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SPECTROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS (CADMIUM) IN AQUEOUS MEDIA

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Abstract

Trace amount of toxic element (Cadmium) was determined by spectrophotometer method using 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt. (Alizarin red S) as a new spectrophotometer reagent. Alizarin red S reacts in slightly acidic solution (0·005 – 0·05M H_2SO_4) with cadmium to give a deep greenish yellow chelate which has an absorption maximum at 422 nm. The reaction is instantaneous and absorbance remains stable for over 24hrs. The average molar absorption co-efficient and sandell's sensitivity were found to he $2{\cdot}24 \times 10^3 L\ mol^{-1}\ cm^{-1}$ and 20 ng cm^{-2} of Cd respectively. Linear calibration graphs were obtained for 0·1 – 40 $\mu g\ mL^{-1}$ of Cd. The stoichiometric composition of the chelate is 1 : 2 (Cd : Alizarin red S). Large excess of over 50 cations, anions, and some common complexing agents (e.g EDTA, oxalate, citrate phosphate, thio-urea, SCN^-) do not interfere in the determination. The method was successfully used in the determination of cadmium in Several Standard Reference Materials (alloys, steels and water) as well as in some environmental waters (In land and surface), biological samples (human blood and urine), soil samples and complex synthetic mixtures. The method has high precision and accuracy. ($S = \pm 0{\cdot}01$ for 0·5 $\mu g\ mL^{-1}$.

Keywords

spectrophotometry; cadmium determination; 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt. (Alizarin red S); alloy; steel; environmental; biological; samples; soil samples.

Introduction

Different types of ligand were used with about 30 toxic metal ions to obtain color chelate through the novel reaction techniques. Finally Trace amount of toxic element cadmium was determined by spectrophotometric method using 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt (Alizarin red S) as a new spectrophotometric reagent.

Cadmium in trace amounts is important industrially [1], as a toxicant [2] and biological non-essential [2], as an environmental pollutant [3] and as an occupational hazard [4] It is an extremely toxic metal, has been responsible for a number of deaths [5]. The symptoms of cadmium poisoning are instantaneous hypertension, shortening of life-span; Kidney damage, bronchitis, retardation of growth, gross abnormalities of the vital organs and the risk of prostatic cancer [6]. It also cause generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers [6]. The most serious situation being the disease called "Itai-Itai" disease which causes gradual weakening of the bone structure, diminution of stature and ultimately the total collapse of the entire skeletal system [7]. Its extreme toxicity towards marine and fresh water organisms is also well known [7]. Cadmium is a potential health hazard due to its presence in urban atmosphere and cigarette smoke [7]. The permissible limit of cadmium in drinking water is 0·05 mgL–1 according to EPA [8]. Increasing Cadmium pollution of the environment resulting from the growth of cadmium based industries and the use of fossil fuels makes the development of method for the trace and ultra-trace analysis of this toxic metal essential.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. 1, 2-dihydroanthraquinone-3-sulphonic acid, sodium salt (Alizarin Red S) has been reported as a spectrophotometric reagent for Arsenic [9] but has not previously been used for spectrophotometric determination of cadmium. This paper reports its use in a very sensitive, highly specific spectrophotometric method for the trace determination of cadmium. The method possesses distinct advantages over existing methods [10-30] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent alizarin red S in slightly acidic solution (0·0005 – 0·05M H2SO4) with cadmium to produce a highly absorbent deep greenish yellow chelate product, followed by direct measurement of the absorbance in aqueous solution. With suitable masking, the reaction can be made highly selective.

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Experimental

Apparatus

A shimadzu (Kyoto, Japan) (Model–1601PC) double beam UV/VIS recording spectrophoto-meter and Jenway (England, U.K.) (Model–3010) pH-meter were used for the measurements of absorbance and pH, respectively. A Shimadzu (Model-AA 6200) atomic absorption spectrophotometer equipped with a micro computer-controlled nitrous oxide-acetylene flame was used for comparison of the results.

Reagents and Solutions

All the chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled de-ionized water, which is non-absorbent under ultraviolet radiation was used throughout.

Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with nitric acid (1 + 1) and rinsed several times with high-purity de-ionized water. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO_3. More rigorous contamination control was used when the cadmium levels in the specimens were low.

Alizarin Red S Solution, 1·39 × 10–3 M

Prepared by dissolving the requisite amount of alizarin red S. (1, 2-dihydroxyanthraqui-none-3-sulphonic acid, sodium salt) (BDH chemicals) in a known volume of de-ionized water. More dilute solutions of the reagent were prepared as required.

Cadmium Standard Solutions

A 100-mL amount of stock solution (1 $mgmL^{-1}$) of divalent cadmium was prepared by dissolving 0·2282mg of AR crystallized cadmium sulfate (3 Cd SO_4, 8 H_2O) (Merck) in doubly distilled de-ionized water. Aliquots of this solution were standardized by EDTA titration using xylenol orange as indicator. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water as and when required.

EDTA Solution

A 100-mL amount stock solution of EDTA (0·01% W/v) was prepared by dissolving 10 mg of A.C.S.-grade (≥ 99%) of disodium dihydrogen ethylenediamine tetraacetate dihydrate in (100-mL) de-ionized water.

Potassium Permanganate Solution

A 1% potassium permanganate solution (Merck) was prepared by disslolving in de-ionized water. Aliquots of this solution were standardized with oxalic acid. Sodium azide solution (2·5% W/v) (Fluka purity > 99%) was also used.

Tartarate Solution

A 100-mL stock solution of tartarate (0·01% W/v) was prepared by dissolving 10 mg of A.C.S grade (99%) potassium sodium tartarate tetrahydrate in (100-mL) de-ionized water.

Aqueous Ammonia Solution

A 100-mL solution of aqueous ammonia was prepared by diluting 10-mL concentrated NH_4OH (28 – 30%, A.C.S grade) to 100-mL with de-ionized water. The solution was stored in polypropylene bottle.

Other Solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their analar grade or equivalent grade water soluble salts (or the oxides and carbonates in hydrochloric acid); those of niobium, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure, Johnson Matthey) according to the recommended procedures of Mukharjee [31]. In the case of insoluble substances, special dissolution methods were adopted [32].

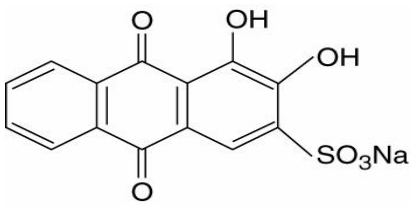
Procedure

To 0·1 – 1·0 mL of a neutral aqueous (pH – 6) solution containing 1 – 300 μg of cadmium in a 10-mL calibrated flask was mixed with 1 : 5 – 1 : 110 fold molar excess of the alizarin red S. reagent solution (preferably 1·0 mL of $1·39 \times 10^{-1}$M) followed by the addition 0·5 – 1·8 mL (preferably 1 mL) of 0·05 M sulfuric acid (or pH 5·5 – 6·1). The mixture was diluted to the mark with de-ionized water. The absorbance was measured at 422 nm against a corresponding reagent blank. The cadmium content in an unknown sample was determined using concurrently prepared calibration graph.

Factors Affecting the Absorbance

Absorption spectra

The absorption spectra of the cadmium-alizarin Red S system in 0·05M H_2SO_4 medium was recorded using the spectrophotometer. The absorption spectra of the cadmium-alizarin Red S is a symmetric curve with the maximum absorbance co-efficient is shown in Fig-1. In all instances measurements were made at 422 nm against a reagent blank. The reaction mechanism of the present method is as reported earlier [33].



Structure of Alizarin red S (1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt.)

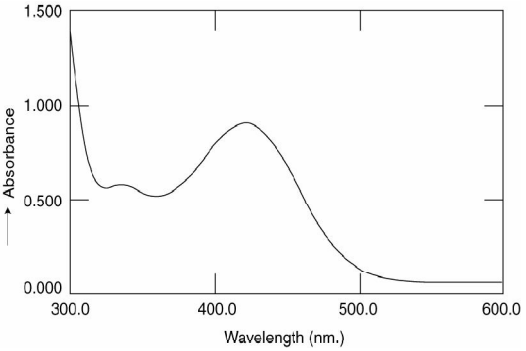


Fig 1. Absorption spectra of the Cadmium-Alizarin red S system and reagent blank (λ_{max} = 422nm) in aqueous solutions.

