

Extractive spectrophotometric determination of trace amounts of cadmium(II) in medicinal leaves and environmental samples using benzildithiosemicarbazone (BDTSC)

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Abstract

A new thiosemicarbazone, benzildithiosemicarbazone (BDTSC), is proposed as a sensitive and selective analytical reagent for extractive spectrophotometric determination of Cd(II). BDTSC reacts with cadmium(II) to give a yellow-colored complex in ammonium chloride–ammonium hydroxide buffer of pH 10.5, which is easily extracted into isoamylalcohol with 1:1 composition having a maximum absorbance at wavelength 360 nm. The molar absorptivity and Sandell's sensitivity are found to be $0.196 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.008 \mu\text{g cm}^{-2}$ of Cd(II), respectively. The instability constant of the method has been calculated by Asmus' method as 5.05×10^{-5} (which is in close agreement with the value obtained by Edmonds and Birnbaum's method) at room temperature. The interfering effect of various cations and anions has also been studied. The method has been successfully applied for the determination of Cd(II) in several standard reference materials as well as environmental samples, medicinal leaves and leafy vegetables.

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1. Introduction

Cadmium is a lustrous, silver–white, ductile and highly malleable metal. It is soluble in acids but not in alkalis. About three-fourths of cadmium is used in Ni–Cd batteries, and the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics [1,2]. Cadmium has been used to electroplate steel and more particularly as a barrier to control nuclear fission. The fact remains that a very large amount of cadmium is released into the environment naturally. About half of this cadmium is released into rivers through weathering of rocks and some of it is released into air through forest fires and volcanoes. The rest of cadmium is released through human activities, such as manufacturing processes and so on. Human intake of cadmium takes place mainly through diet like liver, kidney, mushrooms, shellfish, mussels, cocoa powder and dried

seaweed [3]. One of the main reasons for cadmium accumulating in the body is the extensive use of tobacco.

Trace amounts of cadmium are very important in industrially [4], as a toxicant [5] and biologically non-essential [6], as an environmental pollutant [7] and as an occupational hazard [8]. It is an extremely toxic metal, and the effects of acute cadmium poisoning are manifested in a variety of symptoms including high blood pressure, kidney damage and destruction of red blood cells [9]. The reported cadmium content in the environment is 70–110 ng l⁻¹ in seawater, and 2–960 ng l⁻¹ in fresh water [10].

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, with comparable sensitivity and accuracy, besides having good precision.

There are many organic complexing reagents [11–13], which can be used for the spectrophotometric determination of cadmium, yet these suffer from disadvantages such as low

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

Reagent	pH	λ_{\max} (nm)	ϵ_{\max} ($\times 10^4$ L mol $^{-1}$ cm $^{-1}$)	Remarks	References
1,4,8,11-Tetra-1,4,8,11-tetramethyl cyclotetradecane	NaOH	550	1.1	Interferences were Cu $^{2+}$, Hg $^{2+}$, Ag $^{+}$ and large anions	[8]
<i>p</i> -Nitrophenyldiazo aminoazobenzene	0.2–0.3 mol l $^{-1}$ KOH	480	1.19	Interferences were Hg $^{2+}$, Ag $^{+}$ and large anions	[9]
Polyvinylpyrrolidinone	–	–	–	Interferences were Hg $^{2+}$, Ag $^{+}$ and large anions	[10]
Benzildithiosemicarbazone (BDTSC)	10.5	360	0.196	–	Present method

sensitivity, incomplete extraction and interference 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 thio-phenylthiosemicarbazones in inorganic/analytical chemistry for determination of metal ions [14]. The metal chelates of these sulfur and nitrogen containing organic reagents find a wide range of applications in medicine and agriculture [15]. 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 sensitive reagent benzildithiosemicarbazone (BDTSC) for the first time, for the extractive determination of trace amounts of Cd(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–vis spectrophotometer have been compared with those obtained through the atomic absorption spectrometer. The operating parameters of AAS are presented in Table 2.

2. Apparatus

A Shimadzu (UV-2450 model) UV–vis spectrophotometer with 1.0 cm quartz cell has been used for absorbance measurements. An Elico (model Li-10 India) pH-meter has been used for pH adjustments. A Hitachi model 170-30 atomic absorption spectrophotometer was used for comparison of results.

