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# Spectrophotometric Determination of Copper(II) Using Ammonium Pyrollidine Dithiocarbamate in Anionic Aqueous Solution of Sodium Dodecyl Sulphate

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A simple rapid new spectrophotometric method has been developed for the determination of copper using ammonium pyrollidine dithiocarbamate in presence of anionic aqueous micellar solution 1.0 % sodium dodecyl sulphate. Ammonium pyrollidine dithiocarbamate reacts with copper(II) to form *bis*(ammonium pyrollidine dithiocarbamato) copper complex. The importance of this method is the use of micellar system which replaces the previous solvent extraction steps. Micellar system enhancing the sensitivity, selectivity and the molar absorptivity which reduces the cost and toxicity. The average molar absorption coefficient and Sandell's sensitivity was found to be 1.08 × $10^4$ L $mol^{-1}$ $cm^{-1}$ and 5.83 ng $cm^{-2}$ at $\lambda_{max}$ 447.8 nm respectively. Linear calibration graph was obtained over the concentration range 0.12-4.0 μg $mL^{-1}$, the stoichiometric composition of the complex was 1:2 (Cu:[APDC]$_2$. The developed method was successfully applied for the determination of copper from alloy and brass samples.

**Keywords: Spectrophotometric, Copper, Ammonium pyrollidine dithiocarbamate, Anionic micellar, Sodium dodecyl sulphate.**

## INTRODUCTION

Copper play important role in biological systems and is necessary constituent of many enzymes. It is utilized for production of hemoglobin. It enhances iron absorption and transport in gastrointestinal. Copper is utilized to maintain the level of myelin in nervous process, utilized for brain tissues and bone formation[1,2]. Excess intake of copper is toxic and causes harmful to human kind, also effects the microbiological treatment of waste water[3]. In spectrophotometric analysis of metal ions, the metal is complexed with chelating agent and solublized in solvent extraction is easy method for studying the metal ions because of its simplicity and rapidity[4,5]. Several spectrophotometric methods have been developed to replace the old solvent extraction method by using the surfactants[6]. Micellar methods due to solubility of several metal complexes have shown improvement in the analytical merits of techniques for the determination of metal ions. Micellar media is introduced to enhance the molar absorpitivities, sensivities and replaces the previous steps of toxic solvent extraction[7-15]. Many spectrophotometric methods for the determination of copper using various chelating reagents are available. Some of the recently developed spectrophotometric methods for the determination[16-21] are less selective and less sensitive. We have developed new simple, sensitive and selective spectrophotometric method for the determination of copper(II) in various materials by using ammonium pyrollidine dithiocarbamate (APDC) as chelating agent in anionic micellar aqueous solution of 1.0 % sodium dodecyl sulphate (SDS).

## EXPERIMENTAL

A Cecil CE 9500 UV-visible scanning spectrophotometer equipped with a 10 mm path length quartz cell was utilized. Atomic absorption spectrophotometer (Analyst-100 Perkin Elmer) with multi-elemental hollow cathode lamps was used. I.R. spectrophotometer (260 Hitachi*)* was utilized for study of metal chelates. Besides, pH/conductivity meter (Sension 156 HACH) with Sension Gel-filled pH electrodes was used.

**Preparation of reagents:** Stock working solutions of metal ions Cu(II), Co(II) and Ni(II) 1000 μg $mL^{-1}$ made from their nickel(II) chloride, cobalt(II) nitrate and copper(II) nitrate salts. Ammonium pyrollidine dithiocarbamate (APDC) solutions were made prepared freshly in distilled water before going to acid decomposition. Stock solutions of APDC concentration 8 × $10^{-4}$ M were made by dissolving 0.032 g of APDC in 250 mL volumetric flask and volume was made up to mark. The surfactant 1.0 % SDS was made freshly by taking SDS salt 1.0 g in

100 mL volumetric flask with double distilled water and volume was made up to mark. Insoluble compounds were made dissolved in acids or according to special dissolution method[22]. Buffer solutions of pH 1-10 were prepared by using appropriate methods[23], with appropriate volumes of the mixtures of 0.2 M KCl-0.2 M HCl for (pH 1-4.0), 0.2 M $CH_3COOH$ - 0.2 M $CH_3COONa$ for (pH 5-6.0), 0.1 M $KH_2PO_4$ - 0.1 M NaOH for (pH 6.5-8.0) and 0.025 M sodium borate and 0.1 M HCl for (pH 9-10.0). Chemicals utilized in this study were analytical grade of high purity (Merck/Fluka).

