: The effect of foreign ion is studied by measuring the absorbance of the reaction mixture containing 1.12 µg /ml of cadmium (II) in the presence of different amounts of foreign ions. The results presented in the Table-3**.** An error of ±2% in the absorbance value caused by foreign ions is considered as a tolerable limit.

The effect of various ions 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.

Applications:

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

Table-4. 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**	**R.S.D (%)**
Vepaku (Azadirachta indica) [b]	0.334	0.352	0.00429	1.22
Rampala (Kalanchoe lanceolata) [b]	0.122	0.121	0.00118	0.98
Gaddichamanthi(Tridax Procumbent) [b]	0.156	0.155	0.00204	1.32
Tellagorrak (Sidda cord folia) [c]	0.122	0.123	0.00119	0.97
Papatahommi (Pavetta indica) [c]	0.320	0.319	0.00443	1.39
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-5. Determination of trace amount of Cd (II) in Biological Samples

Sample name		Cd (II) found µg g-I			
	Sample taken (ml)	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

Table-6. Determination of trace amount of Cd (II) in Water Samples

Sample Name	Cd (II) found µg g-I			
	AAS	Proposed method[a]	S.D	R.S.D (%)
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-7. Determination of trace amount of Cd (II) in Soil samples

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

A known aliquot of the above sample solution is taken into a 25 ml separating funnel and the cadmium content is determined as described is given 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 in given Table. 4, 5, 6, & 7 respectively.

CONCLUSION

The literature available indicates that a few thiosemicarbozones have been used for the direct spectrophotometric determination of Cd(II), but not extractive spectrophotometric determination of it. Hence, the authors have introduced a new reagent, 3-MTAT 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 ion 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.

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