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A NOVEL METHOD FOR DETECTION AND ESTIMATION OF COPPER (II) IN WATER

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An improved, simple and sensitive method for quick detection and estimation of Copper (II) in drinking water has been described. The method involves use of ferric thiocyanate along with optimized amount of sodium thiosulphate as field test reagent. The concentration of copper is determined from the time required for disappearance of red brown colour of reagent. The ratio of ferric thiocyanate and sodium thiosulphate solutions should be 1:3 for best results. A time chart is also provided for finding out concentration of copper. The sensitivity limit of reagent for visual observation is 1.0 mg/l. The test is simple, sensitive, rapid, economic and quantitative, hence it can be incorporated in existing water testing field kits.

Keywords: copper (II), water sample, ferric thiocyanate reagent, field test

Introduction

Copper is widely distributed in nature. Copper salts are used in water supply systems to control biological growths in reservoirs and in distribution pipes and to catalyse the oxidation of manganese [1]. Corrosion of copper containing alloys in pipe fittings may introduce measurable amount of copper into the water in a pipe system.

Copper is essential metal required by almost all living organisms in some of their enzyme systems [2]. The adult daily requirement has been estimated as 2.0 mg. Deficiency of copper may lead to certain physiological disorders in both plants and animals, but in higher concentrations it works essentially as a pollutant. Copper poisoning occurs mostly due to homicidal ingestion of copper containing solutions or consumption of acidic beverages stored in containers of copper [3]. Excess of copper in human body is toxic and causes hypertension, sporadic fever, uremia, coma and even death. Copper also produces pathological changes in brain tissue [4]. It is also toxic to most aquatic life and particularly algae are very sensitive to copper. It is toxic to many plants at 0.1 to 1.0 mg/l nutrient solutions. Thus the presence of copper is to be tested in drinking water for suggesting its potability along with other physicochemical parameters. In the present investigation an attempt is made to detect and estimate copper in drinking water. The permissible limit of copper in drinking water is 1.0 mg/l as laid down by WHO [5].

Experimental

Reagents

a. Ferric thiocyanate solution (2.0 g ferric chloride (AR) and 2.5 g potassium thiocyanate (AR) in 100 ml double distilled water).
b. Sodium thiosulphate (AR) solution - 0.1 N (freshly prepared).

Method

To 10 ml water sample add a drop of ferric thiocyanate reagent. A red brown colour appears. Now add 3 drops of sodium thiosulphate solution. Shake, if red brown colour disappears within 5 minutes it indicates that Copper (II) is present above permissible limit i.e. 1.0 mg/l. The quantitative estimation can be done with the help of time chart provided for ready reference. If the colour of reagent does not disappear within 5 minutes it indicates that copper concentration is well within permissible limit. Higher concentration of copper in the tests sample is determined by standard dilution technique.

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Table 2 Copper (Permissible limit = 1.0 mg/l)

	Reagents					
Characteristics	Alizarin blue	Benzidine + Potassium bromide	Ammonium bromide	Dithizone	Ferric thiocyanate + Sodium thiosulphate	Ferric thiocyanate + Sodium thiosulphate* (in optimized ratio)
Medium	Pyridine	Acetic acid	Conc. H_3PO_4	CCl_4	Water	Water
Number of ingredients	2	3	2	2	3	3
Sensitivity (ppm)	5.0	5.0	3.0	1.0	0.01	0.01
Oxidation state	Cu (II)	Cu (II)	Cu (II)	Cu (II)	Cu (II)	Cu (II)
Colour and nature of complex	Blue ppt (Stable)	Blue colour (Stable)	Violet colour (Stable)	Yellow brown colour (Stable)	Brown colour disappears (Stable)	Brown colour disappears (Stable)
Interferences	Co (III), Ni (II) interfere	Au (III), Fe (III) interfere	Many metal ions interfere	Zn (II), Cd (II), Pb (II) interfere	No interference	No interference
Remark	Liquid phase	Liquid phase	Liquid phase	Liquid phase	Liquid phase	Liquid phase

*Modified field test reagent

Table 1 Time Chart

Concentration of COPPER (mg/l)	Time required for disappearance of reagent colours
10.0	Instantaneous
5.0	1 minute
3.0	2 minute
2.0	4 minute
1.0	5 minute
< 1.0	> 5 minutes

Time chart

Standard copper sulphate (AR) solutions were prepared in different concentrations ranging from 1.0 to 10.0 mg/l. The time required by different concentrations of copper for disappearance of reagent colour were taken as reference time in the time chart, as shown in *Table 1*.

Estimation of copper

Standard copper solutions were made from copper sulphate and estimation of Copper (II) was done using atomic absorption spectrophotometric method (AAS) [6].

