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# A simple spectrophotometric determination of trace level cadmium using 1,5-diphenylthiocarbazone in cationic micellar media

**Humaira Khan[1], M.Jamaluddin Ahmed[1,2]*, M.Iqbal Bhanger[1]**

[1]National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, (PAKISTAN)

[2]Department of Chemistry, University of Chittagong, Chittagong-4331, (BANGLADESH)

Fax : 00880-31-726310

E-mail : mjahmed_bd@yahoo.com

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## ABSTRACT

A very simple, selective and highly sensitive direct spectrophotometric method is presented for the rapid determination of cadmium at ultra-trace level using 1,5-diphenylthiocarbazone (dithizone) as a new micellar spectrophotometric reagent($\lambda_{max}$=500nm) in aqueous solution. The presence of micellar system avoids the previous steps of solvent extraction and reduces the cost, toxicity while enhancing the sensitivity, selectivity and the molar absorptivity. The molar absorptivities of the cadmium-dithizone complex formed in the presence of the cationic cetyltrimethylammonium bromide(CTAB) surfactant are almost ten times the value observed in the standard method and the maxima of the absorption are shifted about 20 nm when compared with the standard method, resulting in an increase in the sensitivity of the method. The reaction is instantaneous and the absorbance remains stable for over 24h. The average molar absorption coefficient and Sandell's sensitivity were found to be $1.2\times0^5$ L $mol^{-1}cm^{-1}$ and $5ngcm^{-2}$ of Cd, respectively. Linear calibration graphs were obtained for 0.01-10mg $L^{-1}$ of Cd; the stoichiometric composition of the chelate is 1:2(Cd: dithizone). The method is characterized by detection limit of 3μg $L^{-1}$ of Cd. The interference from over 60 cations, anions and complexing agents has been studied at 1mg $L^{-1}$ of Cd. The method was successfully used in the determination of cadmium in several standard reference materials(alloys and steels, soil, bovine liver and human hair), environmental water samples(potable and polluted), biological samples(human blood and urine), soil samples and complex synthetic mixtures. The method has high precision and accuracy(s=±0.01 for 0.1mg $L^{-1}$). 

## INTRODUCTION

Cadmium is an extremely toxic metal and has been responsible for a number of deaths[1]. It is also responsible for pancreatic cancer even at trace levels[2]. Increasing cadmium pollution of the environment, resulting from the growth of cadmium based industries and the use of fossil fuels, poses danger to public health[3]. On the other hand, the nutrient role of the metal ion is also recently recognized[4]. Therefore, the separation, preconcentration and determination of cadmium in biological and environmental matrices have become subjects of great interest.

Dithizone(diphenyltiocarbazone, $H_2Dz$) is an organic colorimetric reagent that provides basis of sensitive methods for the determination of large number of metal ion[5]. Metal ions combine with dithizone to yield non-polar colored complexes whose colors differ significantly from dithizone. These non-polar complexes are generally extracted into solvents like chloroform and carbon tetrachloride. Extraction spectrophotometry using dithizone as a color-developing reagent is sensitive but suffers from several disadvantages. It is time-consuming and tedious and involves the use of chlorinated solvents. Carbon tetrachloride and chloroform had been used as solvents for these extractions, which

can be classified as toxic and as environmental pallutants[6]. They have been listed as carcinogens by the ATSDR[7] and EPA[8] This problem has been overcome in recent years by introducing a hydrophobic micellar system generated by a surfactant similar to that employed in phase-transfer reactions[9]. Micellar systems are convenient to use because they are optically transparent, readily available, relatively non-toxic and stable[10]. Nevertheless, the addition of surfactants at concentrations above the CMC to an aqueous medium to form a miceller solution is the most commonly preferred procedure today. Micelles enhance the solubility of organic compounds in water by providing local nonpolar environments. This phenomenon of micellar solubilization has been used in the development of many new methods and in modification of existing methods of analysis[11,12]. The use of micelle formation is promising for improving the analytical performance of the spectrophotometric procedures[13]. Organic micellar media are very useful in analytical applications, including the improved analyte sensitivity in UV-visible spectrophotometric methods[14]. Especially, the surfactants have been used to improve UV-visible spectrophotometric determination of metal ions with complexing agents. Generally, the metal-chelate complexes formed in the surfactant media are more stable than those formed in the absence of surfactant[15].