Effect of Acidity

Of the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied. Sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when the 10-mL of solution (1 μg mL^{-1}) contained, 0·5–1·8 mL of 0·05M sulfuric acid at room temperature (25 ± 5)°C. Outside this range of acidity, the absorbance decreased (Fig.-2).

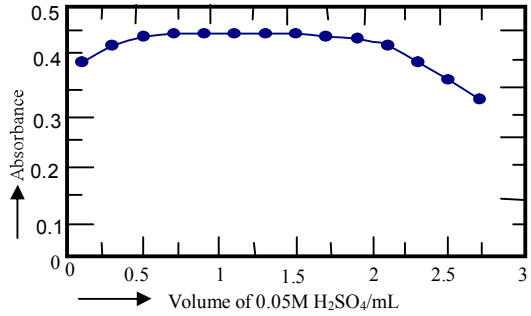


Fig 2. Effect of the acidity on the absorbance of Cd-Alizarin red S system.

Effect of Time

The reaction is instantaneous. Constant maximum absorbance was obtained just after diluting to volume and remained strictly unaltered for 24h (Fig.-3).

Effect of Temperature

The Cadmium-Alizarin Red S system obtained maximum and constant absorbance at room temperature (25 ± 5)°C. Outside this range of temperature, the absorbance decreased.

Effect of Reagent Concentration

Different molar excesses of alizarin Red S were added to fixed metal ion concentration and absorbance were

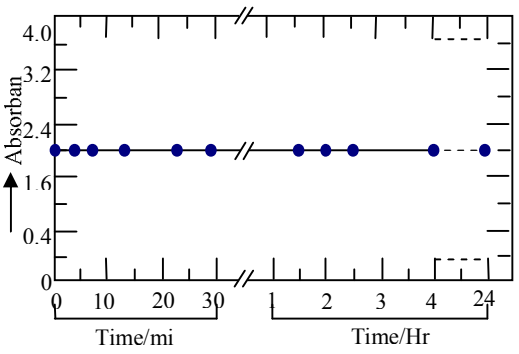


Fig 3. Effect of the time on the absorbance of Cd-Alizarin red S system.

measured according to the standard procedure. It was observed that at the 1 μg mL^{-1} cadmium metal, the reagent molar ratios of 1 : 50 – 1 : 110 produce a constant absorbance of the Cd-chelate (Fig.-4). For all subsequent measurements 1 mL of 1·39 × 10^{-3}M Alizarin red S reagent was added.

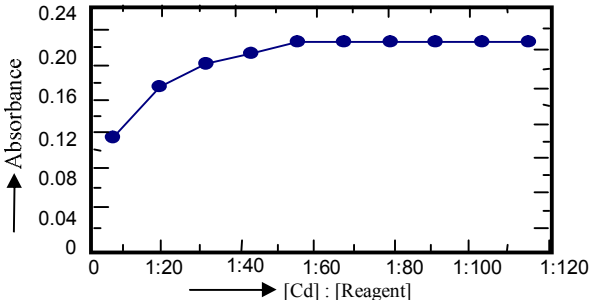


Fig 4. Effect of reagent (Cd : Alizarin red S molar concentration ratio) on the absorbance of Cd-Alizarin red S system.

Calibration Graph (Beer's Law and Sensitivity)

The well-known equation for spectrophotometric analysis in very dilute solution was derived from Beer's law. The effect of metal concentration was studied over 0·1 – 80 μg mL^{-1} distributed in three different sets (0·1 – 1, 0, 1 – 10 and 10 – 80 μg mL^{-1} for convenience of measurement. The absorbance was linear for 0·1 – 40 μg mL^{-1} of cadmium at 422 nm. The molar absorption co-efficient and the sandell's sensitivity [34] were found to be 2·24 × 10^3 L mol^{-1} cm^{-1} and 20 ng cm^{-2} of cadmium, respectively. Of the calibration graph which that showing the limit of linearity range is given in (Fig.-7). The next two was straight-line graphs passing through the origin (Fig.-5, 6).