3. Reagents

All of the chemicals used are of analytical grade; quartz-processed high-purity water has been used throughout the experiment.

Table 2
Operating parameters of the AAS instrument

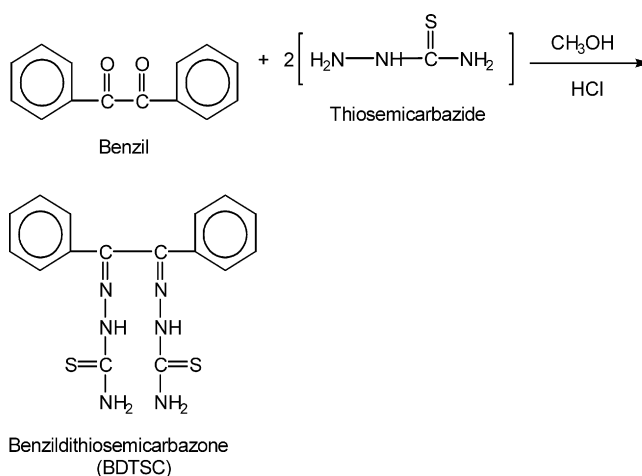
Parameter	Element Cd
Wavelength (nm)	228.8
Slit width	0.7
Pretreatment temperature (°C)	900
Automation temperature (°C)	1600

3.1. Preparation of standard solution of cadmium(II)

A known amount of cadmium acetate is dissolved in water and then diluted to 100 cm 3 with distilled water. The stock solution is then standardized by EDTA titration [16] using xylenol orange as an indicator. Further, required dilute solutions are prepared by diluting the stock solution, suitably with distilled water.

3.2. Synthesis of benzildithiosemicarbazone

Benzildithiosemicarbazone (BDTSC) is synthesized and recrystallized as reported by Reddy et al. [17]. To a refluxing mixture containing 50 cm 3 of methanolic benzil (0.42 g) and 50 cm 3 of aqueous thiosemicarbazide (0.365 g) solutions, 3.0 cm 3 concentrated hydrochloric acid is added. The reaction mixture is kept on a hot water bath for about 30 min, until a light yellow-colored precipitate forms. This product is then separated by filtration and dried. The product is recrystallized from ethyl alcohol. The purity of the reagent is checked by ascertaining the melting point and elemental analysis (melting point 234–236 °C, yield 63%). A 0.1 mol dm $^{-3}$ stock solution is prepared by dissolving 3.24 g of BDTSC in 40% (v/v) aqueous dimethylformamide.



3.3. Buffer solution

2 mol dm $^{-3}$ ammonium chloride and 2 mol dm $^{-3}$ ammonium hydroxide solutions are prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

3.4. General procedure

Known aliquots of 10.0 cm^3 of solution containing constant volumes of 2.0 cm^3 of buffer (pH 10.5), 2.0 cm^3 of $1.601 \times 10^{-3}\text{ mol dm}^{-3}$ BDTSC and 2.0 cm^3 of 0.1 mol dm^{-3} lithium chloride solution and varying amounts of cadmium(II) from 1.0 to $10.0\text{ }\mu\text{g cm}^{-3}$ are prepared. Each solution is then shaken with two 10.0 cm^3 portions of isoamylalcohol for 2 min and then allowed to settle, each time. The combined organic phases of each aliquot are taken in a 25 cm^3 standard flask and made up to the mark with isoamylalcohol. The absorbances of all the organic phases are recorded at 360 nm , against their corresponding reagent blank.

4. Results and discussion

Cadmium reacts with benzildithiosemicarbazone (BDTSC) in ammonium chloride–ammonium hydroxide buffer (pH 10.5) and gives a 1:1(M:L) yellow-colored complex, which can be easily extracted into isoamylalcohol. The complex has a maximum absorbance at 360 nm . The optimum reaction conditions for the quantitative determination of the metal–ligand complex have been established through a number of preliminary studies, such as the effect of pH, choice of 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 Cd(II) at micro gram levels.