The aim of the present study is to develop a simpler direct spectrophotometric method for the trace determination of cadmium with dithizone in the presence of inexpensive cationic micelles, such as cetyltrimethylam monium bromide(CTAB), in aqueous solutions. This method does not requires a solvent-extraction step; hence, the use of carcinogenic carbon tetrachloride or chloroform is avoided. The method described here has recorded for the first time the non-extractive direct spectrophotometric determination of cadmium in aqueous media without the recourse of any "clean-up" step. This method is far more selective, non-extractive, simple and rapid than all of the existing spectrophotometric methods[16-23]. The method is based on the reaction of slightly absorbent dithizone in acidic solution with cadmium to produce highly absorbent brownish-red-chelate product, followed by the direct measurement of the absorbance in aqueous solution. With suitable masking, the reaction can be made highly selective.

## EXPERIMENTAL

### Apparatus

A. Perkin Elmer(Germany)(Model:Lambda-2) double-beam UV/VIS-spectrophotometer and a WTW inolab(Germany)(Model:Level-1) pH-meter with a combination of electrodes were used for measurements of the absorbance and pH, respectively. A Hitachi Ltd., Model 180-50, S.N.5721-2 atomic absorption spectrophotometer with a deuterium lamp back ground corrector, equipped with graphite furnace GA-3, with cadmium hollow cathode lamps of Hitachi, and a Hitachi Model 056 recorder was used for recording analytical data of the metal under investigation. The experimental conditions were: slit width, 1.3nm; lamp current, 7.5 mA; wavelength, 228.8nm; cuvette, cup; carrier gas, 200mL $min^{-1}$; sample volume, 10µL.

### Reagents and solutions

All 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 vessals were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated $HNO_3$ and rinsed several times with de-ionized water. Stock solutions and environmental water samples(1000mL each) were kept in polypropylene bottles containing 1mL of concentrated nitric acid. Biological fluids were collected in polyethane bottles from affected persons. Immediately after collection, they were stored in a salt-ice mixture and later, at the laboratory, were kept at $-20^0C$[24]. More rigorous contamination control was used when one cadmium levels in the specimens were low.

### Cetyltrimethylammonium bromide (CTAB) solution 0.3M

A 500mL of CTAB solution was prepared by dissolving 54.67g of pure cetyltrimethylammonium bromide(E.Merck Darmstadt, Germany) in 250-300mL in doubly distilled de-ionized water, sonicated for 30min and diluted upto the mark with de-ionized water when it became transparent.

### 1,5-Diphenylthiocarbazone(Dithizone) $1.95\times10^{-3}$M

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Prepared by dissolving the requisite amount(0.05%) of diphenylthiocarbazone(E.Merck, Darmstadt) in a known volume of 2-propanol(Fluka, Germany). More dilute solutions of the reagent were prepared as required.

### Cadmium standard solutions($8.89\times10^{-3}$M)

A 100 mL stock solution(1mg/mL$^{-1}$) of cadmium was prepared by dissolving 274.41 mg of cadmium nitrate 4-hydrate[$Cd(NO_3)_2.4H_2O$](E.Merck, Germany) in de-ionized water. Aliquots of this solution were standardized with EDTA using Xylenol Orange as an indicator. More dilute standard solutions were prepared from this stock solution, as and when required.

### Tartrate solution

A 100mL stock solution of tartrate(0.1% w/v) was prepared by dissolving 100mg of potassium sodium tartrate tetrahydrate(E.Merck, Darmstadt) in(100mL) de-ionized water.

### Aqueous ammonia solution

A 100mL solution of aqueous ammonia was prepared by diluting 10mL of concentrated $NH_3$(28-30%) ACS grade to 100mL with de-ionized water. The solution was stored in a polypropylene bottle.

### EDTA solution

A 100mL stock solution of EDTA(0.1% w/v) was prepared by dissolving 128mg of ethylenediaminetetra acetic acid, disodium salt dehydrate(E.Merck, Darm stadt) in (100mL) de-ionized water.

### 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. In the case of insoluble substances, a special dissolution method was adopted[25].

### Procedure

A series of standard solutions of a neutral aqueous solution containing 0.1-100µg of cadmium in a 10mL calibrated flask was mixed with 0.5-1.6mL (preferably 1.0mL) of 0.01M $H_2SO_4$ and 175-350 fold molar excess of a dithizone solution(preferably 1mL of $1.95\times10^{-3}$M) followed by the addition 2-4mL (preferably 3 mL) of 0.3M CTAB. The mixture was diluted to the mark with de-ionized water. The absorbance was measured at 500nm against a corresponding reagent blank. The cadmium content in an unknown sample was determined using a concurrently prepared calibration graph.