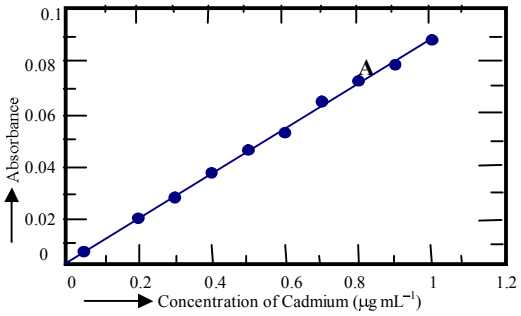


Fig 5. Calibration graph A : 0·1 – 1 μg mL^{-1} of cadmium.

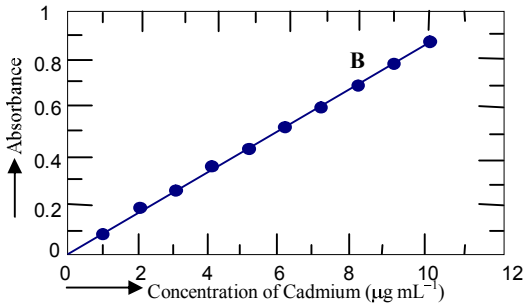


Fig 6. Calibration graph B : 1 – 10 μg mL^{-1} of cadmium.

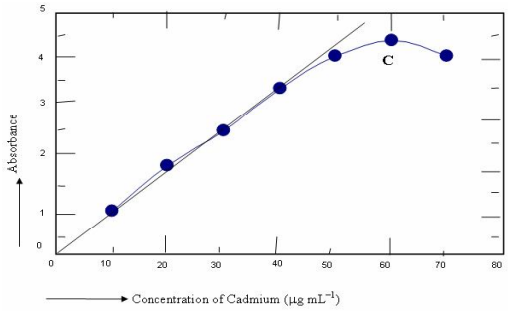


Fig 7. Calibration graph C : 10 – 40 μg mL^{-1} of cadmium.

The selected analytical parameters obtained with the optimization experiments are summarized in table 1.

Precision and Accuracy

The precision of the present method was evaluated by determining different concentrations of cadmium (each analyzed at least five times). The relative standard deviation (n = 5) was 2 – 0% for 1 – 300 μg of cadmium in 10-mL, indicating that this method is highly precise and reproduciable (Table-2). The detection limit (3 S of the blank) and Sandell's Sensitivity (Concentration for 0·001 absorbance unit) for cadmium were found to be 30 ng mL^{-1} and 20 ng cm^{-2}, respectively. Added cadmium was accurately recovered from the other metals (Table-5).

The reliability of our Cd-Chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of a cadmium spike to some environmental water samples was quantitative as shown in (Table-6).

Table 1. Selected analytical parameters obtained with the optimization experiments.

Parameter	Studied range	Selected Value
Wavelength/ λ_{max}(nm)	200 – 800	422
Acidity/M H_2SO_4	0·005 – 0·5	0·01 – 0·1
pH	4·0 – 7·0	5·5 – 6·2
Time/h	0 – 72	24
Temperature/°C	1 – 50	25 ± 5
Reagent (fold molar excess, M : R)	1 : 1 – 1: 110	1 : 50 – 1: 110
Linear range/ μg mL^{-1}	0·01 – 100	0·1 – 40
Detection limit/ng mL^{-1}	1 – 100	30
Reproducibility (% RSD)	0 – 2	0 –2

The method was also tested by analyzing several synthetic mixtures containing cadmium and diverse ions (Table-4). The results of biological analysis by the spectrophotometric method were excellent agreement with those obtain by AAS (Table-7). Hence, the precision and accuracy of the method were found to be excellent.

$$\text{Mean, } \bar{X} = \frac{\Sigma X_1}{N} = \frac{1101{\cdot}5}{11} = 100{\cdot}14$$

