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Simultaneous determination of copper and cadmium as Cu(DDTC)$_2$ Spectrophotometrically after fractional extraction

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ABSTRACT

Copper(II) and cadmium(II) forms M(DDTC)$_2$ complexes (M=Cu, Cd) with diethyldithiocarbamate (DDTC) that is extracted in CHCl$_3$/CCl$_4$. Yellow Cu(DDTC)$_2$ shows maximum absorbance at 435 nm whereas Cd(DDTC)$_2$ has no absorption. Extract was divided into two fractions. Absorption of one fraction is directly measured which is equivalent to Cu(II) present in sample. Addition of excess copper(II) to the second fraction of the extract displaces cadmium quantitatively forming additional Cu(DDTC)$_2$ as its stability is higher than Cd(DDTC)$_2$. The absorbance of second extract is measured subsequently when additional absorbance is equivalent to cadmium. Linear calibration range was obtained 0.05–17 µg mL^{-1} for cadmium and 0.02–12 µg mL^{-1} for copper with the regression coefficient (r^2) 0.998 for each. In the presence of EDTA as masking agent very good selectivity was achieved.

KEYWORDS: Diethyldithiocarbamate, Copper(II), Cadmium(II), Environmental Water and Soil Samples, Biological, Fertilizer and Food Samples

1. INTRODUCTION

A variety of metals in the form of ions (complexes) with variety of toxicity could enter industrial wastewaters as a result of anthropogenic activity. By the biological cycle, some of them through the food chain pass into plants, animals and man, thus affecting them negatively.[1] The determination of heavy metals in environmental, biological, and food samples has drawn significant attention due to the toxic and nutritional effects of these elements or their compounds.[2] Copper functions as a cofactor and is required for structural and catalytic properties of a variety of important enzymes.[3] Nonetheless, excess copper shows some toxicological effects. Food, beverages, and drinking water are potential sources of excess exposure. Exposure to elevated concentrations of copper primarily affects the liver and is typically manifested by the development of liver cirrhosis, episodes of hemolysis, and damage to renal tubules, brain and other organs.[2,4] Again, cadmium can be accumulated in biological systems, becoming a potential contaminant along the alimentary chain. This element has harmful effects on human health, affecting several organ systems, such as nervous, gastrointestinal, reproductive and skeletal, and biochemical activities.[2,5] The need for regular monitoring of these elements in materials has led to an increasing demand for suitably sensitive and selective analytical methods.[6] Diethyldithiocarbamate (DDTC) has been used as complexing agent for the determination of a number of metals, Cu(II), Ni(II), Mn(II) or V(V) alone.[7] The purpose of this work is to describe a spectrophotometric method for simultaneous determination of copper and cadmium using this reagent which has not previously been used. Cd(DDTC)$_2$ complex formed with DDTC possesses no absorption. Hence, cadmium determination indirectly by its quantitative displacement with copper followed by the measurement of additional Cu(DDTC)$_2$ is an interesting attempt. Method was successfully applied to a number of real samples.

2. EXPERIMENTAL

2.1 Chemicals and reagents

High-purity carbontetrachloride, various acids, salts and reagent grade Na-DDTC (Merck) were used. Solutions of a large number of inorganic ions and complexing agents were prepared from their analytical grade, or equivalent grade, water soluble salts. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO$_3$. Complexes, [Cd(TCA-ATP)$_2$], [Cd(sal-pn-sal)], [Cd(HAP-pn-HAP)] and [Cd(HPP-pn-HPP)] were used as reference materials that were prepared following the procedure described by Hasan et al.[8] Blood and urine samples, collected in polypropylene tube, were kindly provided from Chittagong Medical College Hospital, Chittagong.

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2.2 Instrumentation

A Shimadzu UV Visible spectrophotometer (model UV-1800) with suitable settings equipped with 1-cm quartz cells was used for measuring the absorbance. The spectral band length was 1 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction, and the recorder was a computer-controlled in the wavelength range 190–1100 nm. A Jenway (England, U.K) (Model-30100) pH meter were used for the measurement of pH. A Thermo (Model-iCE 3000 C093300131v1.30) AAS spectrophotometer was used for comparing the results.