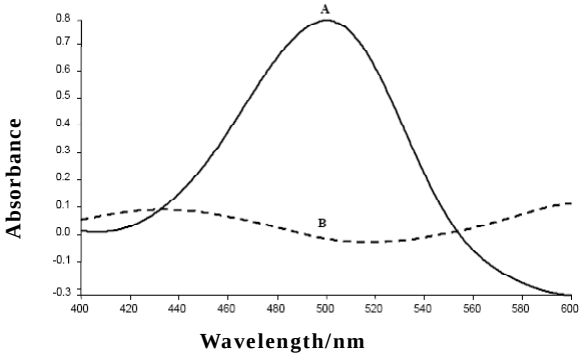


**Figure 1 : A and B absorption spectra of Cd-dithizone system and reagent blank ($\lambda_{max}$=500nm ) in cationic micellar media of cetyltrimethylammonium bromide**

## RESULTS AND DISCUSSION

### Factors affecting the absorbance

### Absorption spectra

The absorption spectra of the cadmium-dithizone system in a $1\times10^{-2}$M sulfuric acid medium were recorded using a spectrophotometer. The absorption spectra of the cadmium-dithizone is a symmetric curve with the maximum absorbance at 500 nm and an average molar absorption coefficient of $1.2\times10^5$L mol$^{-1}$cm$^{-1}$(Figure 1). The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 500nm against a reagent blank. The reaction mechanism of the present method is as reported earlier[26].

### Effect of surfactant

Of the various surfactants[nonionic {polyoxyethyle nedodecylether(Brij-35), polyoxyethylene sorbitan monopalmitate(Tween-40), polyoxyethylene sorbitan mono-oleate(Tween-80), TritonX-100}; cationic {cetyltrimethylammonium bromide(CTAB)}; and anionic{cetylpyridinum chloride(CPC); and anionic sodium dodecyl sulfate(SDS)}] studied, CTAB was found to be the best surfactant for the system. In a 0.3M CTAB medium, however, the maximum absorbance was observed; hence, a 0.3M CTAB solution was used in the determination procedure.

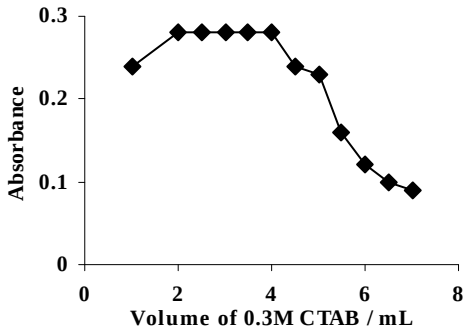


**Figure 2: Effect of a surfactant on the aborbance of the Cd-dithizone system**

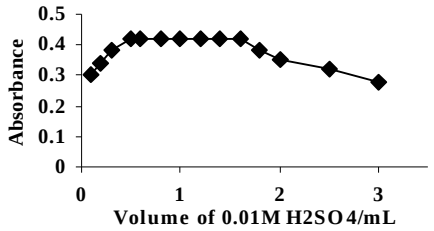


**Figure 3: Effect of the acidity on the absorbance of the Cd-dithizone system**

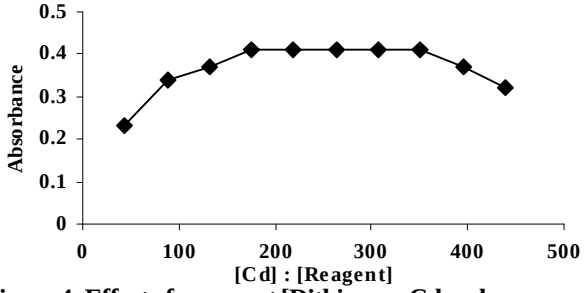


**Figure 4: Effect of a reagent [Dithizone : Cd molar concentration ratio] on the absorbance of the Cd-dithizone system.**