Sandard deviation, S =

$$\sqrt{\frac{\Sigma (X_1 - X)^2}{N-1}} = \sqrt{\frac{13{\cdot}53}{11-1}} = \sqrt{1{\cdot}353} = \pm 1{\cdot}16$$

$$\text{Relative standard deviation } (S_r)\ \% = \frac{S}{X} \times 100.$$

$$= \frac{1{\cdot}16 \times 100}{100{\cdot}14}$$

$$= 1{\cdot}16$$

Effect of Foreign Ions

The effect of over 50 ions and complexing agents on the determination of only 1 μg mL^{-1} of cadmium was studied. The criterion for an interference [35] was an absorbance value varying by more than ± 5% from the expected value for cadmium alone. The results are summarized, in (Table-3). As can be seen, A large

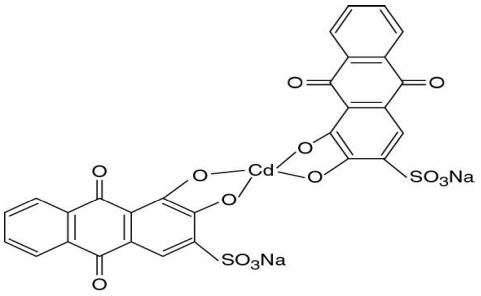
number of ions have no significant effect on the determination of cadmium. The quantities of these diverse ions mentioned (Table-2) were the actual amounts added and not the tolerance limits. The most serious interferences were from V(V), Mo(VI) and Fe(III) ions. Interference from these ions are probably due to complex formation with alizarin Red S.

The greater tolerance limits for these ions can be achieved by using several masking methods. Inorder to eliminate the interference of V(V), Mo(VI) and Fe(III) ions. tartaric acid, EDTA, citric acid or chloride can be used as a masking agent [36]. A 10 fold excess of V(V), Mo(VI) or Fe(III) could be masked with EDTA, tartarate or chloride. During the interference studies, if any precipitate was formed, it was removed by centrifugation. Interference from these three metal ions V(V), Mo(VI) and Fe(III) have been effectively removed by a short single-step ion-exchange separation process, using an

Amberlite XAD-8 resin (100 – 200 mesh) anion exchanger [37].

Composition of the absorbent Complex :

Job's method [38] of continuous variation and the molar-ratio [39] method were applied to ascertain the stoichiometric composition of the complex. A cadmium-Alizarin Red S (1 : 2) complex was indicated by both methods.



Structure of the Cadmium-Alizarin red S complex.

Applications

The present method was successfully applied to the determination of cadmium (II) in a series of synthetic mixtures of various compositions (Table-4) and also in number of real samples, e.g several Certified Reference Materials (CRM) (Table-5). The method was also extended to the determination of cadmium in a number of environmental, biological and soil samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample was analyzed for cadmium content, recoveries in both the 'spiked' (added to the samples before the mineralization or dissolution) and the 'unspiked' samples are in good agreement (Table-6). The results of biological analysis by spectrophotometric method were found to be in excellent agreement with those obtained by AAS (Table-7). The results of soil samples analysis by spectrophotometric method are shown in (Table-8). The precision and accuracy of the method were excellent.

Determination of Cadmium in Synthetic Mixtures :

Several synthetic mixtures of varying compositions containing cadmium and diverse ions of known concentrations were determined by the present method using tartarate or EDTA as a masking agent and the results were found to be highly reproducible. The results are shown in (Table-4). Accurate recoveries were achieved in all solutions.

Determination of cadmium in alloys and Steels.

0·1 g amount of an alloy or steel sample was accurately weighed into a 50-mL flask following a method recommended by parker et al [40]. To it, 10-mL of 20% (V/V) sulfuric acid was added, carefully covering with a watch-glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5-ml of concentrated HNO_3 until all carbides were decomposed. Then 2-mL of 1 : 1 (V/V) H_2SO_4 was added and the solution was evaporated carefully to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25 ± 5)°C. After suitable dilution with de-ionized water, the contents of the flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resulting solution was filtered, if necessary, through a whatman No. 40 filter paper into a 50-mL calibrated flask. The residue was washed with a small volume of hot water and the volume was made up with de-ionized water. A suitable alliquot (0·1 – 1·0 mL) of the above solution was taken into a 10-mL calibrated flask and the cadmium content was determined as described under procedure using EDTA or fluoride as a masking agent. The results are shown in (Table-5). Added cadmium was recovered accurately from the other metals.

