

A rapid extractive spectrophotometric determination of copper(II) in environmental samples, alloys, complexes and pharmaceutical samples using 4-[*N,N*(dimethyl)amino]benzaldehyde thiosemicarbazone

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Abstract 4-[*N,N*-(Dimethyl)amino]benzaldehyde thiosemicarbazone (DMABT) is proposed as an analytical reagent for the extractive spectrophotometric determination of copper(II). DMABT forms yellow colored complex with copper(II) in the pH range 4.4–5.4. Beer's law is obeyed in the concentration range up to $4.7 \mu\text{g mL}^{-1}$. The optimum concentration range for minimum photometric error as determined by Ringbom plot method is $1.2\text{--}3.8 \mu\text{g mL}^{-1}$. The yellowish Cu(II)–DMABT complex shows a maximum absorbance at 420 nm, with molar absorptivity of $1.72 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of the complex obtained from Beer's data is $0.0036 \mu\text{g cm}^{-2}$. The composition of the Cu(II)–DMABT complex is found to be 1:2 (M/L). The interference

of various cations and anions in the method were studied. Thus the method can be employed for the determination of trace amount of copper(II) in water, alloys and other natural samples of significant importance.

Keywords Copper determination · 4-[*N,N*-(Dimethyl)amino]benzaldehyde thiosemicarbazone · Chromogenic reagent

Introduction

Pure copper is used extensively for cables and wires, electric contacts, and a wide variety of conducting parts. The alloys of copper find extensive use in automobile radiators, heat exchangers, home heating systems and panels for absorbing solar energy. Besides, they are also used for pipes, valves, fittings in systems carrying potable water, process water and other aqueous fluids. Further, cupric sulphate is used in the manufacture of pigments, pesticides and medicine. Cuprous chloride is used in the organic synthesis and gas analysis. Cupric oxide is used in the manufacture of glass and enamels and as an oxidizing agent. Biologically, copper is essential in small amounts for the synthesis of haemoglobin. A deficiency of copper causes diseases such as anaemia, while an excess of it causes "Jaundice" and "Wilson disease". As a pollutant, copper is of particular concern because

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of its high degree of toxicity. The reported list of toxic copper species (Sorensen 1991) often includes $\text{Cu}(\text{OH})^+$, $\text{Cu}_2(\text{OH})_2^{2+}$, and CuCO_3 . However, without doubt, Cu^{2+} ions that are present in various aqueous solutions (their presence is a function of pH) are considered to be the most toxic of dissolved copper species (Freemantle 1989, Sorensen 1991). Excess copper in water is not only harmful to human beings but also to aquatic organisms. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, considering these excellent and extensive applications of copper and its compounds, a reliable and rapid method is often essential for the determination of copper in a single stage (Table 1).

Experimental

Apparatus and reagents

A Shimadzu (Model-160A) double beam UV/VIS spectrophotometer with 1.0 cm quartz cell and ELICO pH meter (LI 127) with combined electrodes were used for the measurements of absorbance and pH, respectively. All reagents and chemicals used were of analytical or chemically pure grade.

Stock solution of copper sulphate

A stock solution of copper(II) ($800 \mu\text{g mL}^{-1}$) was prepared by dissolving calculated amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in doubly distilled water containing a few drops of sulphuric acid. The solution was made up to a known volume and standardized gravimetrically by salicyaldoximate method (Vogel 1964) and volumetrically by iodometric method (Vogel 1964). This stock solution was further diluted to give a working solution containing $120 \mu\text{g mL}^{-1}$ of copper(II).

DMABT solution

The reagent, 4-[*N,N*-(Dimethyl)amino]benzaldehyde thiosemicarbazone was prepared and purified

as per the reported procedure (Sah and Daniels 1950). The purity of the compound was checked by the elemental analysis. A twice recrystallised product was used for the preparation of 0.1% reagent solution in acetone.

Buffer solutions

A buffer solution of pH 5.0 was prepared by mixing proper proportions of acetic acid (0.2 M) and sodium acetate solutions (0.2 M).