2.3 Preparation of standards

A 0.1% (5.84×10^{-3}M) stock solution of Na-DDTC was prepared by dissolving 0.1 g sodium diethyldithiocarbamate reagent in approximately 80 mL water heated at 60^0C. Afterwards, the volume was made up to 100 mL by adding distilled water in volumetric flask and filtered. A stock solution of cadmium or copper (100 µg mL^{-1}) was prepared by dissolving 0.5704 g of cadmium sulphate octahydrate or 0.9820 g of copper sulphate pentahydrate (Merck, Germany) in 250 mL doubly distilled deionized water. The working standards of cadmium or copper (100 µg mL^{-1}) were prepared by suitable dilutions of this stock solution.

2.4 General procedure

To determine copper and cadmium, various volume of Cd(II) and Cu(II) solution (100 µg mL^{-1}) was placed in a 25 mL separating flask along with 0.3 mL 0.05M H_2SO_4 and 5 mL DDTC (500 µg mL^{-1}) solution. The mixer was stirred for 10 min. The solid product of Cu(DDTC)$_2$ and Cd(DDTC)$_2$ so formed was extracted carefully with the addition of 10 mL (5×2) CCl$_4$, and separated out. pH value of extract was adjusted to 5 using acetate buffer. The extract solution was divided in two fractions of 5 mL each. The absorbance of one portion was measured by a spectrophotometer at 435 nm against a blank which is equivalent of copper content present. An excess of Cu(II) solution (100 µg mL^{-1}) was added to another portion when cadmium was replaced immediately from Cd(DDTC)$_2$ forming additional Cu(DDTC)$_2$ equivalent to Cd(II) present. The organic phase was further separated after vigorous stirring for 10 min. Additional absorbance obtained is equivalent to the cadmium content present.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectra of the reagent and the complex Cu(DDTC)$_2$ or Cd(DDTC)$_2$ are recorded individually in the range 350–600 nm at pH 5.0 against CCl$_4$ (standard) or reagent blank (real samples). The typical superimposed UV-vis spectra of Cu(DDTC)$_2$ or Cd(DDTC)$_2$ in CCl$_4$ and reagent blank are presented in **figure 1**. The spectra show that Cu(DDTC)$_2$ has an absorption maximum at 435 nm, where as Cd(DDTC)$_2$ or the reagent doesn't show appreciable absorbance. The molar absorptivity (e) and Sandall's sensitivity at this wavelength are 1.94×10^4 mol^{-1} L cm^{-1} and 5.797 ng cm^{-2}, respectively for Cd(II) and the corresponding values are 3.16×10^5 and 3.376 ng cm^{-2}, respectively for Cu(II).
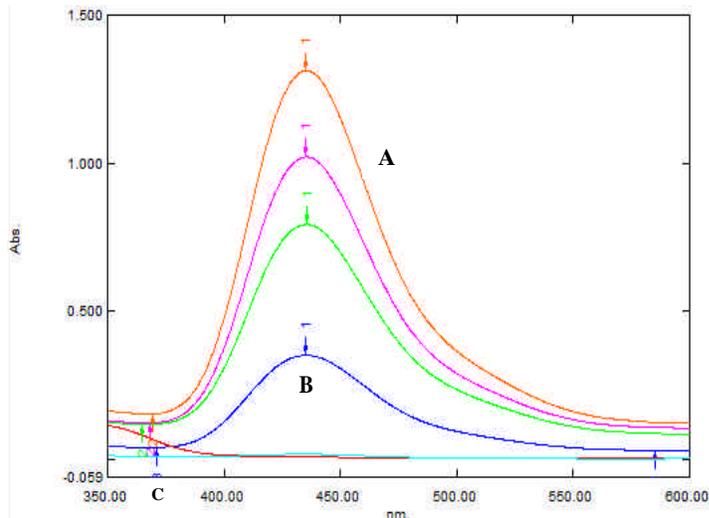

Fig. 1. The typical superimposed UV-vis spectra of (A) Cu(DDTC)$_2$, (B) Cd(DDTC)$_2$ in CCl$_4$ and (C) Reagent blank.

