

Spectrophotometric determination of copper (II) in industrial effluent samples using sulfanilic acid as a ligand system

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A new UV-visible spectrophotometric method was developed for the determination of copper (II) in industrial wastewater samples. The method is based on complex formation of copper (II) with sulfanilic acid in acidic medium at room temperature. The complex showed maximum absorption at a wavelength of 380 nm with a molar absorptivity value of $6.7 \times 10^2 \text{ mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed in the concentration range of 0.3 to 2.1 ppm. Interferences due to zinc (II), cadmium (II), nickel (II), cobalt (II), chromium (III) and several anions were investigated. The proposed method was successfully applied to the determination of copper (II) in industrial effluent samples.

Keywords: Copper (II), Sulfanilic acid (SA), Acidic medium, Beer's Law, Industrial effluent

INTRODUCTION

The entire world is environmental scientist's laboratory. Environmental science deals with the study of atmosphere, water, soil, the release and uptake of materials by plants and animals. It includes various studies on the exchange of chemical species, elements and compounds between the atmosphere, hydrosphere, geosphere and biosphere. This branch has developed, because of the increase in human activities and their effects, frequently not beneficial to the natural environment [1]. Metals, as indispensable components of the nature, constitute about 6 % of the earth. Metals are not biodegradable and have virtually an unlimited lifespan and potential for unlimited recycling. Thus, metals can be considered as renewable materials [2-10]. There are 111 known elements; of these 80 are metals. The important toxic metals and metalloids are: beryllium (Be), osmium (Os), platinum (Pt), mercury (Hg), titanium (Ti), vanadium (V), selenium (Se), chromium (Cr), tellurium (Te), cobalt (Co), copper (Cu), uranium (U), cerium (Ce), silver (Ag), cadmium (Cd), lead (Pb), arsenic (As), antimony (Sb), nickel (Ni), zinc (Zn) and manganese (Mn). Their toxicity varies with threshold limit values (TLV) of $2 \mu\text{g}/\text{m}^3$ to $5000 \mu\text{g}/\text{m}^3$, which are the maximum tolerable limits for human beings. The different metals have different degrees of toxicity. A limited number of these metals are carcinogenic. They lead to cancer of lungs, liver, pleura and thyroid. Some of these

pollutants are encountered in water and air, effluents, solid wastes and sewages [11-13].

Copper is a reddish metal with a face-centered cubic crystalline structure. It has low chemical reactivity [14]. It is an essential metal for plants, microorganisms, animals and human beings to perform specific biological functions [15, 16]. Copper is often added to fertilizers to serve as a supplement to plants. The failure to supply adequate amounts of copper leads to a variety of biochemical and physiological disorders in plants. In humans, it not only facilitates the conversion of iron to haemoglobin but also stimulates the growth of red blood cells. Copper is an integral part of certain digestive enzymes. Copper has received considerable attention owing to its technological and biological significance. It is an essential constituent of about thirty enzymes and glycoproteins. It is required for the synthesis of haemoglobin and for some biological processes. The concentration of copper is crucial for determining its toxicity to many biological systems. It has been reported that the toxic copper species are $[\text{Cu}(\text{OH})]^+$, $[\text{Cu}_2(\text{OH})_2]^{2+}$ and CuCO_3 . Therefore, copper ions present in various aqueous systems are considered to be the most toxic of dissolved copper species. Excess concentration of copper in water systems is harmful to human beings; it affects the self-purification of bulk water and disturbs the microbiological treatment of waste water. Thus, the determination of trace amounts of Cu (II) is becoming increasingly important, because of the increased interest in environmental pollution [17-20]. Copper is an essential element for human

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life, but in high doses it can cause anemia, liver damage, stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes and additives to control algal growth [21]. Long term exposure to copper can cause irritation of nose, mouth, eyes, leading to headache, dizziness, vomiting and diarrhea [14]. Intentional uptake of copper may cause liver and kidney damage and even death. Industrial exposure to copper fumes, dusts and mists may result in metal fume fever, with atrophic changes in nasal mucous membranes. Chronic poisoning with copper results in Wilson's disease, characterized by hepatic cirrhosis, brain damage, renal failure and copper deposition in the cornea [22].