Solutions of foreign ions

The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

Procedure

To an aliquot of the solution containing 10–120 μg of copper(II) in a separating funnel, 10 mL of acetic acid–sodium acetate buffer of pH 5.0 were added. The solution was diluted to 20 mL with distilled water and 2 mL of 0.1% solution of the reagent in acetone was added and shaken well. After adding 5 mL chloroform, the mixture was again shaken well. The mixture was then equilibrated for 2 min. When the equilibrium was reached, the organic layer was separated from the aqueous layer. The aqueous layer was further mixed with two 5-mL portions of chloroform, again equilibrated and the organic layers were separated. All the three portions of the organic phase were mixed, dried with anhydrous sodium sulphate, transferred to a standard flask and finally made up to 25 mL with chloroform. The absorbance of the solution was then measured at 420 nm, using 10 mm matched cell against a reagent blank.

Analysis of copper in alloys

The proposed method was applied for the determination of copper in standard alloys such as Brass, Bronze, copper foil and Gunmetal. About 0.5 g of each oven dried alloy sample was dissolved in conc. HNO_3 . Then about a gram of urea and

Table 1 Comparison of the proposed method with other spectrophotometric method

Reagent	λ_{max} (nm)	pH	Beer's law range $\mu\text{g mL}^{-1}$	Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	M/L	Remarks	Ref.
8-Methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	410	5	1.5–3.8	0.7×10^4	1:1	Less sensitive	Jadhav and Vandre (1995)
2-Carboxybenzaldehyde thiosemicarbazone	346	–	0.5–5.0	1.2×10^4	1:1	Moderately sensitive	Lopez de Alba et al. (1999)
2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone	420	6.0	0–12.7	1.45×10^4	1:1	Moderately sensitive	Desai and Desai (1999)
Benzaldehyde-4-(2-hydroxy-5-sulphophenyl)-3-thiosemicarbazone	325	4.5	7.62	0.74×10^4	1:2	Less sensitive	Patel and Patel (2000)
4-Chlorisonitrosoacetophenone thiosemicarbazone	400	7.5–8.5	0.2–20	2.58×10^4	1:2	Moderately sensitive	Lokhande et al. (2001)
2-acetylthiophene-4-phenyl-3-thiosemicarbazone	385	4.5	0.10–0.51	2.92×10^4	1:1	Moderately sensitive	Prasad et al. (2003)
Benzildithiosemicarbazone	380	4.0	0.5–0.4	1.63×10^4	1:1	Moderately sensitive	Reddy et al. (2003)
Isonitrosopropiophenone thiosemicarbazone	390	10	0.5–0.6	0.582×10^4	1:2	Less sensitive	Kocharekar and Thakkar (2004)
Benzil- α -monoxime thiosemicarbazone	355	4.5	0.25–2.28	0.56×10^4	1:1	Less sensitive	Reddy et al. (2003)
pyridoxal-4-phenyl-3-thiosemicarbazone (PPT)	440	3–5.5	0.2–5.0	2.16×10^4	1:1	Moderately sensitive	Sarma et al. (2005)
2-acetylthiophene thiosemicarbazone	370	5–7	0.2–6.0	1.83×10^4	1:1	Moderately sensitive	Sayaji Rao et al. (2006)
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	380	3	0.4–3.6	2.24×10^4	1:1	Moderately sensitive	Janardhan Reddy et al. (2007)
4-[N,N-(Dimethyl)amino]benzaldehyde thiosemicarbazone	420	4.4–5.4	1.2–3.8	1.72×10^4	1:2	Moderately sensitive	PM

PM present method

one test tube of double distilled water were added, boiled, cooled and made up to a known volume. The stock solution was standardized gravimetrically by the salicylaldoximate method (Vogel 1964) and volumetrically by the iodometric method (Vogel 1964). Aliquots of this solution were used for the estimation of copper as per the proposed procedure. The results are presented in Table 2.

Analysis of copper in pharmaceutical samples

Pharmaceutical samples like supradyn, A to Z, Rediplex and AO-7 were selected for the determination of copper(II) in them. All the above pharmaceutical samples were brought into solution by adopting the following procedure. The samples were treated separately with 10 mL of aqua-regia and heated to near dryness, followed by treatment with 1 mL HClO₄ to decompose the organic matter. Finally, the residue obtained was extracted with 10 mL of 2N HNO₃, the solution was filtered and diluted to a known volume with double distilled water. Aliquots of the solutions were analyzed for copper(II), by using the proposed procedure. The results were checked with certified value and the results are presented in Table 2.