3.2 Method optimization

3.2.1 Optimization of parameters

Acid effect was primarily tested for nitric, sulfuric, hydrochloric and phosphoric while sulfuric acid was supposed to be suitable for complex formation. A maximum absorbance was found at room temperature ($25 \pm 5)^0$C for 0.1×10^{-2} M H_2SO_4. The copper and reagent molar ratios of 1:10 to 1:45 produced a constant absorbance. Therefore, a 20 fold molar excess of DDTC was optimized for constant color development. The reaction was allowed to proceed for varying periods of time at room temperature. The reaction goes to almost completion within 1 min. However for higher precision, the reaction was allowed to proceed for 10 min in all the subsequent experiments. Cu(DDTC)$_2$ was found to be stable for at least 72 hrs.

3.2.2 Optimization of parameters for the extraction of the complex

The influence of pH on the metal exchange reaction and subsequent extraction in organic phase was investigated when optimum pH value for the reaction of Cu(II) and Cd(DDTC)$_2$ is attained at pH 5 and remains constant up to 9 (**figure 2**). The pH value should not be lower than 4 due to the fast decomposition of dithiocarbamate and over 9 would accelerate the Cu(OH)$_2$ precipitation. Acetic acid buffer solution (pH 5) was chosen for the subsequent experiments. The volume of the aqueous phase is an important factor for the extraction of metal ions as Cu(II)-DDTC is sparingly soluble in aqueous phase. The effect of volume of the aqueous phase was studied when solutions containing 2 µg mL^{-1} of Cu(II) were diluted in the volume range from 5 mL to 30 mL with deionized water. Rapid decrease in absorbance was occurred at aqueous volume beyond 15 mL. The efficiency of Cu(DDTC)$_2$ extraction in organic phase depends on the extraction period also. Reaction mixture was extracted at least 10 min for getting maximum recovery of metal content.
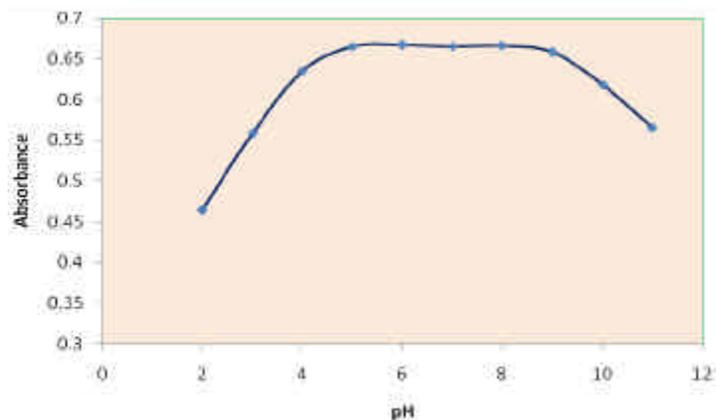
Fig. 2. Effect of pH on the extraction of the Cu(II)-DDTC complex in organic phase.

Summary for the optimization of variables of the proposed spectrophotometric method are given in **table 1**.

3.3 Composition of the complex

Under the optimum conditions the stoichiometry of the reaction between Cu(II) and DDTC was investigated by Job's continuous varia-

against corresponding concentrations for eleven standards containing cadmium or copper ranging from 0.01-20 μg mL^{-1}. Each concentration level was analyzed in triplicate. The linearity range, regression equation and correlation coefficient were obtained by the method of least squares. Good correlation coefficient (r^2) of 0.998 was found for each plot as shown in **figure 3**. The straight line obeyed the equation $y=0.208x+0.0757$ and $y=0.1356x+0.0681$ for copper and cadmium, respectively. Linearity ranges 0.05-17 μg mL^{-1} for cadmium and 0.02-12 μg mL^{-1} for Cu(II). The calibration sensitivity, the limit of detection and the limit of quantitation as well as other analytical characteristics of the procedure are calculated from the calibration curves and summarized in **table 1**.

