

A facile synthesis, characterization of cinnamaldehyde thiosemicarbazone and determination of micro amount of copper (II) in different environmental and vital samples by spectrophotometry in presence of Micellar medium

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ABSTRACT

A rapid, simple, sensitive and selective Spectrophotometric method has been developed for the determination of Copper (II) using Cinnamaldehyde semithiocarbazone (CMTSC). Copper (II) forms a light yellow coloured water-soluble complex with CMTSC in presence of Triton-X (100) (5%) (Micellar medium) and the complex shows maximum absorbance while the reagent blank shows negligible absorbance at λ_{max} 400 nm and at pH 9.0. Beer's law was obeyed in the range 0.095-0.953 mg/mL and the optimum concentration range from ringbom plot was 0.190-0.857 mg/mL of Copper (II). The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be $4.10 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0015\text{-}\mu\text{g.cm}^{-2}$ respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Cu (II): CMTSC] stoichiometry with stability constant 5.0×10^6 . The standard deviation of the method in the determination of $0.381\text{-}\mu\text{g ml}^{-1}$ of Copper (II) was 0.001. First and second order derivative Spectrophotometric methods are developed at λ_{max} 420 nm and 440 nm respectively for the determination of Copper (II), which was more sensitive than the zero order method. The developed method has been used for the determination of Copper (II) in different Environmental and Vital samples like Beer, Wine, Grains, Nuts, Sheep liver, Buffalo milk and Industrial fly ash, Species, Alloy, Biological and Plant samples.

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KEYWORDS

Copper (II);
Spectrophotometry;
Environmental and
Vital samples;
CMTSC;
Micellar medium;
Triton-X 100.

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al^[1]. Hydrazones are important class of known analytical reagents. Derivative spectrophotometry was a very use-

ful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. Hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. A micellar solution has the ability to enhance the stability of metal complex

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and has been utilized as a medium for the spectrophotometric determination of the metal chelate^[2-4].

Copper is utilized in electrical industries, electronic industries and industrially useful alloys. It is widely used in printed circuit boards, generators, transformers, computer heat sinks, coins. Because of its biostatic property it is used as roofing material for houses. Copper knobs are used in hospitals to reduce the transfer of disease. Copper is essential for all plants and animals. It is an essential constituent of about thirty enzymes and glycoproteins and is required for the synthesis of hemoglobin and for some biological processes.

It also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues into plasma, helps to maintain myelin in the nervous system, and is important in the formation of bone and brain tissues. A deficiency of copper causes diseases such as anemia. Though Copper is an essential element, it becomes hazardous when present in excess. Excess of copper causes jaundice and Wilson disease. Excess of copper in water is not only harmful to human beings, but also interferes with the self purification of bulk water and exerts an adverse effect on the microbiological treatment of waste water. Too much Copper in water has also been found to damage marine life.

EXPERIMENTAL PART

Materials and methods

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300-800 nm.

Facile synthesis of CMTSC

The reagent (CMTSC) was prepared by the Sah and Daniels^[5] procedure.

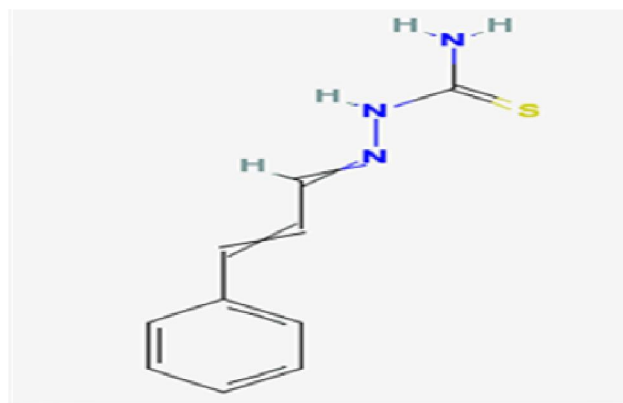
Characterization of CMTSC

The structure and characterization of CMTSC was confirmed by IR, NMR and Mass spectral data.

RESULTS AND DISCUSSION

The chromogenic reagent CMTSC was used for the spectrophotometric determination of the Copper (II). The Copper (II)-CMTSC complex shows the maximum absorbance at 400 nm, where the reagent blank does not absorb appreciably.

The calibration graph follows the straight-line equation $Y = a + bX$; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the Cu (II)-CMTSC complex experimental data in the Beer's law equation, the calibration equations are calculated as $I_{\max} 400 \text{ nm} = 0.64906X + 0.00279$ for zero order data and $I_{\max} 420 \text{ nm} = 0.49291X - 4.37273 \times 10^{-4}$ for first derivative data and $I_{\max} 440 \text{ nm} = 0.73488X + 0.00284$ for second order derivative data which gives the straight lines.