Many analytical techniques are currently available to determine copper concentration in samples with different matrices, such as flame atomic absorption spectroscopy, electrothermal atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry or differential pulse anodic stripping voltammetry. Besides the well-known advantages of these instrumental techniques (precision, accuracy, sensitivity, selectivity, etc.), all of them present a series of disadvantages, such as high investment costs, complexity and difficult *in situ* application. Many spectrophotometric methods have been developed for the determination of Cu(II) based on reactions with reagents such as S,S'-bis(2-aminophenyl) oxalate [23], chloro(phenyl) glyoxime [24], salicylaldehyde acetoacetic acid hydrazone [25], sodium diethyldithiocarbamate [26], neocuproine (2,9-dimethyl-1,10-phenanthroline) [27], etc. Most of the reported spectrophotometric methods are time consuming, employing many reagents to develop the color and to extract the copper complex into organic solvents.

In the present work, a sensitive and simple method of determination of trace copper in industrial wastewater samples by UV-visible spectrophotometry is described, based on the formation of a copper (II) - sulfanilic acid complex. The influence of some analytical parameters including pH, amount of sulfanilic acid and effect of diverse ions, etc., on the complex formation was investigated.

MATERIALS AND METHODS

Spectrophotometry is often used for determining metals in alloys, minerals and complexes, owing to its selectivity. In comparison with atomic emission spectroscopy, atomic absorption spectroscopy and similar techniques, it offers the advantage of

calibration graphs that are linear over a wider range. A very extensive range of concentrations of substances (10^{-2} – 10^{-8} M) may be covered. Color-based identification of materials was probably one of the earliest examples of qualitative molecular absorption spectrophotometry. The recognition that color intensity can be an indicator of concentration was probably the earliest application of molecular absorption spectroscopy for quantitative estimation. This quantitative estimation was done using the human eye as the detector and undispersed sunlight or artificial light as the light source. Later it was found that the accuracy and the precision could be improved by isolating specific frequencies of light using optical filters.

A Systronics UV-visible spectrophotometer 118 with a wavelength range of 200-1000 nm was used for the measurements. It is a single-beam, manual instrument for both qualitative and quantitative absorption spectrometric studies.

All solutions were prepared with analytical reagent-grade chemicals in deionized water. Copper solution was prepared from 2.496 g of analytical reagent-grade copper sulfate crystals dissolved in 100 ml of distilled water. Sulfanilic acid reagent was prepared by solubilizing 1 g of sulfanilic acid in 100 ml of water, slowly by shaking. The pH buffer was prepared from 0.1 g of sodium acetate dissolved in 100 ml of water. Other solutions used for interference studies were prepared by dissolving the required amounts of salts in distilled water.

The procedure followed for the standardization and analysis is as follows:

Add from 0.5 to 5 ml of the copper solution in 20 ml standard flasks (0.15 to 15 ppm of copper). Add 5 ml of sodium acetate solution to each of them. Allow them to stand for a few minutes till the solution gets a whitish color. Add 5 ml of sulfanilic acid solution to the standard flasks. Make up the solution to 20 ml using distilled water and shake well. Then measure the absorbance at 380 nm.

Determination of the suitable pH for complex formation:

All ligands require certain conditions and supporting ions to form the colored complex. In this study it was found that the formation of a complex between copper (II) sulfate and sulfanilic acid solution requires a pH buffer (sodium acetate solution). It brings the system near to neutral pH and allows sulfanilic acid to form a green colored complex with copper (II) ions in the solution.

Determination of the wavelength of maximum absorption of the colored species:

An aliquot of 5 ml of the standard solution containing 0.75 mg L^{-1} of copper (II) was taken in a

20 ml standard flask. Then, 5 ml of sodium acetate solution and 5 ml of sulfanilic acid solution were added and the volume was brought to the mark with distilled water. The solution was mixed well and the absorbance of the colored species was measured at different wavelengths in the range 300-400 nm against the reagent blank, prepared under similar conditions. The absorbance of the colored species was plotted against wavelengths as shown in Figure 1.