3.4.2 Accuracy, precision and specificity

For the accuracy test triplicate measurements were recorded for each of 2, 5, 7, 9 μg mL^{-1} standards. The recovery values were 100.55 – 105.20% (table 2) indicating the high accuracy of the proposed method. For the accuracy check of the proposed method was done by analyzing the certified reference substances (alloy and synthetic compound) and synthetic mixtures also. The found values were very concordant with the certified values. The RSD of the all measurements including

Table 1. Summary for the optimization of variables and validation parameters of the proposed spectrophotometric method

Variables	Studied range	Optimum	Parameter	Values	
				Cadmium	Copper
Acid conc./M	$(0.02\text{-}1.0) \times 10^{-2}$	0.1×10^{-2}	Measurement wavelength (nm)		
Reagent Molar fold excess (M:L)	1:5-1:60	20	Linear range (μg mL^{-1})	0.05-17	0.02-12
Temperature	Ambient	Ambient	Linearity equation	$y=0.1356x+0.0681$	$y=0.208x+0.075$
Time/min	1-20	10	Regression coefficient (r^2)	0.998	0.998
Stability	1 min-72 hrs.		Standard deviation of the slope	0.013	0.003
Wavelength (nm)	350-600	435	Relative standard deviation (%)	4.80	3.92
Extraction variables			Limit of detection, LOD (μg mL^{-1})	0.31	0.28
Extraction period/min	1-30	10	Limit of quantification, LOQ (μg mL^{-1})	0.94	0.77
Aqueous phase volume/mL	5-30	15	Molar absorptivity, ε (L mol^{-1} cm^{-1})	1.94×10^4	3.16×10^5
pH	2–11	5	Sandall's sensitivity (ng cm^{-2})	5.797	3.376

tion and mole ratio methods.[14] The stoichiometry was found to be 1:2 (Copper: Ligand) in both methods.

3.4 Method validation

Method was validated in terms of ICH[15] analytical performance parameters; precision, accuracy, specificity, limit of detection, limit of quantitation, linearity and range, suitability and robustness. To assess validation, its accuracy was checked by analyzing certified reference materials, synthetic compounds and metal alloy. The method was also tested by analyzing several synthetic mixtures containing cadmium and diverse ions. Cd(II) content in these mixtures was compared to that of calculated values.

3.4.1 Preparation of calibration curve and linearity

The calibration curves were constructed by plotting absorbance
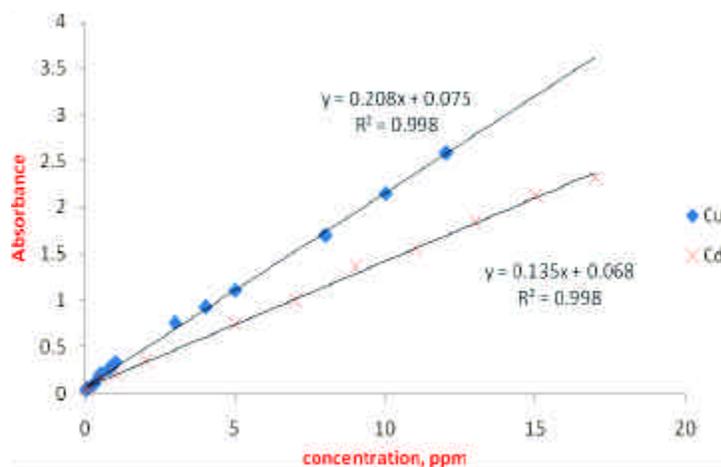

Fig. 3. The calibration curves for both copper and cadmium determination by the proposed method.

within-day and between-day analyses did not exceed 4.8% as shown in **table 2** proving the high precision of the proposed method. The specificity of the proposed method was proved by the satisfactory results obtained for the analysis of copper and cadmium in standard reference materials using suitable masking agent.

Table 2. Determination of cadmium and copper in standard mixture for the intra and inter-day accuracy and precision study.