Determination of Cadmium in Environmental Waters :

Each filtered (with whatman No.-40) environmental water sample (1000-mL) was evaporated nearly to dryness with a mixture of 5 mL of concentrated H_2SO_4 and 10-mL of concentrated HNO_3 in a fume cupboard following a method recommended by Greenberg et al [41], and was then cooled to room temperature. The residue was then heated with 10-mL of de-ionized water inorder to dissolve the salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made upto the mark with de-ionized water.

An aliquot (1 – 2 mL) of this preconcentrated water sample was pipetted into a 10-mL calibrated flask and

the cadmium content was determined as described under procedure using EDTA or chloride as a masking agent. The analyses of environmental water samples from various sources for cadmium are shown .in (Table-6).

Most spectrophotometric method for the determination of cadmium in natural and sea water require preconcentration of cadmium [40] The concentration of cadmium in natural and sea water is a few ng mL^{-1}. A cadmium concentration of 200 μg L^{-1} is toxic to certain fish. The concentration of cadmium found in U. S. drinking water is from 0·4 – 60 ng mL^{-1} [41].

Determination of Cadmium in Biological Samples

Human Serum (5 – 10 mL) .or urine (10 – 20 mL) sample was taken into a 100-mL flask. A glass bead and 10-mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled following a method recommended by stalhr [42]. 1-mL of concentrated sulfuric acid was added carefully followed by the addition of 1–mL of 70% perchloric acid and heating was continued to dense white fumes, repeating nitric acid addition if necessary. Heating was continued for at least $\frac{1}{2}$h and then cooled. The content of the flask was filtered and neutralized with dilute NH_4OH in presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resultant solution was then filtered and transferred quantitatively into a 10-mL calibrated flask and made upto the mark with de-ionized water.

Suitable aliquots (1 – 2 mL) were transferred into a 10-mL calibrated flask and the cadmium content was determined as described under procedure using EDTA or chloride as a masking agent. The results of biological analysis by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are shown in (Table-7).

Determination of Cadmium in Soil Samples

An air-dried homogenized soil sample (100g) was weighed accurately and placed in a 100-mL flask. The sample was digested in the presence of an oxidizing agent, following the method recommended by Jackson [43]. The content of the flask was filtered through a whatman No. 40 filter paper into a 25-mL calibrated flask and neutralized with dilute NH_4OH solution. It was then diluted upto the mark with de-ionized water.

Suitable aliquots (1 – 2 mL) were transferred into a 10-mL calibrated flask and a calculated amount of 0·05M H_2SO_4 (needed to give a final acidity of 0·0025M H_2SO_4) was added followed by 1 – 2 mL of 0·01% (W/V) tartarate or thiocyanide solution as a masking agent. Cadmium content was then determined by the above procedure and quentified from a calibration graph prepared concurrently. The results are shown in (Table-8).

Conclusion

In this paper a new simple, sensitive, selective and inexpensive method with Cd-Alizarin Red S complex was developed for the determination of cadmium in industrial, environmental, biological and soil samples for continuous monitoring. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP–AES, and ICP–MS, are available for the determination of cadmium at trace level in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables etc. have caused spectrophotometry to remain a popular techniques particularly in laboratories of developing countries with limited budgets. The sensitivity in terms of relative standard deviation of the present method are reliable for the determination of cadmium in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5)°C.