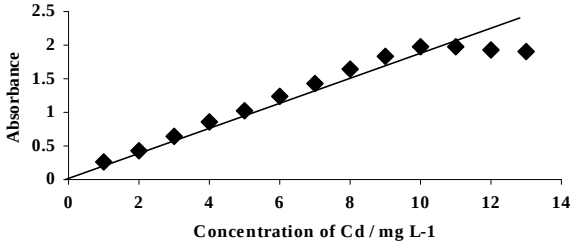


**Figure 5: Calibration graph: C, 1-10mg $L^{-1}$ of Cd**

Different volumes of 0.3M CTAB were added to a fixed metal ion concentration, and the absorbance was measured according to the standard procedure. It was observed that at 1mg $L^{-1}$ Cd-chelate metal, 2-4mL of 0.3M CTAB produced a constant absorbance of the Cd-chelate. Outside this range of surfactant the absorbance decreased (Figure 2). For all subsequent measurements, 3mL of 0.3M CTAB was added.

## 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 a 10 mL of solution(1mg $L^{-1}$) contained 0.5-1.6mL of $1\times10^{-2}$ M sulfuric acid(or pH 2.5-3.07) at room temperature($25\pm5^0$C). Outside this range of acidity, the absorbance decreased (Figure 3). For all subsequent measurements, 1mL of $1\times10^{-2}$ M sulfuric acid(or pH 2.63) was added.

## Effect of time

The reaction is very fast. Constant maximum absorbance was obtained just after dilution to volume, and remained strictly unaltered for 24h.

## Effect of temperature

The absorbance at different temperatures, 0-$50^0$C, of a 10mL solution(1mg $L^{-1}$) was measured according to the standard procedure. The absorbance was found to be strictly unaltered throughout the temperature range of 10-$40^0$C. Therefore, all measurements were performed at room temperature ($25\pm5^0$C).

## Effect of the reagent concentration

Different molar excesses of dithizone were added to a fixed metal-ion concentration, and the absorbances were measured according to the standard procedure. It was observed that at 0.1mg $L^{-1}$ Cd metal(optical path length, 1cm), reagent molar ratios 1:175 and 1:350 produced a constant absorbance of the Cd-chelate (Figure 4). The effect of reagent at different concentration of Cd(1mg $L^{-1}$) was also studied but similar effect was observed. For all subsequent measurements, 1mL of $1.95\times10^{-3}$M dithizone reagent was added.

## Calibration graph (Beer's law and sensitivity)

The effect of metal concentration was studied over 0.01-100mg $L^{-1}$, distributed in four different sets (0.01-0.1, 0.1-1, 1-10, 10-00mg/$L^{-1}$) for convenience of the measurement. The absorbance was linear for 0.01-10mg $L^{-1}$ of cadmium at 500nm. From the slope of the calibration graph, the average molar absorption coefficient was found to be $1.2x10^5$ $Lmol^{-1}/cm^{-1}$. The Sandell's

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sensitivity[27](concentration for 0.001 absorbance unit) was found to be 5ng $cm^{-2}$. Of the three calibration graphs, the one showing the limit of the linearity range is given in figure 5; the next two were straight-line graphs passing through the origin($R^2$=0.9965). The selected analytical parameters obtained with the optimization experiments are summarized in TABLE 1.

**TABLE 1 Selected analytical parameters obtained with optimization experiments**

| Parameter | Studied range | Selected value |
|---|---|---|
| Wavelength, λ/nm | 200-800 | 500 |
| Acidity/M $H_2SO_4$ | $1 \times 10^{-4}$-$3\times10^{-3}$ | $5\times10^{-4}$-$1.6\times10^{-3}$ (preferably $1\times10^{-3}$M) |
| pH | 1-4 | 2.5-3.07 (preferably 2.63) |
| Surfactant/M Cetyltrimethylammonium bromide (CTAB) | 0-0.21 | 0.06-0.12 (preferably 0.09) |
| Time/h | 0-24 | 1min-24h (preferably 5min) |
| Temperature/°C | 0-60 | 10-40 (preferably 25± 5) |
| Reagent (fold molar excess, M:R) | 1:1-1:500 | 1:175-1:350 (preferably 1:220) |
| Linear range/mg $L^{-1}$ | 0.001-100 | 0.01-10 |
| Molar absorption coefficient/L $mol^{-1}$ $cm^{-1}$ | $1.0\times10^5$-$1.4\times10^5$ | $1.2\times10^5$ |
| Sandell's sensitivity/ng $cm^{-2}$ | 1-100 | 5 |
| Detection limit/μg $L^{-1}$ | 1-100 | 3 |
| Reproducibility(%RSD) | 0-5 | 0-2 |
| Correlation coefficient ($R^2$) | 0.991-0.998 | 0.9965 |