4.1. Absorption spectra

The absorption spectra of Cd(II)–BDTSC complex and reagent show maximum absorbances at 360 nm and 320 nm , respectively (Fig. 1). The reagent showed a minimum

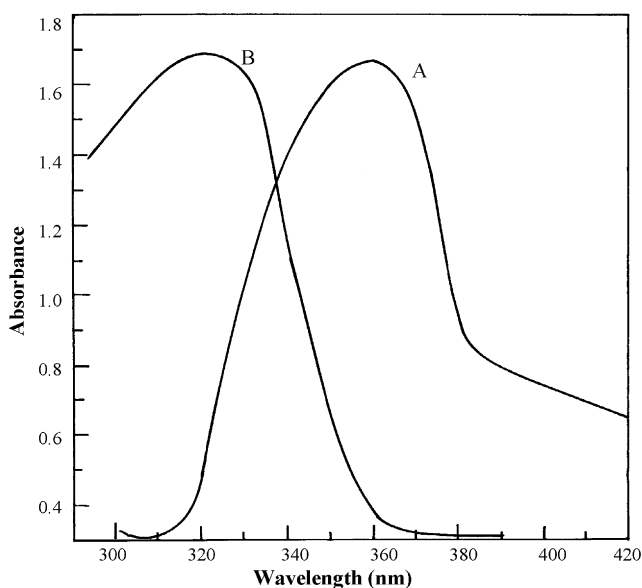


Fig. 1. Absorption spectra of (A) Cd(II)–BDTSC complex and (B) BDTSC–solvent complex. Cd(II): 1 cm^3 of $1.013 \times 10^{-3}\text{ mol dm}^{-3}$; BDTSC: 1 cm^3 of $1.011 \times 10^{-2}\text{ mol dm}^{-3}$; solvent: isoamylalcohol; pH: 2 cm^3 of 10.5.

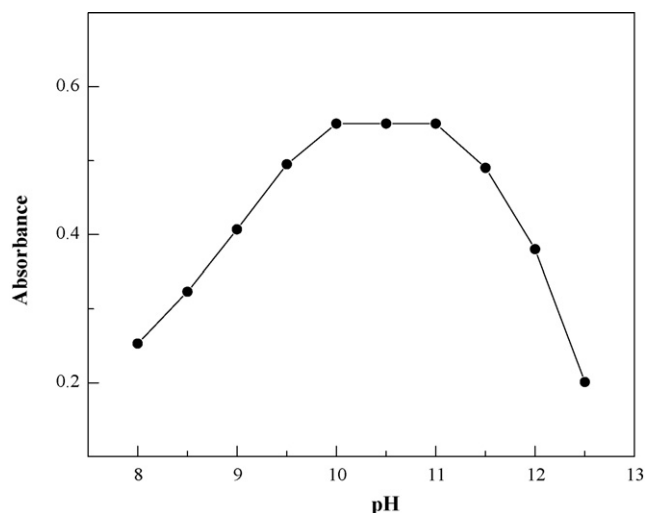


Fig. 2. Effect of pH: Cd(II)–BDTSC complex. Cd(II): 1 cm^3 of $1.013 \times 10^{-3}\text{ mol dm}^{-3}$; BDTSC: 1 cm^3 of $1.011 \times 10^{-2}\text{ mol dm}^{-3}$; solvent: isoamylalcohol; pH: 2 cm^3 of 10.5.

absorbance at the maximum absorbance of the complex. Hence, all the spectral measurements of the complex have been carried out at 360 nm .

4.2. Effect of pH

The influence of pH on the Cd(II)–BDTSC complex is studied to find out the optimum pH range for cadmium determination. The pH studies are carried out using ammonium chloride–ammonium hydroxide buffer.