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Table 2. Standard deviation and relative standard deviation of cd(ii) alizarin red s system

Sample No.	Cd(II) taken $\mu g L^{-1}$	Cd(II) Found X_1 μg L^{-1}	Mean $\bar{X}$ μg L^{-1}	$X_1 - \bar{X}$	$\left(x_1 - \bar{X}\right)^2$	Standard deviation ($\pm$ s)	Relative standard deviation (s_r)%
1	100·0	99		1·14	1·29		
2	100·0	98·5		1·64	2·67		
3	100·0	101·		0·86	0·75		
4	100·0	100·5		0·36	0·13		
5	100·0	99·5		0·64	0·41		
6	100·0	101·5		1·36	1·85		
7	100·0	101	100·14	0·86	0·74	± 1·16	1·16
8	100·0	99·5		0·64	0·41		
9.	100·0	98·5		1·64	2·69		
10	100·0	101·5		1·36	1·85		
11	100	101		0·86	0·74		
N = 11		ΣX_1 = 1101·5		$\Sigma X_1 - \bar{X}$ = 11·364	$\Sigma \left(x_1 - \bar{X}\right)^2$		

Table 3. Table of tolerance limits[1] of foreign ions, tolerance ratio. [Species (x)]/ cd (w/w).

Species X	Tolerance ratio X/Cd	Species X	Tolerance ratio X/Cd
Ammonium (I)	100	Chromium (III)	50^{+}
Arsenic (III)	100	Chromium (VI)	25^{+}
Ascorbic Acid	100	Copper (II)	100^{++}
Azide	100	Vanadium (V)	10^{+}
Chloride	500	Selenium (IV)	50^{+}
Fluoride	1000	Selenium (VI)	25
Barium	200	Nickel (II)	25^{+}
Nitrate	500	Iodide	200
nitrite	100	Cesium	500
Bismuth (III)	100	Cerium	200
Citrate	500	Thiocyanate	100
Tartrate	200	Sodium	500
Bromide	100	Zinc	200
Cobalt (II)	50	Mercury (II)	25^{++}
Cobalt (III)	25	Calcium	1000
Iron (II)	50	Potassium	500
Iron (III)	10^{+++}	Molybdenum (VI)	10^{++}
Silver (I)	25^{+++}	Arsenic (V)	50
EDTA	100	Lead (II)	75
Oxalate	500	Thallium (I)	50
Phosphate	100	Gallium	25
Aluminium	100	Tungsten (VI)	50^{+}
Manganese (II)	200	Tungsten (VI)	50^{+}

[*] Tolerance limit was defined as ratio that causes less than 5 per cent interference.

'+' with 10 μgmL^{-1} tartrate

'++' with 10 μgmL^{-1} EDTA

'+++' with 10 μgmL^{-1} chloride.

Table 4. Determination of cadmium in some synthetic mixtures.

Sample No.	Composition of Mixture/ μg mL^{-1}	Cadmium/μg mL^{-1}		Recovery ± SD[b]%
		Added	Found[a]	
A	Cd	0·50	0·49	98 ± 0·5
		1·00	0·99	99 ± 0·2
B	As in A + $Mn^{2+}_{(25)}$ + $Na_{(25)}$ + $EDTA_{(10)}$	0·50	0·49	98 ± 0·3
		1·00	1·01	101 ± 0·7
C	As in B + $Hg^{2+}_{(50)}$ + $Ni^{2+}_{(50)}$ + $EDTA_{(10)}$	0·50	0·53	106 ± 1·0
		1·00	1·02	103 ± 0·8
D	As in C + $Zn_{(25)}$ + $K_{(25)}$	0·50	0·54	108 ± 1·2
		1·00	1·04	104 ± 1·0
E	As in D + $Ba_{(25)}$ + $Br^{-}_{(50)}$	0·50	0·56	112 ± 1·3
		1·00	1·08	108 ± 1·5

[a]Average of five analyses of each sample.

[b]The measure of precision is the standard deviation (SD).

Table 5. Determination of cadmium in Standard Bronze, Brass and Steel Sample Solutions.