## Effect of foreign ions

The effect of over 60 cations, anions and complexing agents on the determination of only 1 mg $L^{-1}$ of Cd was studied. The criterion for interference[28] was an absorbance value varying by more than ±5% from the expected value for Cd alone. There was no interference from the following: 1000 fold amounts of ascorbic acid, thiocyanide or bromide; a 200-fold amounts of EDTA, chloride, iodide, nitrate, sulfate, sulfite or ammonium(I). EDTA prevented the interference of 200-fold aluminum, 100-fold of indium, 50-fold of lead(II), 25-fold of cobalt (III & IV) or copper(II), 20-fold of bismuth (III) or palladium(II), 10-fold of chromium(VI), cerium (III & IV), manganese or zinc. EDTA & ascorbic acid remove the interference of 10-fold of molybdenum. A 10-fold excess of Fe(II & III) could be masked with ascorbic acid and tetra sodium pyrophosphate. Bromide could be masked 5-fold excess of mercury(II). However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned in TABLE 2.

**TABLE 2 : Tolerance limits of foreign ions[a]**

| Species x | Tolerance ratio[b] x/Cd | Species x | Tolerance ration[b] x/Cd |
|---|---|---|---|
| Ascorbic acid | 1000 | Cobalt(II&III) | 25[c] |
| Ammonium(I) | 100 | Calcium | 100 |
| Azide | 25 | Cerium(III&IV) | 10[c] |
| Acetate | 50 | Cesium | 50 |
| Bromide | 1000 | Copper (II) | 25[c] |
| Chloride | 200 | Indium (III) | 100[c] |
| Carbonate | 200[c] | Iron (II) | 10[d+e] |
| EDTA | 200 | Iron (III) | 10[d+e] |
| Iodide | 200 | Lead (II) | 50[c] |
| Nitrate | 200 | Lanthanum | 50 |
| Phosphate | 100 | Manganese(II) | 100 |
| Sulfite | 200 | Manganese(VII) | 10[c] |
| Sulfate | 200 | Mercury (II) | 5[d] |
| Tartrate | 100 | Molybdenum(VI) | 10[c+d] |
| Thiocyanide | 1000 | Magnesium | 100 |
| Ammonium(I) | 200 | Nickel (II) | 100 |
| Antimony (III) | 100 | Potassium | 100 |
| Aluminum | 20 | Palladium(II) | 20[c] |
| Arsenic (III) | 100 | Strontium | 100 |
| Arsenic (V) | 100 | Silver(I) | 100 |
| Beryllium (II) | 100 | Sodium | 200 |
| Barium | 100 | Thallium(I) | 100 |
| Bismuth (III) | 20[c] | Tin (II) | 100 |
| Chromium (III) | 100 | Vanadium(V) | 10 |
| Chromium (VI) | 10[c] | Zinc | 10[c] |

**[a]Tolerance limit was defined as ratio that causes less than 5 percent interference; [b]Tolerance ratio, [Species (x)]/Cd (w/w); [c]With 25μg $mL^{-1}$ EDTA; [d]With 25μg $mL^{-1}$ ascorbic acid; With 25μg $mL^{-1}$ tetra sodium pyrophosphate; [e]With 25μg $mL^{-1}$ bromide**

## Composition of the absorbance.

Job's method[29] of continuous variation and the molar-ratio[30] method were applied to ascertain the stoichiometric composition of the complex. A Cd-dithizone (1:2) complex was indicated by both methods.

## 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 0.1-100μg of Cd in 10mL, indicating that this method is highly precise and reproducible. The detection limit[31](3s of the blank) and Sandell's sensitivity[27](concentration for 0.001 absorbance unit) for cadmium were found to be 3μg $L^{-1}$ and 5ng $cm^{-2}$, respectively. The results of the total cadmium in a number of real samples were in good agreement with the expected values. The reliability of our Cd-che-