Analysis of copper in complexes

Copper complexes with salicylaldoxime, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, ethylenediamine and ammonia were prepared and purified as per the reported procedure (Gadag and Gajendragad 1978; Vogel 1964; Gopalan and Ramalingam 2003). A known weight of the complex was carefully decomposed with aqua-regia and evaporated to near dryness. The residue was dissolved in distilled water and made up to a known volume. The stock solution was standardized gravimetrically by the salicylaldoximate method (Vogel 1964) and volumetrically by the iodometric method (Vogel 1964). Aliquots of this solution were used for the estimation of copper as per the proposed procedure and the results are presented in Table 2.

Determination of copper in environmental water samples

Water samples were collected in polythene bottles from tap water, river water, spring water taken from different locations. After collection nitric acid (1 cm³/dm⁻³) was added as a preservative and filtered (with Whatman filter paper No. 40). Each filtered environmental water samples (1,000 mL) was evaporated nearly to dryness with a mixture

Table 2 Analysis of copper(II) in alloys, complexes and pharmaceutical samples ($n = 5$)

Sample	Copper present ^a (%)	Copper found (%)	Relative error (%)
Brass	62.59	62.50	-0.14
Bronze	89.79	89.71	-0.08
Copper foil	99.01	99.00	-0.01
Gun metal	87.85	87.69	-0.18
^b Cu(C ₇ H ₆ O ₂ N) ₂	18.93	18.90	-0.15
^c Cu(C ₉ H ₅ N ₄ S)	32.98	32.88	-0.30
^d Cu(C ₅ H ₉ N ₄ S)	28.78	28.71	-0.24
[Cu(en) ₂ (H ₂ O) ₂]I ₂	15.36	15.32	-0.26
[Cu(NH ₃) ₄]SO ₄ .H ₂ O	34.90	34.88	-0.05
A-Z (Alchem)	2.5 (mg/tablet)	2.485 (mg/tablet)	-0.60
AO-7 (Nicholas India)	2 (mg/tablet)	1.991 (mg/tablet)	-0.45
Supradyn (Nicholas India)	0.863 (mg/tablet)	0.861 (mg/tablet)	-0.23

^aEstimated by salicylaldoximate method and iodometric method

^bCopper complexes of Salicylaldoxime

^cCopper complexes of 4-amino-5-mercapto-3-methyl-1,2,4-triazole

^dCopper complexes of 4-amino-5-mercapto-3-propyl-1,2,4-triazole

Table 3 Determination of copper in environmental water samples

Sample	Copper ^a $\mu\text{g mL}^{-1}$		Recovery (%)
	Added	Found ^a	
Distilled water		ND	
	0.480	0.477	99.4
River water	0.640	0.639	99.8
		0.311	
Lake water	0.480	0.790	99.8
	0.640	0.949	99.7
Well water		0.334	
	0.480	0.812	99.7
	0.640	0.972	99.8
		0.241	
	0.480	0.719	99.7
	0.640	0.880	99.8

ND nondetectable

^aAverage of five determinations

of 2 mL of Con.H₂SO₄ and 5 mL of Con.HNO₃. After cooling, addition of 5 mL of Con.HNO₃ were repeated and heating to a dense white fumes continue or until the solution becomes colorless. The solution was then cooled and neutralized with dil.NH₄OH in the presence of 1–2 mL of a 0.01% (w/v) tartrate solution. The resulting solution was then filtered and quantitatively transferred into 100-mL standard flask and make up to the mark with distilled water. Suitable volumes of these solutions were taken and analyzed as per the proposed procedure are given the Table 3.

Analysis of copper in synthetic mixtures of ions

Several synthetic mixtures of varying compositions containing copper(II) and diverse ions of known concentrations were analysed for copper

as per the proposed method and the results are presented in Table 4.