Results and Discussion

The methods for estimation of copper [7-20] involve the use of different reagents like Alizarin blue, Benzidine, Dithizone, Ammonium bromide and ferric thiocyanate etc. Laboratory studies on these reagents were conducted in view of their adaptability for field determinations, stability, ease and sensitivity of test at different dilutions specially near permissible limit. The results are given in *Table 2*.

It is clear from the *Table 2* that ferric thiocyanate reagent is most suitable under field conditions while others are not suitable due to their complexity, unstability and other limitations.

Chemistry Involved in Ferric Thiocyanate Test

In the ferric thiocyanate test when a solution of ferric salt reacts with a solution of an alkali thiosulphate a transient red brown colour appears which is unstable, slowly disappears after considerable time. The reaction takes place in two steps:

$$Fe^{3+} + 2S_2O_3^{2-} \longrightarrow \underset{\text{Red brown complex}}{[Fe(S_2O_3)_2]^-} \quad \text{(rapid)} \qquad (1)$$

$$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow \underset{\text{Almost colourless}}{2Fe^{2+} + S_4O_6^{2-}} \quad \text{(slow)} \qquad (2)$$

$$2Fe^{3+} + 2S_2O_3^{2-} \longrightarrow 2Fe^{2+} + S_4O_6^{2-} \quad \text{(slow)} \qquad (3)$$

Copper (II) accelerate the second partial reaction and therefore speed up total reaction. Consequently the red brown colour due to $[Fe(S_2O_3)_2]^-$ ion disappears far more rapidly when copper ions are present. The velocity of reaction (disappearance of colour) increases with increase in concentration of Copper (II). The chemistry involved is as follows:

$$\begin{aligned}&[Fe(S_2O_3)_2]^- + Cu^{2+} \longrightarrow \\ &\longrightarrow Cu^+ + Fe^{2+} + S_4O_6^{2-} \quad \text{(rapid)}\end{aligned} \qquad (4)$$

$$Cu^+ + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+} \quad \text{(rapid)} \qquad (5)$$

$$\begin{aligned}&[Fe(S_2O_3)_2]^- + Fe^{3+} \xrightarrow{Cu^{2+}} \\ &\longrightarrow 2Fe^{2+} + S_4O_6^{2-} \quad \text{(rapid)}\end{aligned} \qquad (6)$$

Table 3 Comparative studies of Rapid Field Test and Standard Method (AAS) using standard copper solutions

Parameters	Standard samples having different concentration of Cu (II)				
Sample No.	a	b	c	d	e
Time required for disappearance of reagent colour after adding field test reagent (in minutes)	5	4	2	1	inst.
Concentration of copper using time chart in field test method (mg/l)	1.0	2.0	3.0	5.0	10.0
Concentration of copper estimated by standard AAS method (mg/l)	0.988	2.001	3.005	5.001	10.001

Table 4 Comparative studies of Rapid Field Test and Standard Methods using some natural water samples

Source of Water sample	Concentration of Cu (II) (mg/l)	
	AAS	Field test
Tapi Baori	0.0	0.0
Lal Sagar	0.01	< 1.0
Fateh Sagar	0.04	< 1.0
Dev Kund	0.00	0.00
Umed Bhawan	0.03	< 1.0
Kailana	0.00	0.00
Gulab Sagar	0.21	< 1.0
Gorinda Baori	2.02	2.00
Jalap Baori	3.34	3.00
Chandpole Jhalra	0.04	< 1.0
Nagadari Mandore	0.00	0.00
Jhalara Mahila Bagh	0.11	< 1.0
Kurbija Baori	4.45	5.00
Ranisar Padamsar	0.01	< 1.0
Balsamand	0.00	0.00
Shiv Mandir	0.02	< 1.0
Kabutaron Ka Chowk	0.00	0.00
Police Line Ratanada	0.01	< 1.0
Jain Bhawan Ratanada	1.35	2.00
Subhash Chowk Ratanadda	0.01	< 1.0
Baiji Ka Talab	2.20	2.00

To make the test quantitative and specific:

The ratio of number of drops of reagent 1 (ferric thiocyanate solution) and reagent 2 (sodium thiosulphate) solution) was optimized. It was found that 1:3 ratio is optimum. With this optimized concentration ratio the test becomes sensitive upto permissible limit.

Comparative studies of standard methods like Atomic Absorption Spectrophotometric method and rapid field test undertaken on standard Copper (II) solutions have shown (*Table 3*) that the visual colour test exhibited by this method is quite reliable under field conditions.

Laboratory and field trials on surface water, ground water and irrigation water using this reagent have also been extensively conducted during last two years successfully as shown in *Table 4*. Thus this rapid test can be used in field areas for assessing Copper (II) in drinking water. The test is simple, reliable, sensitive and quantitative too and can easily be performed by a person of normal scientific temper. So the test will be a good addition in existing water testing field kits [21].

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