Structure of CMTSC

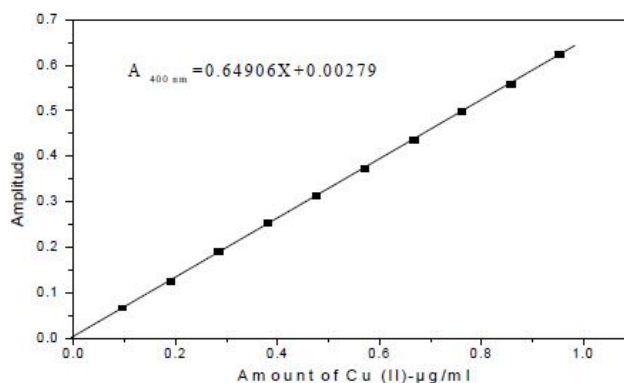
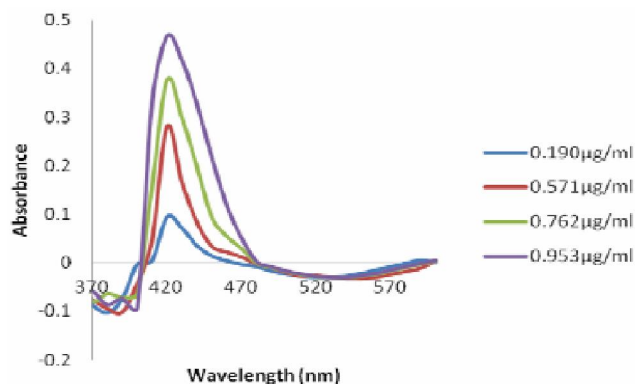


Figure 1 : Absorbance Vs Amount of Cu (II) $Cu(II) = 1.5 \times 10^{-6} \text{ M}$ CMTSC = $3 \times 10^{-3} \text{ M}$; Triton-X100 (5%) = 0.5 ml pH = 9.0; $\lambda_{\max} = 400 \text{ nm}$.

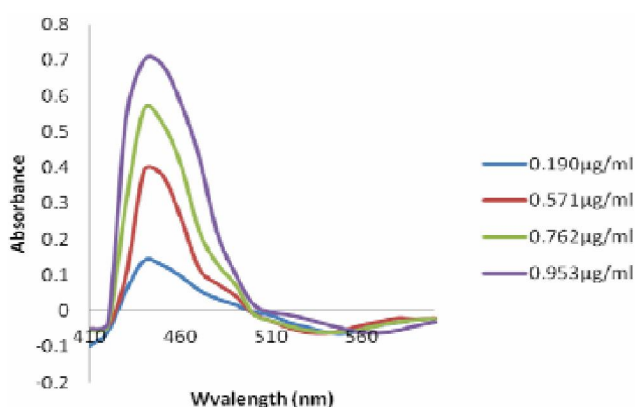
Interference

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which



Cu (II) = 1.5x10⁻⁶ M; CMTSC = 3x10⁻³ M; Triton-X100 = 0.5 ml; pH = 9.0; λ_{max} = 420 nm

Figure 2 : Cu (II)-CMTSC-first derivative spectra



Cu (II) = 1.5x10⁻⁶ M; CMTSC = 3x10⁻³ M; Triton-X100 = 0.5 ml; pH = 9.0; λ_{max} = 440 nm

Figure 3 : Cu (II)-CMTSC-second derivative spectra

often accompany Cu (II) was examined by carrying out the determination of 0.476 µg/ml of Cu (II) in the presence of foreign ions for CMTSC. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ± 2% in the absorbance or amplitude. The data obtained in the derivative method was also incorporated. The data suggest that several associated anions and cations do not interfere when they were present in large excess, such as Iodide, Nitrate, Thiocyanide, and Bromide, Strontium (I), Selenium (II), Barium (II), Strontium (V) and Tungsten (VI). The tolerance limit values for many anions and cations were more

TABLE 1 : Spectrophotometric determination of copper (II) in beer and wine

Sample name	Certified value	*Amount of Cu (II) found (µg/ml)					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Beer	5.32	5.312	-0.15	3.317	-0.09	3.319	-0.03
Wine	7.45	7.43	-0.26	7.44	-0.13	7.44	-0.13

TABLE 2 : Spectrophotometric determination of copper (II) in some grains

Sample name	AAS value	Copper quantity					
		Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Phaseolus Sp	24.38	24.35	0.12	24.37	0.04	24.37	0.04
Vicia Faba	26.4	26.34	0.22	26.37	0.11	26.39	0.03

TABLE 3 : Determination of copper (II) in sheep liver, buffalo milk and industrial fly ash

Sample name	Certified value	*Composition of Cu (II) found (%)					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Sheep liver	16.81	16.83	0.11	16.85	0.23	16.89	0.47
Buffalo milk	4.10	4.09	-0.24	4.12	0.48	4.12	0.48
Industrial fly ash	6.0	5.98	-0.3	6.01	0.16	6.03	0.49