Metal	Added	Intraday (n=5)			Inter-day (n=5)		
	($\mu g\ mL^{-1}$)	Average ($\mu g\ mL^{-1}$)	RSD (%)	Accuracy (%)	Average ($\mu g\ mL^{-1}$)	RSD (%)	Accuracy (%)
Cadmium	2.00	1.99±0.01	3.7	99.6	2.10±0.02	4.8	105.2
	5.00	4.98±0.02	3.7	99.6	5.15±0.02	3.3	103.0
	7.00	6.88±0.02	2.2	98.2	7.03±0.03	2.8	100.5
	9.00	9.00±0.02	1.7	100.1	9.20±0.03	2.7	102.2
Copper	1.00	0.96±0.01	3.8	95.8	0.97±0.01	3.1	97.4
	5.00	4.78±0.01	1.4	95.9	4.80±0.05	3.9	92.5
	8.00	7.70±0.05	3.1	96.3	7.62±0.08	3.6	93.7

3.4.3 Sensitivity
The limit of detection and the limit of quantification were calculated from calibration graph by the formula $LOD = 3 \cdot S_{xy}/a$ and $LOQ = 10 \cdot S_{xy}/a$, respectively. Where, S_{xy} is the standard deviation of the response and (a) is the slope of the calibration curve. The lower detection and quantification limit for Cd(II) were found as $0.29\ \mu g\ mL^{-1}$ and $0.94\ \mu g\ mL^{-1}$, respectively. And the corresponding values for copper determination were $0.23\ \mu g\ mL^{-1}$ and $0.77\ \mu g\ mL^{-1}$, respectively.

3.4.4 Robustness, ruggedness and system suitability
Robustness was examined by evaluating the influence of small variation in the method variables reagent conc., buffer pH, and reaction and extraction period on its analytical performance. Recovery was $(99.87 - 101.41) \pm (0.26 - 0.66)\%$ indicating that small variation in the method variables did not significantly affect the procedures. At five different concentration levels of standard within $1.0-10.0\ \mu g\ mL^{-1}$ maximum wavelength of absorption was found as 435.52 ± 0.33 and their relative standard deviation was found to be 0.077%. The result of cadmium determination in whole blood and urine obtained by the proposed method was compared to that obtained from pre-validated AAS method. Inter method variation competes the analytical agreement. Both indicate the excellent system suitability and ruggedness for the proposed method.

3.5 Effect of diverse ions
Experiment was carried out by the determination of $1\ \mu g\ mL^{-1}$ copper and cadmium in the presence of foreign ions. The tolerance limit of a foreign ion is taken as the amount that caused an error in the absorbance value of =10%. Among the various ions studied, the anions and the cations, Li(I), Na(I), K(I), Cs(I), Zn(II), Ba(II), Mn(II), Ca(II), Ce(VI), Ti(IV) and Al(III) do not interfere even when present in more than 100 fold excess. Co(II), Ni(II), Cr(III), Bi(III), Pb(II), V(V), Mo(VI) and

Fe(III) ions interfered seriously at all proportions due to complex formation with DDTC. Interference from Co(II), Ni(II), Cr(III), Bi(III), Pb(II) can be eliminated using EDTA as masking agent up to 50 fold excess. In order 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 when 10 fold excess of them could be masked.

3.6 Application: standard and real sample
The application was also extended to the determination of cadmium and copper in a number of environmental water and soil samples, biological, food, vegetable and tobacco samples. The results of the analyses gave the satisfactory RSD within analytical agreement.

3.6.1 Cadmium in synthetic mixtures
Synthetic mixtures of varying compositions containing $2\ \mu g\ mL^{-1}$ of cadmium and diverse ions of known concentrations were prepared and cadmium was determined using EDTA as a masking agent (table 3). The recovery was achieved in all solutions with maximum RSD value of 2.54% for triplicate measurements.

3.6.2 Cadmium in reference materials (Alloy or synthetic compounds)
20 mg of each synthetic complex or 0.1 g of an alloy was accurately weighed and acid decomposition was performed in a 50 mL Erlenmeyer flask. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature $(25\pm5)^{0}C$. After suitable dilution with deionized water, solution was neutralized with a dilute NH_4OH solution. The resulting solution was filtered if necessary. An aliquot of 2 mL decomposed solution was taken into a calibrated flask and the copper and cadmium content was determined under general procedure using EDTA as masking agent. The average percentage recovery and RSD values for five replicate analyses were in good agreement with the certified values (**table 3**) indicating good accuracy and precision of the measurements.