**TABLE 3 : Determination of cadmium in some synthetic mixtures**

| Samp. | Composition of mixtures/mg $L^{-1}$ | Cadmium/$mgL^{-1}$ | | Recovery ± $s^b$,(%) |
|---|---|---|---|---|
| | | Added | Found[a] | |
| A | Cd | 0.50 | 0.49 | 98±0.4 |
| | | 1.00 | 1.00 | 100± 0.0 |
| B | As in A+Ca (20)+Na (20)+K(20) | 0.50 | 0.495 | 99±0.5 |
| | | 1.00 | 0.99 | 99 ± 0.3 |
| C | As in B+$Cr^{3+}$(20)+$As^{3+}$ (20)+$NO_3^-$ (20) | 0.50 | 0.50 | 100 ± 0.0 |
| | | 1.00 | 0.98 | 98 ± 0.6 |
| D | As in C+$Mg^{2+}$ (20)+$Sn^{2+}$ (20)+Mg (20) | 0.50 | 0.52 | 104 ± 0.7 |
| | | 1.00 | 1.03 | 103 ± 0.6 |
| E | As in D+Ba (20)+ $Co^{2+}$(20)+EDTA (50) | 0.50 | 0.54 | 108 ± 1.5 |
| | | 1.00 | 1.06 | 106 ± 1.0 |

[a]Average of five analyses of each sample. [b]The measure of precision is the standard deviation

**TABLE 4 : Determination of cadmium in certified reference material**

| Certified reference material (Composition) | Cadmium | | R.S.D. (%) |
|---|---|---|---|
| | Certified value | Found (n=5) | |
| BCR-397. Human hair (Cd, Hg, Pb, Se and Zn) | 0.521[a]±0.024 | 0.515[a]±0.021 | 1.2 |
| BCR-185 R, Bovine liver (As, Cd, Cu, Mn, Pb, Se and Zn) | 0.544[a]±0.017 | 0.539[a]±0.015 | 1.5 |
| BCR-483, Soil amended with sewage sludge(Cu, Cd, Cr, Ni, Pb and Zn) | 24.3[a]±1.3 | 24.15[a]±1.8 | 1.6 |
| GBW 01620- High-tensil steel[c] (Cd, Ag, As, Bi, Ca, Ga, In, Mg, Pb, Sb, Sn, Te, Ti and Zn) | 4.60[b] | 4.48[b]±0.05 | 2.2 |

[a]Value in mg $kg^{-1}$ [b]Value in percentage, [c]This CRM obtained from Beijing NCS Analytical Instruments Co. LTD., China

late procedure was tested by recovery studies. The average percentage recovery obtained for the addition of a cadmium spike to some environmental water samples was quantitative, as shown in TABLE 5. The method was also tested by analyzing several synthetic mixtures containing cadmium and diverse ions. The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by AAS (TABLE 6). Hence, the precision and accuracy of the method were excellent.

## Applications

The present method was successfully applied to the determination of cadmium in a series of synthetic mixtures of various compositions(TABLE 3), and also in a number of real samples, e.g. several standard reference materials, e.g. alloys and steels, soil, bovine liver and human hair (TABLE 4). The method was also extended to the determination of cadmium in a number of environmental, biological, food and soil samples. In view

**TABLE 5 : Determination of cadmium in some environmental water samples**

| Sample | | Cadmium/$\mu gL^{-1}$ | | Recovery ±s(%) | $s_r$[b] (%) |
|---|---|---|---|---|---|
| | | Added | Found[a] | | |
| Tap water | | 0 | 0.0 | | |
| | | 100 | 102.0 | 102±0.1 | 0.31 |
| | | 500 | 504.0 | 100.8±0.2 | 0.25 |
| Well water | | 0 | 4.5 | | |
| | | 100 | 103.0 | 98.6±0.4 | 0.35 |
| | | 500 | 505.0 | 100±0.2 | 0.29 |
| River water | Indus (upper stream) | 0 | 14.8 | | |
| | | 100 | 115.0 | 100.2±0.5 | 0.36 |
| | | 500 | 514.8 | 100 ± 0.0 | 0.00 |
| | Indus (lower stream) | 0 | 15.5 | | |
| | | 100 | 115.0 | 99±0.5 | 0.39 |
| | | 500 | 518.0 | 100.5±0.6 | 0.29 |
| Sea water | Arabian sea (upper) | 0 | 4.0 | | |
| | | 100 | 104.0 | 100±0.0 | 0.00 |
| | | 500 | 506.0 | 100.4±0.5 | 0.17 |
| | Arabian sea (lower) | 0 | 5.5 | | |
| | | 100 | 106.0 | 100.5±0.6 | 0.27 |
| | | 500 | 506.0 | 100±0.2 | 0.18 |
| Lake water[c] | | 0 | 33.5 | | |
| | | 100 | 135.0 | 101±0.6 | 0.45 |
| | | 500 | 540.0 | 101.2±0.5 | 0.23 |
| Drain water (Pulp industry)[b] | | 0 | 53.5 | | |
| | | 100 | 155.0 | 100.9±0.7 | 0.32 |
| | | 500 | 560.0 | 101.2±0.8 | 0.46 |