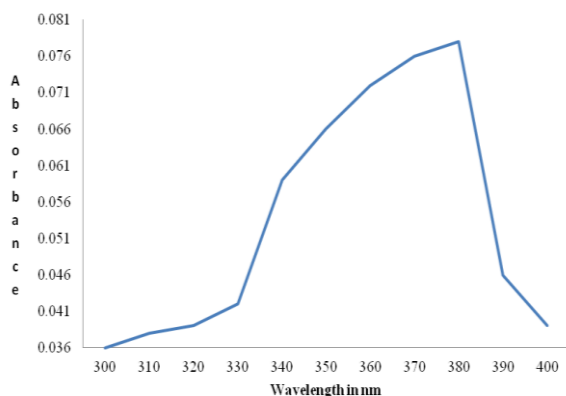


Fig. 1. Absorption spectrum of Cu (II) SA (Cu^{+2} , 0.75 ppm)

Determination of effective sulfanilic acid concentration:

Different aliquots from zero to 10 ml of the standard copper (II) solution were added to 20 ml standard flasks giving solutions of strength 0.3-3 ppm. 5 ml of the 0.1% sodium acetate solution and 5 ml of 1% sulfanilic acid solution were added to each flask. The volume was diluted to the mark with distilled water. The solutions were mixed well and the absorbance of the colored species was measured at 380 nm against the reagent blank, as shown in Figure.2.

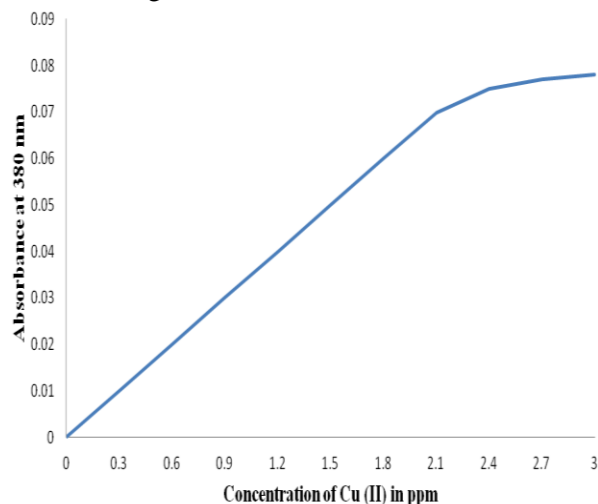


Fig. 2. Effective concentration of Cu (II) with the reagent sulfanilic acid

Preparation of a calibration graph for copper (II):

Different aliquots from zero to 5 ml of the standard solution containing zero to 1.5 ppm of copper (II) were transferred to a series of 20 ml standard flasks. Then, 5 ml of 0.1% sodium acetate and 5 ml of 1% sulfanilic acid solutions were added and the contents were diluted upto the mark with distilled water and mixed well. The absorbance of the colored species was measured at 380 nm against the reagent blank. A calibration graph of absorbance against the concentration of copper (II) was plotted (Figure 3). The calibration graph was used for the determination of copper (II) in various matrices of unknown concentrations.

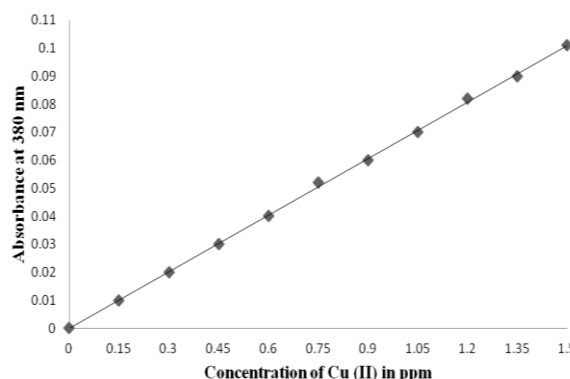


Fig. 3. Beer's law plot of the Cu (II) - sulfanilic acid system

Analysis of industrial effluent:

Copper-containing electro-plating industrial effluent was collected. Suitable aliquots of the sample solutions were analyzed according to the procedure for determining copper (II).

Discussion:

The detailed investigation of the reaction between sulfanilic acid and copper (II) showed that the latter oxidizes sulfanilic acid in sodium acetate medium to a green colored species with an absorbance maximum at 380 nm.