In each case, a mixture containing 1.0 cm^3 of $1.013 \times 10^{-4}\text{ mol dm}^{-3}$ Cd(II), 2.0 cm^3 of 0.1 mol dm^{-3} lithium chloride, 2.0 cm^3 of different pH of ammonium chloride–ammonium hydroxide buffer and 1.0 cm^3 of $1.011 \times 10^{-3}\text{ mol dm}^{-3}$ BDTSC solution is taken and the volume is adjusted to 10.0 cm^3 with distilled water. It is shaken with 4.0 cm^3 of isoamylalcohol for about 2 min and then allowed to separate into two layers. The organic phase is collected in a 10 cm^3 standard flask and made up to the mark with isoamylalcohol. The experiment is repeated with buffers of different pH from 8.0 to 12.5. The absorbances are measured at 360 nm , using the reagent as blank. A plot is drawn between pH and the absorbance, which is shown in Fig. 2. It is observed that the extraction of metal ion into organic phase increases as the pH increases from 8.0 to 10.0 and remains constant from 10.0 to 11.0. However, it decreases from 11.0. Hence, pH 10.5 has been selected for further studies.

4.3. Effect of reagent concentration

Different molar excesses of BDTSC are added to fixed metal ion concentrations, and the absorbances are measured adopting the standard procedure. It is observed that a 16-fold molar excess of reagent with respect to metal is necessary to get maximum absorbance. Hence, a 16-fold molar excess of reagent has been used for further experimental studies.

4.4. Analytical features

A well-known equation for extractive spectrophotometric analysis for the determination of cadmium(II) at very low concentrations has been derived from Beer's Law. The effect of metal concentration has been studied in the range 1.0–10.0 $\mu\text{g cm}^{-3}$. The absorbance is found linearly increasing from 1.0 to 6.0 $\mu\text{g cm}^{-3}$ of cadmium(II) at 360 nm. The molar absorptivity and the Sandell's sensitivity are found to be $0.196 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.008 \mu\text{g cm}^{-2}$ of cadmium(II), respectively.

4.5. 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 have been tried experimentally to study the effect of metal complex extraction into the organic phase in a single step. It is observed that the presence of 2.0 cm^3 of 0.1 mol dm^{-3} of lithium chloride facilitates maximum extraction. Hence, cadmium(II) has been quantitatively extracted into the organic phase with lithium chloride as a salting-out agent and a 16-fold molar excess of reagent. The aqueous phase is tested with EDTA titration using xylenol orange, which confirms the absence of cadmium(II) in it.

4.6. Ringbom's plot for the Cd(II)–BDTSC complex

Ringbom's plot is the standard adopted to know the optimum range of concentration for a system, which emaciates Beer's law. Adopting the standard procedure, a plot is drawn between $\log C$ of Cd(II) and $(1 - T)$, where " T " is the transmittance (Fig. 3). The plot has a sigmoid shape with linear segment at intermediate absorbance values 0.335–0.995, which indicates that cadmium(II) is precisely determined in the range 2.0 – $4.0 \mu\text{g cm}^{-3}$. The slope of the Ringbom plot is 0.466. Based

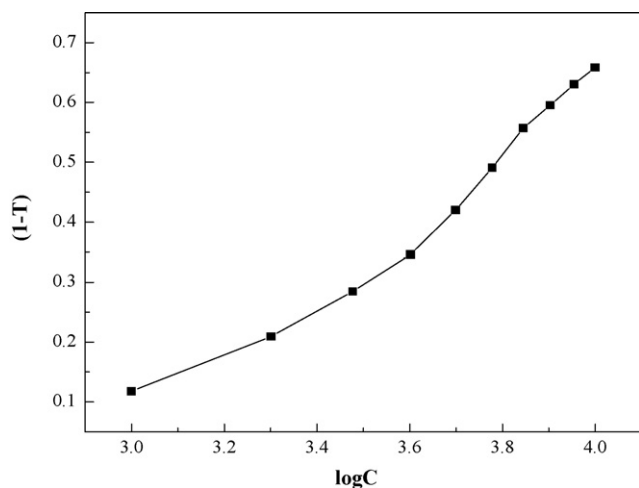


Fig. 3. Ringbom Plot of Cd(II)–BDTSC complex. Cd(II): 1000 – $10,000 \mu\text{g dm}^{-3}$; BDTSC: 1 cm^3 of $1.601 \times 10^{-3} \text{ mol dm}^{-3}$; solvent: isoamylalcohol; pH: 2 cm^3 of 10.5.