TABLE 4 : Spectrophotometric determination of copper (II) in some nuts

Sample name	AAS value	Copper quantity					
		Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Juglans Sp	8.50	8.45	0.59	8.48	0.23	8.45	0.23
Prunus amygdalus	29.26	29.23	0.10	29.25	0.04	29.24	0.04
Pistacia Sp	16.90	16.85	0.29	16.87	0.17	16.89	0.05

TABLE 5 : Spectrophotometric determination of copper (II) in some spices

Sample name	AAS value	Copper quantity					
		Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Sumac	1.65	1.64	0.61	1.643	0.42	1.645	0.30
Curry Powder	0.7	0.63	11.11	0.67	4.47	0.69	1.49
Maggi	2.9	2.83	2.47	2.87	1.04	2.89	0.34

TABLE 6 : Spectrophotometric determination of copper (II) in biological materials

Biological Sample	AAS Method	* Copper (II) found (µg/g)					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Ground nut oil	1.098	1.093	-0.45	1.095	-0.27	1.097	0.09
Mustard oil	2.251	2.247	-0.17	2.249	-0.08	2.249	-0.08
Sesame seed	12.640	12.545	-0.75	12.613	-0.21	12.34	-0.04
Ground nut seed	5.466	5.426	-0.73	5.456	-0.18	5.462	-0.07
Chocolates (Eclairs)	2.007	1.973	-1.69	1.98	-0.36	2.005	-0.10

*Average of five determinations

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in derivative method. The interference of associated metal ions such as Iron (III) and Copper (II) was decreased by adding masking agent phosphate.

Applications

The method proposed in the present studies was applied for the determination of Copper (II) in Beer,

TABLE 7 : Spectrophotometric determination of copper (II) in alloy samples

Alloy Sample	Certified value	*Amount of Cu (II) found ($\mu\text{g/ml}$)					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
(a) BCS 179/3a	58.50	58.47	-0.05	58.49	-0.01	58.49	-0.01
(b) BCS 180/2b	68.12	68.09	-0.04	68.11	-0.15	68.11	-0.01
(c) Tin base white metal	4.58	4.53	-1.11	4.55	-0.65	4.57	-0.21
(d) Devard's alloy (Berther alloy)	48.91	48.78	-0.26	48.83	-0.16	48.89	-0.04
(e) BAS 106	4.10	4.05	-1.23	4.08	-0.49	4.09	-0.24
(a) BCS 179/3a	58.50	58.45	-0.08	58.47	-0.05	58.49	-0.01

TABLE 8 : Spectrophotometric determination copper (II) in different plant samples

Sample name	AAS	Copper quantity					
		Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Spinacia oleraca	1.5	1.48	1.35	1.487	0.874	1.49	0.67
Beta vulgaris v.cilca	1.23	1.21	1.65	1.22	0.82	1.22	0.82
Aplum gravealens	1.08	1.06	1.88	1.07	0.93	1.07	0.93
Raphanus sativus	1.08	1.07	0.93	1.075	0.46	1.079	0.09
Hibiscus esaculuntus	6.80	6.73	1.04	6.78	0.29	6.78	0.29
Foeniculum vulgare	17.01	16.93	0.43	16.95	0.35	16.98	0.17
Visit	1.3	1.275	1.91	1.282	1.40	1.289	0.85
Helianthus annuus	8.42	8.35	0.83	8.37	0.59	8.40	0.23
Raphnus sativus	11.40	11.32	0.70	11.37	0.26	11.39	0.08
Lepidoum sativum	28.80	28.75	0.17	28.79	0.03	28.79	0.03
Foeniculum vulgare	19.30	19.23	0.36	19.27	0.15	19.29	0.05
Lactuca sativa	9.30	9.25	0.54	9.28	0.21	9.28	0.21
B.oleracea V.Capitata	12.5	12.42	0.80	12.45	0.64	12.49	0.40
B.oleracea V.Botry tis	14.5	14.45	0.34	14.48	0.13	14.48	0.13

Wine, Grains, Nuts, Sheep liver, Buffalo milk and Industrial fly ash, Specis, Alloy, Biological and Plant samples.

CONCLUSION

The proposed methods are simple, accurate and have advantages over the reported methods which suffer from interference by large number of ions or require either heating or extraction or are less sensitive. Some factors such as initial cost of instrument, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of these techniques, particularly in laboratories with limited budget in developing countries and for fieldwork are to be taken as the consideration for the determination of Copper (II) at microgram quantities, a number of hydrazone deriva-

tives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry are employed. Among them Spectrophotometric methods are preferred because they are cheaper and easy to handle. In general the technique of solvent extraction was widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction.

PRECISION AND ACCURACY

The precision and accuracy of the proposed methods are studied by analyzing (10 replicates) of Copper

(II) and the RSD value was found to be 0.39%.

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