Sample No.	Certified Reference Material (Composition, %)	Cd Spiked		Recovery ± S[b] (%)
		Added (μg mL^{-1})	Found[a] (μg mL^{-1})	
1.	BAS – 32a, Al-Bronze Alloy	0·10	0·102	100 ± 0·2
	Cu = 85·9, Zn = 0·94, Mn = 0·27	0·50	0·48	96 ± 0·5
	Fe = 2·67, Ni = 1·16, Al = 8·8			
2.	BAS – 10g HT Brass	0·10	0·103	103 ± 0·6
	Cu = 60·0, Fe = 1·56, Sn = 0·31	0·50	0·49	98 ± 0·5
	Pb = 3·34, Zn = 32·0. Mn = 1·36			
3.	BAS – 646, High speed steel.	0·10	0·102	100 ± 0·2
	Te = 0·90, Cr = 4·55	0·50	0·50	100 ± 0·0
	Mo = 4·95, V = 1·99			
4.	Brass – 5f	0·10	0·105	105 ± 1·6
	Cu = 70·8, Zn = 24·2, Sn = 1·85	0·50	0·54	108 ± 0·8
	Pb = 2·52, Fe = 0·31, P = 0·06			

[a]Values given represent the average of triplicate determination.

[b]The measure of precision is the standard deviation (S).

Table 6. Determination of cadmium in some environmental water samples.

Sample		Cadmium/μg L^{-1}		Recovery ± S (%)	S_r^b (%)
		Added	Found[a]		
	Tap water	0	3·5	± 0·2	0·25
		100	105·0	99 ± 0·1	0·24
		500	504·0	100 ± 0·3	0·31
	Pond water	0	5·0		
		100	107·0	100·9 ± 0·4	0·24
		500	508·0	100 ± 0·0	0·00
	Rain water	0	5·5		
		100	105·5	99·4 ± 0·3	0·37
		500	504·0	100 ± 0·5	0·38
River water	(i) Burigonga (Upper stream)	0	12·0		
		100	120·0	99 ± 0·2	0·29
		500	522·0	100·2 ± 0·5	0·31
	(ii) Burigonga (Lower stream)	0	13·5		
		100	114·8	100·1 ± 0·3	0·21
		500	519·0	100 ± 0·5	0·00
Sea water	(i) Bay of Bengal (Upper)	0	15·0		
		100	113·0	98 ± 0·3	0·45
		500	515·0	100·3 ± 0·6	0·22
	(ii) Bay of Bengal (lower)	0	12·0		
		100	114·0	100·9 ± 0·3	0·25
		500	518·0	101 ± 0·6	0·17
Drain water	(i) Berger paints (Dhaka)	0	120		
		100	225	100·8 ± 0·5	0·28
		500	640	99·5 ± 0·8	0·34
	(ii) Asian paints	0	30		
		100	135	100·0 ± 0·00	0·26
		500	540	100·7 ± 0·1	0·32

[a]Average of five replicate determinations.

[b]The measure precision is the relative standard deviation (Sr).

Table 7. Concentration of cadmium in blood and urine sample.

Serial No.	Sample	Cadmium/μgL^{-1}		Sample Source
		AAS (n = 5)	Proposed method (n = 5)	
1	Blood	230·5	231 ± 1·3	Kidney disease patient (male)
	Urine	60	58 ± 1·0	
2	Blood	350	348 ± 1·5	Prostatic cancer Patient
	Urine	320	319 ± 0·8	
3	Blood	32	35 ± 1·0	Hypertension Patient (Female)
	Urine	25	23 ± 1·2	
4	Blood	4	3·2 ± 0·5	Normal Adult (Male)
	Urine	2	1·2 ± 0·4	

Table 8. Determination of cadmium in some surface soil samples.[ab]

Serial No.	Cadmium ($\mu g\ g^{-1}$)	Sample Source
S_1^C	2·1 ± 0·7	Traffic Soil (Saidabad Bus Terminal Dhaka)
S_2	0·60 ± 0·2	Agriculture Soil (Kamrangi char, Dhaka)
S_3	1·2 ± 0·5	Road Side Soil (Chittagong–Dhaka Highway)
S_4	1·8 ± 0·8	Industrial Soil (Asian Paints (Bd) Ltd.)
S_5	4·0 ± 1·0	Contaminated Soil (Steel Mill Area)
S_6	0·35 ± 0·05	Marine Soil (Bay of Bengal)

[a]Average of five analyses of each sample.

[b]The measure of precision is the standard.

[c]Composition of the soil samples : C, N, P, K, Na, Ca, Mg, Cu, Pb, NO_3^-, Zn, SO_4, Mn, Mo, Co, etc.