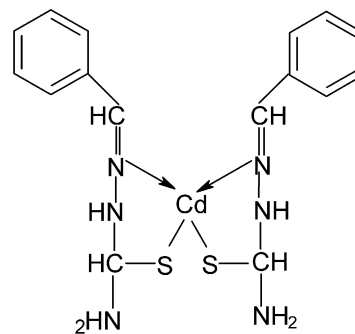
on this value, the ratio between the relative error in concentration and photometric error is 4.94, for a photometric error of one percent $\Delta p = 0.01$. Hence, the relative error in concentration is 0.049.

4.7. Precision and accuracy

To assess the precision and accuracy of the method, estimations are carried out for a set of five determinations, with different concentrations of cadmium(II), under optimum conditions. The results show that the standard deviation of the method is not more than 0.0021 and relative standard deviation is less than 0.68%. These results indicate that this method has good precision, besides being accurate.

4.8. Composition of the Cd(II)–BDTSC complex

Job's method of continuous variation and molar-ratio method have been applied, to ascertain the stoichiometric composition of the complex. It is found that BDTSC forms a 1:1 complex with cadmium(II) as shown in Fig. 4. From experimental results the structure of complex derived exists as:



Structure of BDTSC–Cd(II) complex

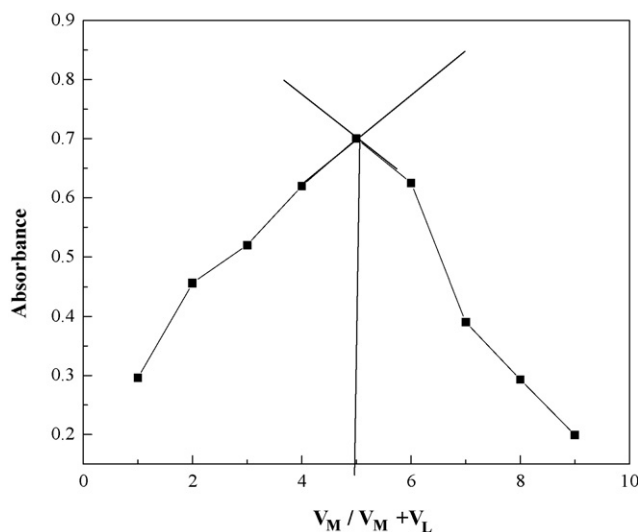


Fig. 4. Job's method of continuous variation Cd(II)–BDTSC. Cd(II) and BDTSC 1 cm^3 of $1.011 \times 10^{-4} \text{ mol dm}^{-3}$; solvent: isoamylalcohol; pH: 2 cm^3 of 10.5.

Table 3
Effect of foreign ions

Foreign ion	Added as	Tolerance Limit ($\mu\text{g/ml}$)
Mn(II)	MnSO ₄ ·7H ₂ O	250
Al(III)	Al ₂ (SO ₄) ₃ (NH ₄) ₂ SO ₄ ·24H ₂ O	250
Cu(II)	CuSO ₄ ·5H ₂ O	None
Zn(II)	ZnSO ₄ ·7H ₂ O	15
Pd(II)	PdCl ₂	10
Fe(III)	NH ₄ Fe(SO ₄) ₂ ·12H ₂ O	200
Zr(IV)	ZrO(NO ₃) ₂ ·2H ₂ O	200
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄	50
Mg(II)	MgSO ₄ ·7H ₂ O	250
Ni(II)	(NH ₄) ₂ SO ₄ NiSO ₄ ·6H ₂ O	25
Cr(III)	Cr ₂ (SO ₄) ₃	50
Ti(IV)	TiF ₄	250
U(VI)	UO ₂ (CH ₃ COO) ₂ ·2H ₂ O	250
V(V)	NH ₄ VO ₃	100
W(VI)	Na ₂ WO ₄ ·2H ₂ O	250
Co(II)	CoSO ₄ ·7H ₂ O	50
Bromide	KBr	250
Chloride	NaCl	200
Citrate	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	100
EDTA	Na ₂ EDTA	None
Flouride	NaF	250
Iodide	KI	200
Nitrate	KNO ₃	250
Oxalate	(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	None
Phosphate	NH ₄ H ₂ PO ₄	None
Sulphate	K ₂ SO ₄	200
Tartrate	(NH ₄) ₂ C ₂ H ₄ O ₆ ·4H ₂ O	200
Thiocyanate	NH ₄ SCN	50
Thiosulphate	Na ₂ S ₂ O ₃ ·5H ₂ O	250
Thiourea	NH ₂ CSNH ₂	200

Amount of cadmium(II) = 5.0 $\mu\text{g/ml}$.