**Determination of Cu(II) ions with APDC in 1.0 % SDS:** Metal ions standard solutions of 0.06-10 µg mL$^{-1}$ were taken in 10 mL calibrated flasks, added with appropriate volume 6 × 10$^{-4}$ M APDC, buffer volume 2.0 mL (pH 8) and added 1 mL 1.0 % SDS was shaken and made up volume up to mark. The absorbance of the metal complexes were recorded.

**Determination of Cu(II) ion with APDC using $CCl_4$:** Metal ions solutions of varying concentration were taken in calibrated volumetric flask, added 6 × 10$^{-4}$ M APDC and buffer solution volume 2.0 mL (pH 8) and 10 mL of $CCl_4$ were mixed for the complex formation in the solvent extraction method. The sample solutions were extracted thrice in separating funnel with $CCl_4$ and the absorbance of complex was measured.

**Infrared:** A series of standard solutions of metal ions in volumetric flask were mixed with 6 × 10$^{-4}$ M APDC and buffer solution 2.0 mL of varying (pH 8). IR absorbance spectra of metal-chelates were investigated in the region 4000-250 cm$^{-1}$ with IR spectrophotometer (260 Hitachi) in $CCl_4$. IR parameter modes were adjusted at 2 gain, band slit 0.1 nm and speed 20 nm/sec. Cuvets used for the sample solutions of complexes were made of NaCl. NaCl cells used for metal-PAN chelates using reagent APDC as reference. The important IR bands and assignments of ligands and their complexes were observed corresponding to M-S=C.

**Presence of foreign interferences:** The interfering effect of foreign metal ions and anionic salts NaF, $Na_2C_2O_4$, KSCN, $Na_2$tartarate, $KClO_3$, KCN, $Na_2$citrate, Cd(II), Pb(II), Zn(II), Al(III), Mg(II), Mn(II) and Cr(III) were studied separately and collectively up to 1000 µg mL$^{-1}$ in the flask containing complexes and the absorbance was measured. Various masking agent EDTA and ascorbic acid were added in the complex formation for the removal of the interference of foreign ions. Interference of many species was reduced by using masking agents and by changing the pH of the complex formation. Interferences of foreign metal ions and salts by APDC in 1.0 % SDS are given in Table-1.

TABLE-1
EFFECT OF FOREIGN IONS ON Cu(II)-[APDC]$_2$

| Ion/salt | Cu(II) |
|---|---|
| KSCN, $KClO_3$, $Na_2$tartarate | 1000 |
| Mg(II) | 800 |
| NaF | 600 |
| Al(III), Zn(II) | 100 |
| Zn(II) | 50 |
| Cr(III) | 30 |
| Cu(II) | – |
| Cr(IV) | 8 |
| Ni(II) | 5 |
| Fe(III) | 5 |
| Co(II) | 5 |
| Pb(II) | 3 |
| Cd(II) | 2 |

**Determination of copper ions in alloys sample:** Alloy sample of copper ions 0.1-0.5 g of reference material Mallory was digested with concentrated HCl (15 mL) and concentrated $HNO_3$ (5.0 mL) in beakers. The sample solution was heated to reduce the volume to 5 mL on a hot plate. Then mixed 10 mL concentrated HCl, solutions in the sample solutions by filtering and diluting to a final volume of 25 mL. Alloy sample of reference material having the composition as Mallory (Cu 99.2, Cr 0.81)[29] results are shown in Table-2.