[a]Average of five replicate determinations; [b]The measure precision is the relative standard derivation ($s_r$); [c]The Manchar Lake, Hyderabad, Sindh; [d]Oriented Pulp Industry, Karachi.

**TABLE 6 : Determination results for human fluids**

| S. no. | Sample | Cadmium/$\mu gL^{-1}$ | | Sample source[b] |
|---|---|---|---|---|
| | | AAS | Proposed method[a] | |
| 1 | Blood | 55.7 | 56.5±1.5 | Kidney disease patient (Female) |
| | Urine | 13.9 | 15.8±1.2 | |
| 2 | Blood | 48.8 | 49.5±1.3 | Hypertension patient (Male) |
| | Urine | 12.2 | 12.5±1.2 | |
| 3 | Blood | 21.6 | 22.3±1.4 | Tuberculosis patient (Male) |
| | Urine | 5.5 | 5.8±1.0 | |
| 4 | Blood | 18.7 | 19.8±1.5 | Smoker (Male) |
| | Urine | 4.6 | 5.1±1.2 | |
| 5 | Blood | 12.8 | 13.5±1.3 | Traffic constable (Male) |
| | Urine | 3.5 | 3.8±1.0 | |
| 6 | Blood | 7.2 | 6.8±1.4 | Normal adult (Male) |
| | Urine | 1.8 | 1.7±0.5 | |

[a]Average of five replicate determination ± s; [b]Samples were from LUMHS Hospital, Hyderabad

of the unknown composition of environmental water samples, the same equivalent portions of each sample were analyzed for cadmium content; the recoveries in both the "spiked" (added to the samples before the mineralization or dissolution) and the "unspiked" samples are in good agreement (TABLE 5). The results of bio-

**TABLE 7 : Content of cadmium in soil samples**

| S. no. | Cadmium/mgkg$^{-1}$ | | Sample source |
|---|---|---|---|
| | Fond(n=5) | RDS, % | |
| $S_1$[a] | 1.35 | 1.5 | Traffic soil (Hyderabad bus terminal) |
| $S_2$ | 0.711 | 0.8 | Agricultural soil (Dadu district) |
| $S_3$ | 10.9 | 1.8 | Lake soil (The Manchar Lake Hyderabad) |
| $S_4$ | 1.58 | 1.2 | Industrial soil (Pakistan oil mill, Hyderabad) |
| $S_5$ | 0.39 | 0.5 | Marine soil (Arabian Sea) |

[a]**Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu, Co, Mn, Zn, Fe, Mo, Pb, Cd, Hg, Mo, $NO_3^-$, $Cl^-$ and $SO_4^{2-}$ etc.**

logical analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS(TABLE 6). The results of soil-samples analyses by the spectrophotometric method were found to be highly reproducible(TABLE 7).

## 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 EDTA or ascorbic acid as a masking agent; and the results were found to be highly reproducible. The results are shown in TABLE 3. Accurate recoveries were achieved in all solutions.

## Determination of cadmium in alloys and steels, soil, bovine liver and human hair (certified reference materials)

A 0.1g amount of a alloy and steel, soil, bovine liver or human hair sample was accurately weighed and placed in a 50-mL Erlenmeyer flask following a method recommended by Parker[32]. To this, 10mL of concentrated $HNO_3$ and 5mL of concentrated HCl was added, carefully covering the flask with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after the addition of 5mL of concentrated $HNO_3$, until all carbides were decomposed. The solution was evaporated carefully to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature(25±5$^0$C). After suitable dilution with de-ionized water, the contents of the Erlenmeyer flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute $NH_4OH$ solution. The resulting solution was filtered, if necessary, through a Whatman no. 40 filter paper into a 25-mL calibrated flask. The residue was washed with a small volume of hot water and the volume was made up to the mark with de-ionized water.