4.9. Calculation of instability constant of Cd(II)–BDSTC complex

Edmands and Birnbaum's method [18] as well as Asmus' method [19] has been employed to determine the instability constant of Cd(II)–BDTSC complex. The absorbance values of

Table 5
Determination of cadmium(II) in soil samples

Samples	Cadmium(II) ^a ($\mu\text{g g}^{-1}$)
Agricultural soil (Tiruchanoor)	0.28 ± 0.4
Roadside soil (Tirupati)	0.58 ± 0.5
Industrial soil (Srikalahasthi)	1.3 ± 0.6
Contaminated soil (Renigunta)	0.0 ± 1.5

^a Average of the five determinations.

the extracts are obtained at 360 nm after shaking the solution containing fixed volumes of Cd(II) ($1.01 \times 10^{-4} \text{ mol dm}^{-3}$), buffer (pH 10.5) and lithium chloride (0.1 mol dm^{-3}) with different known volumes of 0.5–2.0 cm³ of $1.01 \times 10^{-4} \text{ mol dm}^{-3}$ BDTSC solution, into isoamylalcohol. The instability constant of Cd(II)–BDSTC complex is calculated and found to be 5.97×10^{-5} at room temperature, following Edmonds and Birnbaum's method. In Asmus' method, the instability constant of Cd(II)–BDTSC complex is calculated and found to be 5.05×10^{-5} , at room temperature, which is in close agreement with the value obtained by Edmonds and Birnbaum's method.

4.10. Effect of foreign ions on the extraction of the Cd(II)–BDTSC complex

The effect of foreign ions is studied by measuring the absorbance of the reaction mixture containing 5.0 $\mu\text{g cm}^{-3}$ of cadmium(II) in the presence of different amounts of foreign ions. The results are presented in Table 3. An error of $\pm 2\%$ in the absorbance value caused by foreign ions is considered as a tolerable limit.

The interference of metal ions has been tested up to 50-fold excess. The results show that Al(III), Mn(II), W(IV), Mg(II), Ti(IV) and U(VI) do not interfere. The tolerated limits for other metal ions are Fe(III) and Zr(IV) up to 40-fold excess, Co(II), Cr(III) and Mo(VI) up to 10-fold excess, Cu(II), Ni(II), Ag(I), Pd(II) and Zn(II) less than 5-fold excess. 1.0 cm³ of 4% cit-

Table 4
Determination of trace amounts of Cd(II) in medicinal leaves and leafy vegetables

Sample	Cd(II) found ($\mu\text{g g}^{-1}$)		Standard deviation	Relative standard deviation (%)
	AAS	Proposed method ^a		
Vepaku (<i>Azadirachta indica</i>) ^b	0.334	0.352	0.0043	1.22
Ramapala (<i>Kalanchoe lanceolata</i>) ^b	0.122	0.121	0.0012	0.98
Gaddi Chamanti (<i>Tridax procumbens</i> L.) ^b	0.156	0.155	0.002	1.32
Tellagorak (<i>Sida cordifolia</i> L.) ^c	0.122	0.123	0.0012	0.97
Papatahommi (<i>Pavetta indica</i> L.) ^c	0.32	0.32	0.004	1.39
Bangi (<i>Tagetes erecta</i> willd) ^b	0.12	0.123	0.0012	0.99
Thotakura (<i>Amaranthus gangeticus</i>) ^c	0.125	0.123	0.002	1.56
Chukkaku (<i>Rumex vesicarius</i>) ^b	0.1	0.1	0.002	1.98
Tutikura (<i>Ipomoea reptans</i>) ^b	0.33	0.342	0.0042	1.23
Cauliflower green (<i>Brassica deraceavar, botntis</i>) ^c	0.18	0.178	0.0031	1.7
Khesari (<i>Latyrus sativus</i>) ^b	0.53	0.545	0.011	2.02
Kappatega (<i>Taliacora acuminata</i> L.) ^c	0.35	0.362	0.007	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 6
Determination of trace amounts of Cd(II) in water samples