Results and discussion

Absorption spectra

4-[N,N-(Dimethyl)amino]benzaldehyde thiosemicarbazone forms a sparingly soluble complex with copper(II). The complex can readily be extracted quantitatively into chloroform in the pH range 4.4–5.4. It is evident from the spectrum that the yellow solution of the complex in chloroform shows an absorption maximum in the visible region at 420 nm. The reagent has a negligibly small absorbance at the λ_{max} of the complex and, hence, does not interfere with the determination of copper. Thus, further absorbance measurements of the complex were made at 420 nm.

Effect of pH

To study the effect of pH on maximum color development and also on quantitative extraction of the colored complex into chloroform, the color reaction and the extraction were carried out at different pH values. A series of buffer solutions, each differing by 0.2 pH units were prepared and in the presence of these buffers, the color was developed and then the complex was extracted into chloroform layer as per the procedure. The absorbance values of each of the extracted solutions were measured. It is seen from that the extraction of the complex into chloroform is quantitative and the complex shows maximum absorbance in the pH range 4.4–5.4. The complete extraction of

Table 4 Analysis of copper(II) in synthetic mixtures of ions (n = 5)

Composition of mixtures ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	Relative error (%)
Cu(II) (2.35 $\mu\text{g mL}^{-1}$) (A)	2.349	-0.04
(A) + Pb(II) (10 $\mu\text{g mL}^{-1}$) + Zn(II) (12 $\mu\text{g mL}^{-1}$)	2.348	-0.08
(A) + Zn(II) (5 $\mu\text{g mL}^{-1}$) + Cd(II) (5 $\mu\text{g mL}^{-1}$)	2.350	0.00
(A) + Rh(III) (10 $\mu\text{g mL}^{-1}$) + Fe(II) (1 $\mu\text{g mL}^{-1}$)	2.350	0.00
(A) + Rh(III) (12 $\mu\text{g mL}^{-1}$) + Ni(II) (8 $\mu\text{g mL}^{-1}$)	2.349	-0.04
(A) + Ni(II) (5 $\mu\text{g mL}^{-1}$) + Fe(II) (1 $\mu\text{g mL}^{-1}$)	2.349	-0.04
(A) + Cd(II) (5 $\mu\text{g mL}^{-1}$) + Fe(II) (0.5 $\mu\text{g mL}^{-1}$)	2.350	0.00

the complex into chloroform is confirmed by the fact that the aqueous phase does not show any absorbance. However, outside this pH range, it is observed that either the extraction of the complex into chloroform is incomplete or the solution does not attain the maximum color. For all subsequent studies, therefore, the pH is maintained at an optimum level of 5.0.

Composition of the complex and effect of reagent concentrations

The composition of the Cu(II)–DMABT complex was studied by Job's method of continuous variation and also by the mole ratio method. In these methods, equimolar solutions of Cu(II) and DMABT were used. The continuous variation method shows a maximum at the mole fraction 0.333 of copper, indicating the formation of a 1:2 complex (Cu–DMABT). Further support to this, comes from the results of mole ratio method.

In order to study the effect of reagent concentration on the intensity of the color developed, the experiments were carried out by treating the copper(II) solution with varying amounts of the reagents, extracting the complex into chloroform and then measuring the absorbance at 420 nm. The results of these studies reveal that a minimum 10-fold excess of the reagent is needed for maximum color development. Further, the absorbance of the solution is not affected substantially, even on addition of more than ten fold excess of the reagent.

Order of addition of reagents, rate of reaction and stability of color

The order of the addition of the reagent did not have any effect on the absorbance of the complex. The color reaction between copper(II) and the reagent is found to be rapid and the maximum color development takes place instantaneously at room temperature. During extraction, the equilibrium between the two layers is reached in less than two minutes. It is also observed that the extraction of copper(II) complex into chloroform is almost complete in a single extraction. However, to ensure complete extraction, two additional

extractions were carried out. The color of the complex in chloroform is found to be stable at least for 24 h without any significant change in the absorbance value.