3.6.3 Cadmium and copper in environmental water and soil samples
250 mL of industrial (TSP, Eastern refinery, CUFL and BSRM) or battery water was mixed with 10 mL of conc. HNO_3, 2 mL of conc. H_2SO_4 and 2 drops $HClO_4$ acid in a distillation flask. The sample was digested until a paste was formed. Other water (250 mL) samples (Tap water, Karnafuli river water and Bay of Bangle water) were pre-concentrated by simple evaporation. Ammonia buffer solution was added

Table 3. Determination of cadmium in Certified Substances and synthetic mixture by the proposed spectrophotometric method.

Certified substance/ synthetic mixture	Cadmium ($\mu g\ mL^{-1}$)			
	Certified values	Expt. values	RSD (%)	Recovery (%)
Alloy-1	3.00	2.70±0.05	1.8	90.0
Alloy-2	3.00	2.88±0.10	3.4	96.0
[Cd(TCA- ATP)$_2$]	8.15	8.36±0.20	2.4	102.5
[Cd(Sal-pn-Sal)]	11.39	11.14±0.08	0.7	97.8
[Cd(HAP-pn-HAP)]	10.63	10.71±0.20	1.8	100.7
[Cd(HPP-pn-HPP)]	9.97	9.79±0.40	4.1	98.2
$Cd^{2+} + Ni^{2+} + SO_4^{2-} + EDTA$		2.01±0.02	1.0	100.6
$Cd^{2+} + Ni^{2+} + Mg^{2+} + SO_4^{2-} +EDTA$		1.96±0.05	2.5	98.4
$Cd^{2+} + Ni^{2+} + Mg^{2+} + K^+ + SO_4^{2-} + Cl^- + EDTA$		2.03±0.03	1.4	101.7
$Cd^{2+} + Ni^{2+} + Mg^{2+}+K^+ +As^{3+} + SO_4^{2-} + Cl^- + EDTA$	2.00	2.09±0.02	1.0	104.7
$Cd^{2+} + Ni^{2+} + Mg^{2+} + K^+ + As^{3+} + V^{5+}+ SO_4^{2-} + Cl^- + EDTA$		2.04±0.04	1.9	102.4

to precipitate iron as hydroxide. The resulting solution was then filtered and quantitatively transferred into a 50 mL calibrated flask and made up to the mark with deionized water.[9] 2 g of soil sample was placed into a 250 mL flask. 0.2 mL of sulfuric acid, 1 mL of nitric acid and 1 mL of perchloric acid were added. The mixture was heated to 180°C for 3 hrs on a hotplate. After cooling, 1 g of ammonium chloride and 20 mL of 0.5 N HCl were added, evaporated to approximately 10 mL and filtered into 50 mL plastic bottles through an ashless 5B filter paper. Ammonia buffer solution was added (not exceeding pH 8) to this solution to precipitate iron as hydroxide. An aliquot (2 mL) of pre-concentrated environmental water or acid digested soil sample was pipetted into a calibrated flask and the copper and cadmium content was determined under the general procedure using EDTA. Triplicate measurements possess good precision (RSD not greater than 6%) (**table 4**).

3.6.4 Cadmium and copper in biological samples
2 mL of human blood, 25 mL of urine or 5 g human hair[10] of the affected persons was taken into beaker. 10 mL of conc. HNO_3 and 2 mL of conc. H_2SO_4 were added and the beaker was placed on the digester under gentle heating. The solution was heated to dryness. After cooling 1 mL of conc. HNO_3 and 10 mL distilled water were added and volume

was reduced at 3-4 mL. The content of the beaker was filtered and neutralized with dilute ammonia. Each resultant solution was then transferred quantitatively into a 50 mL calibrated flask and made up to the mark with deionised water. An aliquot (2-mL) of digested biological sample was pipetted into a calibrated flask and the metal content was determined under the general procedure using EDTA as masking agent. The result given in **table 5** indicates the good reproducibility of the method. **Figure 4** indicate inter method variation of proposed and AAS method for cadmium measurements.