**Determination of copper(II) ions in brass sample:** The brass sample 1 g was digested with concentrated $HNO_3$ (15 mL) in to a 250 mL beaker and mixed deionized water 25 mL, samples were dissolved by heating on hot plate and samples were taken to a volumetric flask of 1000 mL and made the maximum volume diluted up to maximum. Brass solution of 1 mL was diluted in 1000 mL volumetric flask. Diluted brass sample after complex formation was investigated as given in Table-3.

**Copper(II) ions in stream water sample:** The stream water solution was collected from Khairpur, Sindh city of Pakistan. The sample solution was filtered with filter paper and acidified with dil. $HNO_3$. The 5 mL sample was transferred to three different volumetric flasks of 10 mL and then added the optimized concentration of APDC, appropriate buffers and SDS for complex to the determination of Cu(II) ions by present method as given in Table-4.

**Determination of Cu(II) in tap water samples:** Sample solution of tap water was collected from Sukkur city, Pakistan. Then samples were filtered through 0.45 µm filter paper and then were acidified with 1 mL concentrated $HNO_3$ to avoid precipi-tation. Copper metal was skipped in tap water in the volumetric flask added appropriate volumes of APDC, 2 mL

TABLE-2
DETERMINATION OF COPPER(II) IN ALLOY SAMPLES

| Alloy certified (%) composition | Metal ion | Metal (µg) present | Metal (µg) found | RSD (%) | Relative error (%) | Recovery (%) |
|---|---|---|---|---|---|---|
| Mallory | Cu(II) | 25.00 | 24.98 | 0.91 | 0.08 | 99.92 |

TABLE-3
DETERMINATION OF COPPER(II) IN REAL SAMPLES

| Sample | Analyte ion | Proposed method (µg mL$^{-1}$) | RSD (%) | AAS method (µg mL$^{-1}$) | RSD (%) | Recovery (%) |
|---|---|---|---|---|---|---|
| Diluted brass sample | Cu(II) | 0.655 | 0.4 | 0.664 | 0.4 | 98.64 |

TABLE-4
DETERMINATION OF COPPER(II) IN STREAM WATER SAMPLE

| Sample | Spiked (ng mL$^{-1}$) | Amount found (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Stream water | 0.0 | 1.70 | |
| | 50.0 | 51.50 | 99.61 |

buffer solution of pH 8 and 2.0 mL 1.0 % SDS for the complex formation. Results are given in Table-5.

TABLE-5
PERCENTAGE RECOVERY OF KNOWN AMOUNT OF Cu(II)

| Metal ions | Amount added (µg mL$^{-1}$) | Amount found (µg mL$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Cu(II) | 0.50 | 0.49 | 98 |

## RESULTS AND DISCUSSION

Ammonium pyrollidine dithiocarbamate reacts with Cu(II) forms metal-chelate. Ammonium pyrollidine dithiocarbamate is bidentate ligand have the bonding sites to the Cu(II) ion, are two sulphur atoms of the APDC group after deprotonation[26]. The structure of Cu(II) ions with APDC is shown in Fig. 1[27]. UV-visible spectra of APDC ligand solution shows strong sharp peak absorption ($\pi \rightarrow \pi^*$ transitions) transfer from one ligand-to another ligand. Here charge transfer (LLCT) due to sulphur atom of thio group at UV region $\lambda_{max}$ 279.2 ($\pi \rightarrow \pi^*$ transitions) of C=C group, C=S double bonds in 1.0 % SDS is given in Fig. 2[28]. UV-visible spectra of copper(II)-PDC complex showed, PDC being shifted to a bathochromic shift to longer wave length of C=CN group and S=S group showed red-shifted by 68 nm broad absorption peaks ($\pi \rightarrow \pi^*$). Transitions of charge transfer from ligand-to metal (LMCT) was observed to empty (dπ) orbital of cobalt and filled ligand molecular orbital (pπ) at $\lambda_{max}$ 447.8 nm (ε 10800 mol$^{-1}$ cm$^{-1}$)[28]. UV-visible spectra of copper(II)-PDC show that sulphur atoms of the thio group after deprotonation are taking part in PDC-chelate are shown in Fig. 3[28].