Validity of Beer's law, molar absorptivity and Sandell's sensitivity

In order to determine the concentration range in which Beer's law is valid, absorbance values were measured at various concentrations of Cu(II) in the solution. The Beer's plot shows that, Beer's law is obeyed up to $4.7 \mu\text{g mL}^{-1}$ of Cu(II). The optimum working range, obtained from Ringbom plot (Ringbom et al. 1939) was found to be $1.2\text{--}3.8 \mu\text{g mL}^{-1}$. Molar absorptivity of the complex was calculated to be $1.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of the method was found to be $0.0036 \mu\text{g cm}^{-2}$.

Precision and accuracy of the method

To assess the precision and accuracy of the method, determinations were carried out for a set of six measurement of $1.41\text{--}3.76 \mu\text{g mL}^{-1}$ of Cu(II), under the optimized experimental condition. These results reveal that the relative error and co-efficient of variation do not exceed $\pm 0.60\%$ and 0.37% , respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

The influence of the presence of diverse ions on the absorbance value of Cu(II)–DMABT complex system was studied with $2.82 \mu\text{g mL}^{-1}$ Cu(II) in the presence of foreign ions. An error of $\pm 2\%$ in the absorbance value was considered as tolerance limit. It is evident from the results that anions such as fluoride ($800 \mu\text{g mL}^{-1}$), chloride (2,000), bromide (1,000), nitrate (2,000), sulphate (3,000), phosphate (1,500), tartarate (1,000), acetate (5,000) and borate (1,800) do not show any interference. Similarly, cations like Tl(I) ($1,100 \mu\text{g mL}^{-1}$), Zn(II) ($1,200 \mu\text{g mL}^{-1}$), Pb(II) (1,000), Ca(II) (10), Ba(II) (500), Fe(II) (50), Co(II) (1,000), Ni(II) (800), Cd(II) (200), Mg(II) (1,000), Mn(II) (150), Sr(II) (1,200), Al(III) (20),

Rh(III) (1,000), Cr(III) (500), Ru(III) (5,000), Ir(III) (10), Ce(III) (400), Bi(III) (50), Zr(IV) (50), Th(IV) (400), Ti(IV) (40), U(VI) (1,000) and Mo(VI) (40) do not interfere in the method.

Among the anions studied, thiosulphate, oxalate, citrate and thiocyanate show severe interference at all levels of concentration. Among halides, iodide alone shows interference. EDTA also shows severe interference at all levels of concentrations. Among the metal ions, Ag(II), Hg(II), Pd(II), Sn(II) and Pt(IV) show severe interference at all levels. Except Sn(II), the interference of others is due to the formation of colored complexes with the reagent. In the presence of Sn(II), the intensity of the color is found to be decreased. Ca(II) and Al(III) do not interfere up to 10 and 20 $\mu\text{g mL}^{-1}$, respectively. The presence of $\nu(\nu)$ prevents the color reaction. Ir(III) also interfere when present above 10 $\mu\text{g mL}^{-1}$.

Suitability of organic solvents as extractants

In order to find out the most suitable non-aqueous extractant for the present work, extraction of the Cu(II)–DMABT complex and measurements of absorbance were carried out by the proposed procedure, using common solvents such as chloroform, benzene, xylene, toluene, carbon tetrachloride, nitrobenzene etc. Of the several such solvents tried for extraction, chloroform is found to be the most suitable solvent for the system studied and exhibited good sensitivity, selectivity and stability. In other solvents, either, the complex shows lower absorbance or the complex is not easily extracted into the solvent, therefore, in all subsequent determinations; chloroform is used as the extractant.

Conclusions

The DMABT forms a 1:2 yellow complex with Cu(II) in the pH range 4.4–5.4. Beer's law is valid up to 4.7 $\mu\text{g mL}^{-1}$ and optimum concentration range for the determination is 1.2–3.8 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity of the method are found to be $1.72 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0036 \mu\text{g cm}^{-2}$, respectively. The relative error and coefficient of variation ($n = 6$)

for the method do not exceed $\pm 0.60\%$ and 0.37% , respectively. Since the method tolerates a number of metal ions commonly associated with copper, though the method involves extraction of the colored complex into chloroform. The extraction process is very fast. The color reaction is completed instantaneously at the laboratory temperature itself. Thus, the method can be employed for the determination of trace amount of copper(II) in water, alloy samples and other natural samples of significant importance.

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