3.6.5 Cadmium and copper in cigarette tobacco and food (Tea/Vegetables/Honey)
0.73 g of tobacco from cigarette was dissolved in 2 mL conc. H_2SO_4 and heated about 20 minutes. 0.1 g Tea sample (Ispahani Mirzapur) was taken in a Porcelin crucible and heated for about 50 minutes on a hot plate.[12,13] The residue obtained was well grounded with a glass rod. 10 g of wet radish, 25 g wet cabbage or 2 mL honey was digested in 10 mL conc. HNO_3 on a hot plate till all organic matter was completely eliminated. The residue obtained was diluted by adding 20 mL distilled water and filtered. The filtrate was treated with dilute ammonia solution in order to neutralize the excess acid. 2 mL of the solution was taken to determine the concentration of copper and cadmium by the general procedure using EDTA as a masking agent. Result of triplicate measurements with well RSD is shown in **table 6**.

3.6.6 Cadmium and copper in fertilizer
1 g finely grounded TSP (Triple Super Phosphate) fertilizer was dissolved in 5 mL conc. HNO_3 by gentle heating or 1 g MOP (Muret of Potash) fertilizer was dissolved in water and the solution was taken in a 100 mL calibrated flask. Volume was made up to the mark with doubly distilled deionised water. The solution was neutralized by NH_4OH solution and filtered. 2 mL of each solution was analyzed for copper and cadmium content by general procedure of the proposed method. Results of triplicate measurements given in table 6 indicate RSD well enough for the determination.

Table 4. Determination of cadmium and copper in environmental samples by the proposed method.

Sample	Source		Cadmium Conc. (µg mL⁻¹)	RSD (%)	Copper Conc. (µg mL⁻¹)	RSD (%)
Water	**Industrial**	TSP	1.81±0.04	2.2	4.13±0.05	1.21
		CUFL	1.62±0.05	3.1		
		Eastern Refinery	1.20±0.03	2.5		
		BSRM	1.41±0.04	2.8	2.13±0.05	2.3
	Environmental	Tap water	0.08±0.005	6.2		
		River water	1.18±0.06	5.1		
		Sea water	0.73±0.04	5.5		
		Battery water	5.82±0.10	1.7	5.72±0.1	1.7
Soil	**Industrial**	TSP	1.40±0.02	1.4		
		Eastern Refinery	1.24±0.03	2.4		
	Environmental	Ship Yard	0.77±0.02	2.6	0.67±0.01	1.5
		Road-side	0.42±0.006	1.4		
		Agricultural	0.94±0.05	5.3		
		Marin soil	0.84±0.03	3.5	1.37±0.05	3.6

Table 5. Biological sample analysis for the determination of cadmium and copper by proposed method.

Sample	Proposed Method Patients	Conc. of Cd (µg mL⁻¹)	RSD (%)	AAS (µg mL⁻¹)	Inter method variation (%)	Copper Conc. of Cu (µg mL⁻¹)	RSD (%)
Blood	Lung	1.66±0.04	2.4	1.55	6.58	1.66±.05	3.0
	Stroke	1.74±0.03	1.7	1.73	0.57	1.23±0.05	4.0
	Kidney	0.61±0.02	3.3	0.60	2.64	0.486±0.02	4.1
	Hypertension	1.51±0.05	3.3			1.12±0.01	0.9
Urine	Lung	1.60±0.02	1.2	1.71	-6.48	0.730±0.03	4.1
	Stroke	1.43±0.03	2.1	1.30	8.51	1.23±0.03	2.4
	Kidney	1.32±0.01	0.7	1.41	-7.14	0.836±0.02	2.4
Hair	Male	0.26±0.01	3.8	-	-	2.18±0.03	1.4