Sample	Cd(II) found ($\mu\text{g g}^{-1}$)		Standard deviation	Relative standard deviation (%)
	AAS	Proposed method ^a		
River water (Swarnamukhi)	1.92	2.01	0.012	0.61
Waste water (Tiruchanoor)	2.3	2.51	0.132	0.73
Sea water (Marina Beach)	1.90	0.91	0.132	0.725

^a Average of the five determinations.

rate has been employed as a masking agent for Ni(II), Pd(II), Zn(II). The interference of copper(II) has been eliminated by using 1.0 cm^3 of 2% thiosulphate as the masking agent. Ag(I) has to be removed as silver chloride, prior to the extraction of cadmium(II).

Anions like bromide, chloride, fluoride, iodide, nitrate, sulphate, tartrate, citrate, thiocyanate, thiosulphate and thiourea have no effect on the extraction of Cd(II), even when they are present in 50-fold excess or more. However, EDTA, oxalate and phosphate interfere seriously.

5. Applications

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

5.1. Determination of Cd(II) in medicinal leaves and leafy vegetables

The medicinal leaves and leafy vegetables analyzed have been procured from the city grocery stores. The samples are cleaned and dried in open air, protecting them from mineral contamination. The dried samples are pulverized to finely powder particles in a mortar for the analysis of Cd(II). 10.0 g of powdered sample is taken in a silica crucible, heated in order to oxidize the organic matter and ashed at $550\text{ }^\circ\text{C}$ in a muffle furnace for 4–5 h. The ash is dissolved in 10 cm^3 of 2 mol dm^{-3} hydrochloric acid, heated and filtered through an acid washed filter paper. Then the residue is washed with hot water. The filtrate and washings are collected into a 25 cm^3 volumetric flask and finally made up to the mark with double distilled water and analyzed for Cd(II) using the recommended general procedure. The results are checked with parallel determinations by direct atomic absorption spectrometry. The data obtained in the analysis of medicinal leaves and leafy vegetables are given in Table 4.

5.2. Determination of cadmium(II) in soil samples

Soil samples like agricultural soil, roadside soil, industrial soil, and contaminated soil have been selected for the determination of Cd(II). The air-dried homogenized soil samples have been weighed, 100 g each accurately and taken in 100 cm^3 micro-Kjeldahl flasks. The samples are digested in the presence of an oxidizing agent (65% HNO_3). The content of the flasks are filtered through Whatman No.41 filter paper into 25 cm^3

calibrated flasks and neutralized with dilute NH_4OH solution. They are then diluted, made up to the mark with distilled water.

A known aliquot of each of the above sample solutions is taken into a 25 cm^3 separating funnel and Cd(II) has been determined following the specified general procedure. The data obtained in the analysis of soil samples are given in Table 5.

5.3. Determination of cadmium(II) in water samples

A choice of three water samples in and around the city of Tirupati has been made. Each filtered environmental water sample is evaporated nearly to dryness with a mixture of 5.0 cm^3 concentrated H_2SO_4 and 10 cm^3 concentrated HNO_3 in a fume cupboard and then cooled to room temperature. The residue is then heated with 10.0 cm^3 of deionized water, in order to dissolve the salts. The solution is cooled and neutralized with dilute NH_4OH in the presence of $1\text{--}2\text{ cm}^3$ of 0.01% tartrate solution. The resulting solution is filtered and quantitatively transferred into a 25 cm^3 calibrated flask and made up to the mark with deionized water.

A known aliquot of the above sample solution is taken into a 25 cm^3 separating funnel and the cadmium content is determined as described in the general procedure. The data obtained in the analysis of water samples is given in Table 6.

6. Conclusion

The literature available indicates that a few thiosemicarbazones 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, BDTSC for the extractive spectrophotometric determination of cadmium(II). The selectivity of the reagent is improved by the use of masking agents to suppress the interference of metal ions like Ag(I), Pd(II), Zn(II), Ni(II), Cu(II), U(VI), V(V), Mn(II) and Ti(IV).

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

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