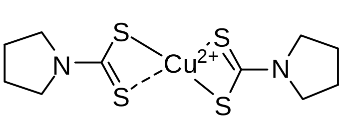

Fig. 1. Structure of *bis*(ammonium thiocarbamato) copper

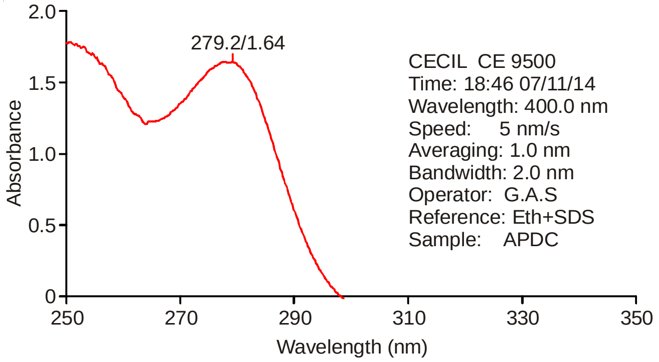

Fig. 2. UV-vis spectrum of APDC at ($\lambda_{max}$ 279.2 nm) in 1 % SDS

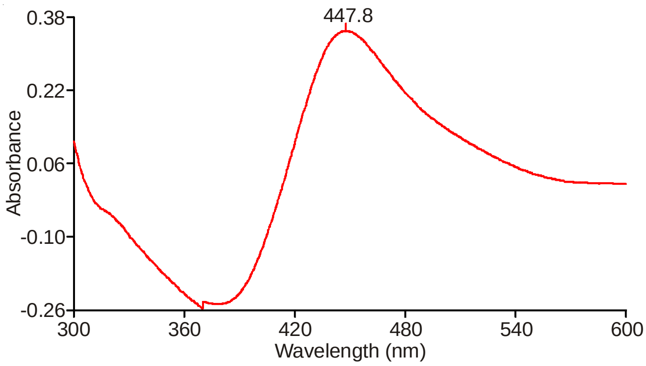

Fig. 3. UV-vis spectrum of Cu(II)-[APDC]$_2$ complex at ($\lambda_{max}$ 447.8 nm)

Stochiometric metal-chelates compositions were determined by Job's method of continuous variation by varying the concentrations of the metal and chelates by the molar-ratio method[29,30]. Composition of metal against ligand ratio in the complex formation was 1:2 (M:L$_2$)[31]. The APDC concentration effect was determined by keeping the varying APDC concentrations over the range 0.5 to 10.0 × 10$^{-4}$ M, while concentration of Cu(II) ions was 1 mmol. 1 mmol metal ions with reagent molar ratio 1:6 × 10$^{-4}$ M formed the metal-chelate have the maximum constant absorbance. Concentration of APDC 6 × 10$^{-4}$ M for Cu complex showed maximum constant absorbance as given in Fig. 4. 1.0 % SDS solution 2 mL of surfactant in 2 mg L$^{-1}$of Cu ions in Cu(II)-APDC, showed maximum constant absorbance[28]. The concentration 1 % SDS was optimized for the proposed procedure which is greater the cmc value 8.3 × 10$^{-3}$ M[32]. In terms of selectivity optimum pH 8 was optimized for Cu(II)-(PDC)$_2$complex and this value was kept constant[32]. The metal-complex production was rapid absorbance measurement was constant maximum up to 60 min. At ordinary temperature and metal-chelates showed unaltered absorbances until 24 h. Calibration of concentration graph ranges 0.12-4.0 µg mL$^{-1}$, the correlation coefficients with observed data was 0.9997 is shown in Fig. 5. The average molar absorption coefficient was determined 1.83 × 10$^4$ mol$^{-1}$ cm$^{-1}$ at $\lambda_{max}$ 447.8 is given in Table-6. Sandell's sensitivity was determined to be 5.83 ng cm$^{-2}$ is given in Table-6. Results showed good improvement than reported[33]. Detection limits (3 of the blank) were determined to be 5.83 ng mL$^{-1}$is given in Table-6. Cadmium(II) and nickel(II) have greater interferences with Cu(II)-chelate formation, which were removed with the use of 2 mL 0.1 M EDTA masking agents by forming stable metal complexes with Cd and Ni[28]. KClO$_3$, KSCN and Na$_2$tartarate showed no interference till the concentration reached at 1000 µg mL$^{-1.}$ Cu(II) and Cd(II) produced higher interference at low trace level that was removed with addition of masking agent 0.01 M NaCN volume 1.0 mL given in Table-1. IR spectra of APDC showed absorption peak of ν(C=C) and C=S appeared at 1700 cm$^{-1}$. The absorption peaks of ν(C=S) were observed near 1413 and1300 cm$^{-1}$. These absorption peaks suggested group (C=S) are shown in Fig. 6. The spectra of Cu(II)-chelates were compared with the ligands; the ν(C=S) bands being changed to higher wave numbers by 60-70 cm$^{-1}$ due to the thio-sulphur bonding. The ν(C=S) changed to higher wave numbers by 60-70 cm$^{-1}$ near1485 and at 1360 cm$^{-1}$ ν(C=S) bands showed PDC bonding with Cu(II) ions ν(M-S)[34,35]. New peaks near 1500 and 1440 cm$^{-1}$ suggested the ν(M-S) stretching for Cu(II)-PDC complexes are shown in Fig. 6. Ammonium