Optimization of experimental variables:

In order to establish the optimum conditions for the formation of copper-sulfanilic acid species, the effect of several experimental variables was studied and is discussed in the following paragraphs.

Absorption spectrum:

The absorption spectrum of the copper-sulfanilic acid colored species in 0.1% sodium acetate solution is shown in Fig.1. Sulfanilic acid with the amino group in para position has an absorbance maximum at 356-380 nm. Therefore, the absorbance measurements were made at 380 nm. Under similar conditions, the reagent blank does not absorb at this wavelength.

Effect of medium and its concentration:

To develop a quantitative method based on this reaction, a study was conducted to determine the most effective acid species and optimum acid concentration to be employed. The green-colored species was unstable in either sodium oxalate or ammonium acetate medium and does not give maximum color intensity in other media. Sodium acetate medium was found to be the most effective buffer compared to the other two. In sodium acetate medium the green color was stable for 25 min and subjected to less interferences from foreign ions.

Effect of the metal ion concentration:

The effect of concentration of copper (II) ions was studied by measuring the absorbance at 380 nm for a solution containing a fixed amount of sulfanilic acid and varying amounts (0.3 to 3 ppm) of copper (II). Below the concentration of 0.09 ppm, copper (II) does not give maximum intensity and above 2.4 ppm, the concentration had no effect on the absorbance values. Hence, a working concentration range up to 1.5 ppm of copper (II) can be estimated. The results of these studies are presented in Figure.2.

Reaction rate and effect of time:

The time required for obtaining the green colored species of copper and sulfanilic acid was examined. Under the optimum conditions, full color development occurred instantaneously and the developed color was found to be stable for a period of 25 minutes.

Effect of diverse ions:

In order to assess the possible analytical applications of the method, the effect of some ions which often accompany copper, was studied. Different amounts of the diverse ions were added to a 0.75 ppm copper (II) solution. An error of less than 2 % in the absorbance values was considered

to be tolerable. The tolerance limits of the foreign ions tested are given in Table 1.

The major advantage of this method was that sulfanilic acid can be used as a selective reagent for the determination of copper in the presence of large amounts of cations like Ni (II), Zn (II), Be (II), and Cd (II) and anions like chlorides (Cl⁻), nitrates (NO₃⁻), sulfates (SO₄²⁻) and phosphates (PO₄³⁻) which are associated with copper in electro-plating industries.

The results also indicate that Cr (IV) and sulfate ions interfere seriously. However, the interference of these ions can be avoided using appropriate masking agents.

APPLICATIONS:

The developed method was applied for the determination of copper in an industrial effluent by the procedure described above. The results are presented in Table 2

CONCLUSIONS:

The proposed method for determination of copper (II) offers the advantage of simplicity, rapidity and sensitivity without the need for heating or extraction. The developed color is stable for 25 min.

This procedure permits a clear determination of color in presence of copper and hence the proposed method can be successfully applied to the determination of trace amounts of copper in industrial effluents.

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Table 1: Effect of different ions on the determination of 0.75 ppm of copper (II)

Cations	Tolerance limit in ppm	Anions added	Tolerance limit in ppm
Zn(II)	6	Cl ⁻	25
Cd(II)	20	SO ₄ ²⁻	15
Ni(II)	25	PO ₄ ³⁻	20
Co(II)	30	NO ₃ ⁻	25
Cr(IV)	4	EDTA	0.40

Table 2 Copper (II) concentrations found in the industrial effluent samples

Sample of industrial effluent	Copper certified (ppm)	Copper found (ppm)
Sample 1	0.3	0.27
Sample 2	0.45	0.45

REFERENCES:

1. B. Barbara, Kebbekus Somenath Mitra *Environmental Chemical Analysis* CRC Press, New York, 1997.
2. World Commission on Environment and Development, *Our Common Future*, New York, Oxford University press (1987).
3. C. Baird, *Environmental Chemistry*, W.H Freeman and Company, New York (1995).
4. Gore, *Earth in the Balance: Ecology and the Human Spirit*, New York, Houghton Mifflin (1992).
5. A.K. De, *Environmental Chemistry*, New Age International (P) Limited, New Delhi (1998).
6. G.S. Fell, *Metals in the Environment 2*, Chem. Britain, 167, (1980) 323.
7. K Schwartz, *Clinical Chemistry and Chemical Toxicology of Metals*, Elsevier, (1977).
8. S.D. Lee, *Biochemical Effects of Environmental Pollutants*, Ann Arbor Science Publishers. Inc., Ann Arbor, Mich. (1977).
9. J.L. Casarett and John Doult, *Toxicology: The Basic Science of Poisons*, Macmillan Publishing Co., New York (1975).
10. Ei-Ichiro Ochiai, *Bioinorganic Chemistry*, Allyn and Bacon Inc., Boston Mass (1977).
11. Dayananda B P Ph.D Thesis University of Mysore, Mysore, 2007.
12. S M Khopakar, *Envirnmental Pollution Analysis*, New Age International(P) Ltd., New Delhi, (2001).
13. Kiran Kumar T N Ph.D Thesis University of Mysore, Mysore, 2009.
14. Shanthalakshmi K Ph.D thesis University of Mysore, Mysore, 2009
15. Hashem E Y, Seleim M M, Ahmed M. El-Zohry, *Gre. Chem Let. Revi.*, **4**, 241, (2011),.
16. Prafullachandra Tekale, Smruti Tekale, Sudheer Lingayat and P N Pabrekar, *J. Sci Res Rep.*, **1**, 83, (2011).
17. Lutfullah, Saurabh Sharma, Nafisur Rahman, Syed Najmul Hejaz Azmi, Bashir Iqbal, Maisa Ismail Bilal Bait Amburk, Zuweina Masoud Hilal Al Barwani, *J. Chin Chem Soc.*, **57**, 622, (2010).
18. Freemantle, M. H. *Chemistry in Action*, Macmillan Educa Education Ltd.: London, 1989.
19. Sorensen, E. B. M. *Metal Poisoning in Fish*, CRC Press: Boston, MA, (1991).
20. Scheinberg, I. H, Morell, A. G. *In Inorganic Biochemistry*, Eichhorn G.L Eds, Elsevier, New York, **1**, 306, (1973).
21. Orhan Turkoglu and Mustafa Soylak, *J. Chin Chem Soc.*, **5**, 575 (2005).
22. Rekha D, Suvadnan K, Suresh Kumar K, Prasad P. Reddy, Jayaraj B, Chiranjeevi P, *J. Serb. Chem. Soc.*, **72**, 299, (2007).
23. Sinan Nohut, Serdar Karabocek, Saadettin Guner, Yasar Gok, *J. Pharm Biomed Ana.*, **20**, 309, (1999).
24. Srilalitha Vinnakota, Raghavendra Guru Prasad Aluru, Ramana Kumar Kakarla, Seshagiri Vahi Ravindranath Lakshmana Rao, Krishna Rao, *Ovid Uni Ann. Chem*, **22**, 5, (2011).
25. Jankiewicz B, Ptaszyński B, Turek, *Poli J. Envi Studies*, **8**, 35, (1999).
26. Central Pollution Control Board, *Guide Manual: Water and Wastewater Analysis*, New Delhi, India, 2012.

СПЕКТРОФОТОМЕТРИЧНО ОПРЕДЕЛЯНЕ НА МЕД (II) В ПРОБИ ОТ ПРОМИШЛЕНИ
ОТПАДЪЦИ С ПОМОЩТА НА СУЛФАНИЛОВА КИСЕЛИНА КАТО ЛИГАНД

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(Резюме)

Разработен е нов UV-Vis спектрофотометричен метод за определяне на мед (II) проби от промишлени отпадъчни води. Методът се основава на комплексобразуване на медни йони (II) със сулфанилова киселина в кисела среда при стайна температура. Комплексите показват максимална абсорбция при дължина на вълната 380 nm с моларна абсорбция $6.7 \times 10^{-2} \text{ mol}^{-1} \text{ cm}^{-1}$. Законът на Beer се спазва в обхват от концентрации 0.3 до 2.1 ppm. Изследвано е пречещото влияние на цинк (II), кадмий (II), никел (II), кобалт (II), хром (III) и няколко аниона. Предложеният метод е приложен успешно за определянето на мед (II) в проби от промишлени отпадъчни води.