A suitable aliquot(1-2mL) of the above solution was taken into a 10-mL calibrated flask and cadmium content was determined as described under a procedure, using EDTA or ascorbic acid as masking agent. The results are shown in TABLE 4. The certified cadmium value in alloys and steels, soil, bovine liver and human hair were obtained from a calibration graph. The results for total cadmium were in good agreement with certified values (TABLE 4).

## Determination of cadmium in environmental waters

Each filtered (with Whatman no. 40) environmental water sample(100mL) evaporated nearly to dryness with 10mL of concentrated $HNO_3$ in a fume cupboard following a method recommended by Mitra[31] and was heated with 10mL of de-ionized water in order to dissolves the salts. The solution was then cooled and neutralized with dilute $NH_4OH$ solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2mL) of this solution was pipetted into a 10-mL calibrated flask, and the cadmium content was determined as described under a procedure using EDTA or ascorbic acid as a masking agent. The analysis of environmental water samples from various sources for cadmium and the results are given in TABLE 5.

Most spectrophotometric methods for the determination of cadmium in natural water and sea water require the pre-concentration of cadmium[33]. The concentration of cadmium in natural water and sea water is a few μg $L^{-1}$. The concentration of cadmium found in U.S. drinking water is from 0.4-60μg $L^{-1}$[33].

## Determination of cadmium in biological samples

Human blood (5-10 mL) or urine (10-20mL) was collected in polyethane bottles from the affected persons. Immediately after collection, they were stored in a salt-ice mixture and later, at the laboratory, were kept at -20$^0$C. The samples were taken into a 100-mL micro-Kjeldahl flask. A glass bead and 10mL of concentrated nitric acid were added and the flask was placed

on the digester under gentle heating following a method recommended by Stahr[34]. When the initial brisk reaction was over, the solution was removed and cooled. Five milliliters of concentrated $HNO_3$ was added carefully, followed by the addition of 0.5mL of 70% $HClO_4$, and heating was continued to dense white fumes, repeating $HNO_3$ addition if necessary. Heating was continued for at least ½h and then cooled. The content of the flask was filtered and neutralized with dilute ammonia. The resultant solution was then transferred quantitatively into a 10-mL calibrated flask and made up to the mark with de-ionized water.

A suitable aliquot(1-2mL) of the final solution was pipetted out into a 10-mL calibrated flask, and the cadmium content was determine as described under procedure using EDTA, ascorbic acid and tetra sodium pyrophosphate as a masking agent. The results of biological (human fluids) analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are given in TABLE 6.

**Determination of cadmium in soil samples**

An air-dried homogenized soil sample(100g) was weighed accurately and placed in a 100-mL micro-Kjeldahl flask. The sample was digested in the presence of oxidizing agent, following the method recommended by Jackson[35]. 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 up to the mark with de-ionized water.

Suitable aliquots(1-2mL) were transferred into a 10-mL calibrated flask. The cadmium content was then determined, as described under procedure, using EDTA or ascorbic acid as a masking agent. The results are shown in TABLE 7.

## CONCLUSIONS

In the present work, a simple, sensitive, selective and inexpensive micellar method with the Cd(II)-dithizone complex was develop for the determination of cadmium in industrial, environmental, biological and soil samples. The presence of a micellar system (altered environment) avoids the previous steps of solvent extraction, and reduces the cost and toxicity while enhancing the sensitivity, selectivity and molar absorptivity. The molar absorptivities of the cadmium-dithizone complex formed in presence of the cationic CTAB surfactants are almost ten-times $3.99\times10^5$L mol$^{-1}$cm$^{-1}$ the value observed in the standard method($1.9\times10^4$L mol$^{-1}$/cm$^{-1}$) and the maxima of absorption is shifted by about 20 nm when compared with standard method, resulting in an increase in the sensitivity of the method. With suitable masking, the reaction can be made highly selective. Cadmium in environmental and biological samples has been determined by pulse polarography, NAA, ICP-AES, ICP-MS and AAS. The first four methods are disadvantageous in terms of costs and instruments used in routine analysis. AAS is often lacking in sensitivity and affected by matrix conditions of samples such as salinity. The proposed method using dithizone in the presence of aqueous micellar solutions not only is one of the most sensitive methods for the determination of cadmium but also is excellent in terms of selectivity and simplicity. Therefore, this method will be successfully applied to the monitoring of trace amounts of cadmium in environmental, biological and soil samples.

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