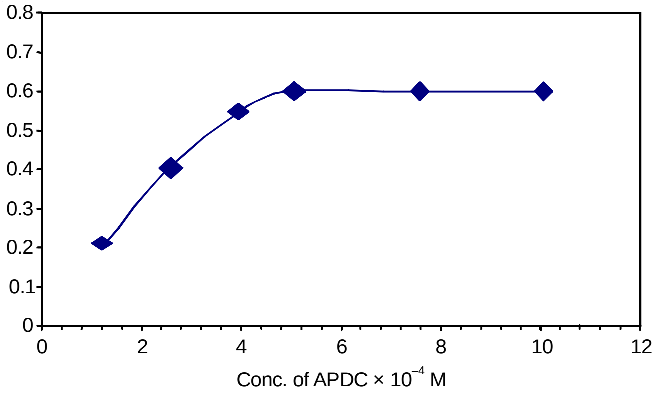

Fig. 4. Effect of APDC conc. on the absorbance of Cu(II)-APDC conc. of APDC × $10^{-4}$ M

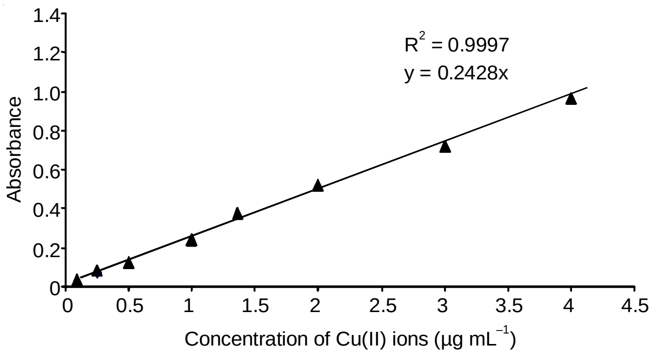

Fig. 5. Calibration graph of Cu(II)-APDC complexes in 1.0 SDS

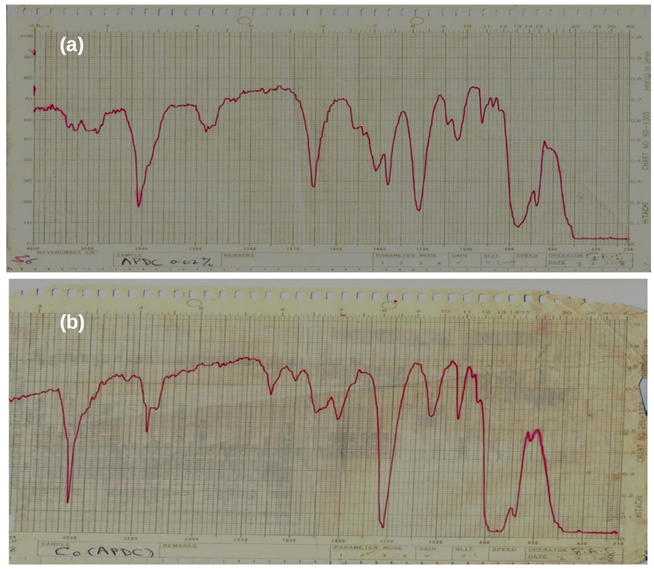

Fig. 6. IR spectra of (a) APDC (b) Cu(II)-APDC complex

pyrollidine dithiocarbamate is bidentate bonded to Cu(II) ion by the sulphur atom of PDC (Fig. 6)[33].

TABLE-6
ANALYTICAL PARAMETERS OF Cu(II)-[APDC]$_2$

| Parameters | Cu(II) |
|---|---|
| Wavelength (nm) | 447.8 |
| pH | 8 |
| Concentration of SDS (%) | 1.0 |
| APDC concentration (1×$10^{-4}$ M) | 6 |
| Reagent (M:R) | 1:2 |
| Linear range (µg mL$^{-1}$) | 0.12 -4 |
| Molar absorption coefficient (mol$^{-1}$cm$^{-1}$) | 1.83 × $10^4$ |
| Sandell's sensitivity (ng cm$^{-2}$) | 5.83 |
| Detection limit (µg mL$^{-1}$) | 5.83 |
| Correlation coefficient (R$^2$) | 0.9997 |
| Reproducibility (% RSD)* | 0.002 |

**Precision and accuracy:** Certified reference, namely Mallory was investigated. The procedure reliability was checked with recovery test % age method with the addition of spiked quantity of Cu(II) ions in water samples are given in Table-2. The average Cu(II) ions contents were found (n 7) in the reference material with a precision; RSD value up to 0.28 % of relative standard deviation[28].

**Validation of method:** Present developed method was assessed with % age recovery test and with method of standard addition. Data value showed well comparison with AAS and have good agreement of the both values to each method[28]. The results data were checked by statistically with t-test and f-test at 95 % confidence levels as given in Table-2.