In tap water cadmium was 0.08 µg mL⁻¹ but in Karnafuli river water it was present 1.18 µg mL⁻¹ which is too much larger than tap water. In case of kidney patient the amount of cadmium in blood was 0.61µg mL⁻¹. On the other hand the amount of cadmium of 1.66 µg mL⁻¹ in blood of lung patient is larger than that of kidney patient. Vegetable and other food samples contained small amount of cadmium, while the tea sample contained high amount of copper (4.54 µg mL⁻¹). Among the cigarette tobacco samples, Gold Leaf and Navy
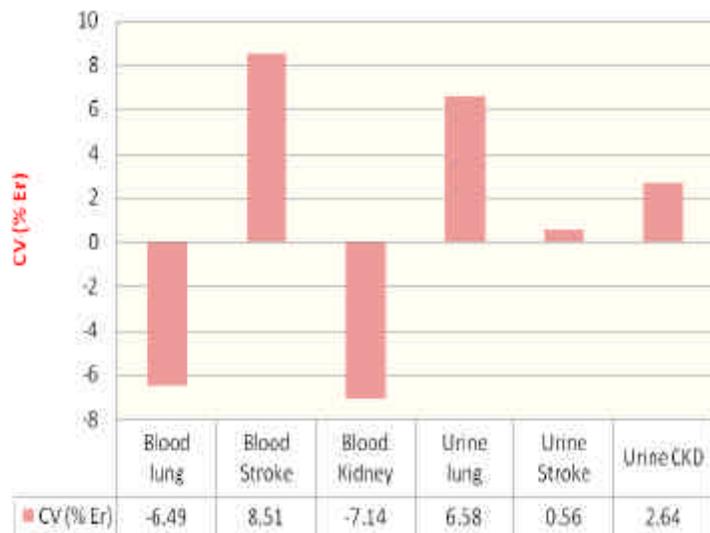
Fig. 4. Inter method variations in percentage of error in cadmium measurements by the proposed method and AAS.

contained relatively higher amount of cadmium and copper than Banson. Though the values of both cadmium and copper concentration in environmental water and soil samples were not very high, but the respective responsible authorities in Bangladesh should have an attention to control environmental pollution due to cadmium and copper exposure.

Table 6. Determination of Cadmium and Copper in cigarette tobacco, food and fertilizer by the proposed method.

Samples		Cadmium Conc. ($\mu g\ g^{-1}$)	RSD (%)	Copper Conc. ($\mu g\ g^{-1}$)	RSD (%)
Brand Name cigarette	Gold Leaf	0.500±0.02	4.0	0.45±0.02	4.4
	Banson	0.340±0.02	5.9	0.35±0.01	2.8
	Navy	0.508±0.03	5.9	1.72±0.05	2.9
Food	Radish Flesh	0.04±0.003	6.9	-	-
	Cabbage	0.28±0.02	7.1	-	-
	Honey	0.102±0.006	5.8	1.92±0.05	2.6
	Tea	0.76±0.02	2.6	4.54±0.04	0.8
Fertilizer	TSP	2.82±0.02	0.7	0.87±0.04	4.5
	MOP	5.60±0.06	1.0	1.50±0.05	3.3

Dithiocarbamates are more suitable than other complexing reagents because of their selectivity towards Cd(II) and Cu(II). Metal determination in the different matrices based on the direct measurement of maximum absorption at 435 nm is not susceptible to potential interferences from the matrix excipients. Therefore, the method described herein has many advantages: it is simple and rapid, it has high accuracy and sensitivity, it uses inexpensive reagents available in any analytical laboratory. The method is practical and valuable for its wide application. As complex stability was at least 72 hrs it allows the processing of large batches of samples and their comfortable measurements with convenience. This gives the high throughput property to the proposed method when applied for analysis of large number of samples in quality control/analytical laboratories.

4. CONCLUSION

Though techniques ICP-MS, ICP-AES and AAS likely to be the most widely employed are reliable and sensitive, they suffer from the limitation of being rather costly, time-consuming and not always readily available. Contrary, in laboratories of developing countries like us the choice of any analytical methods depends on not only the sensitivity, selectivity, accuracy but also the availability of reagents, cost effectiveness of instruments and the time required for analysis as well as safety and ease of operation. Simple spectrophotometric method which is less costly and labor-intensive is viable alternatives to those methods requiring more sophisticated instrumentation. A spectrophotometric procedure for the simultaneous determination of cadmium(II) and copper(II) using diethyldithiocarbamate (DDTC) as ligand is described. Primarily Cu (II) complex was extracted with CCl_4 and the absorbance was measured at 435 nm. Cadmium measurement is based on the quantitative displacement of cadmium from cadmium-DDTC complex by copper. Under the optimized conditions method meets the excellent validation criteria. In the presence of EDTA very good selectivity was achieved for the simultaneous determination of copper and cadmium.

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