## Conclusion

The copper(II) determination results obtained were comparable with the reported methods, while the present method is more sensitive than reported[27, 33]. The method has proved significant improvement in the results Beer's law concentration linear range and in the detection limits than the reported methods in Table-7[27,36]. Selectivity and sensitivity of the proposed method was higher than reported time-consuming expensive, solvent extraction method to the determination of metal ions[36]. The present technique is precise, sensitive, selective, reproducible, non-extractive simple, rapid and versatile than reported spectrophotometric methods[5,27,36].

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TABLE-7
REVIEW OF APDC/DDTC FOR DETERMINATION OF COPPER(II)

| Metal | Method | Reference |
|---|---|---|
| Cu | DDTC in aqueous $\lambda_{max}$ 540 nm, ε 5.5 × $10^3$ mol$^{-1}$ cm$^{-1}$ | 37 |
| Cu | CTAB with DDTC, ε 12.7 × $10^3$ mol$^{-1}$ cm$^{-1}$, D.L. 40.6 ng mL$^{-1}$ | 27 |
| Cu | SDS with DDTC, $\lambda_{max}$ 446 nm, ε 1.37 × $10^4$ mol$^{-1}$ cm$^{-1}$, D.L 98.9 ng mL$^{-1}$ | 4 |
| Cu | Tween 80, $\lambda_{max}$ 445 nm, linear concentration 0.05-8.0 µg mL$^{-1}$, D.L. 0.0393 µg mL$^{-1}$ | 28 |
| Cu | SDS, $\lambda_{max}$ 447.8 nm, ε 1.08 × $10^4$ mol$^{-1}$ m$^{-1}$, linear concentration 0.12-4.0 µg mL$^{-1}$, D.L 5.83 ng mL$^{-1}$ | Present method |

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