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Full Length Research Paper

Development of a sensitive spectrophotometeric method for determination of copper

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Simple and rapid spectrophotometeric procedure have been established for quantitation of Cu (II).This method is based on the reaction between alizarin red S and boric acid in the solution of pH 8.5 to produce a red complex which place between organic and aqueous phases. In presence of Cu (II), the complex of alizarin red S and boric acid is dissociated and new complex between alizarin red S and metal ions formed which can be measured at the optimum wavelength. All variables were studied to optimize the reaction conditions. Regression analysis of beer's low plot showed good correlation in concentration range 0.6 - 15 µg.mL^{-1}. The molar absorptivity and detection limit are calculated. The interference effects of the foreign cation have been examined.

Key words: Extraction, copper, trace elements, water samples, Alizarin red S

INTRODUCTION

The direct determination of heavy metals at trace level in saline samples by flame atomic absorption spectrometer (FAAS) or electrothermal atomic absorption spectrometer (ETAAS) (Stalikas, 2002; Ghaedi et al., 2005; Jahromi et al., 2007; Sakai et al., 1998) has been failed due to particularly their low concentrations and matrix effects. Many authors indicated that matrix interferences are possible and to overcome them, the addition of different matrix modifiers (Ghaedi et al., 2006) as well as the use of preconcentration–separation procedures (Ghaedi et al., 2006; Stafilov, 2000; Nakamura et al., 1988; Lazaru et al., 1993; Dadfarnia et al., 2006) . Preconcentration and separation techniques, such as liquid–liquid extraction, ion exchange, co-precipitation, cloud point extraction, solid phase extraction, etc. can solve these problems and lead to a higher confidence level and easy determination of the trace elements (Ghaedi et al., 2006; Stafilov, 2000; Nakamura et al., 1988; Lazaru et al., 1993; Dadfarnia et al., 2006; Rojas et al., 2007; Lahiri et al., 2007; Yaman et al., 2006; Li et al., 2007). Some of these methods suffer from inconveniences such as, lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi stage, lower enrichment factor and consumption of organic harmful solvents. These problems can be overcome by replacement of filtration or centrifugation by flotation. The major advantages of the flotation preconcentration method are the rapidity in addition to excellent recoveries of analytes. The equipments necessary for flotation preconcentration are simple and inexpensive. The small amount of a surfactant and the tiny air bubbles require to perform the proper flotation prevent serious contamination risks, which could be manifested by the high blank value. Because the physical and chemical properties of aragonite aqueous solution are similar to those of the natural waters with higher water hardness, a method of flotation is applied as the second way to eliminate the matrix effects (Aki et al., 2006; Lazaru et al., 1997; Stafilov et al., 2000) . Several methods have been developed for the flotation of heavy metal ions (Caballero et al., 1990; Cundeva et al., 2000; Paneva et al., 2005; Zendelovska et al., 2001; Karimi et al., 2008; Zhao et al., 2008).

Copper determination in water and biological materials is a good tool for environmental and toxicological monitoring (Duran, 2007; Prabhakaran and Subramanian, 2003; Lemos, 2003; Guo, 2004; Tewari and Singh, 2001; Kumar, 2000; Venkatesh and Singh, 2005; Safavi et al., 2006). Generally determination of trace metal is very important in the context of environmental Protection, food

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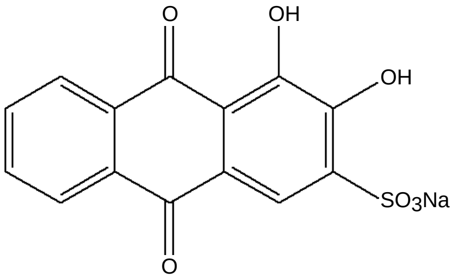

Figure 1. Structure of Alizarin red S

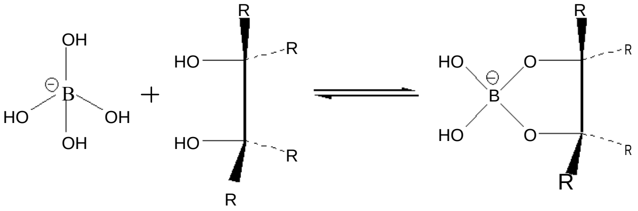

Figure 2. Cyclic ester formed from the reaction of 1, 2-diols with borate.

and agricultural chemistry and high purity materials. Flame atomic absorption spectrometry and spectrophotometeric have been widely used for the determination of trace metal ions because of the relativity simple and inexpensive equipment required.

The application of UV-Vis absorption to the determination of metals is still popular in many laboratories. The technique provides easy determination of many metals from low to high concentration at affordable cost.

Many new organic reagents have been synthesized and various highly sensitive methods developed with molar absorptivities of 10^5 -10^6 L. mol^{-1}.cm^{-1} or even higher. In studies for establishing new methods, much attention paid to sensitivity. However specificity and selectivity are also very important.

In this paper UV-Vis spectrophotometeric method is proposed for determination of Cu (II) in aqueous solution. The method based on the reaction Cu (II) and alizarin red S (Figure 1). The proposed method is simple, sensitive and the complex formed is stable.

EXPRIMENTAL

Materials

Chloroform, boric acid, sodium monohydrogen phosphate, sodium dihydrogen phosphate, mercury (II) chloride, silver sulfide, copper (II) sulfate pentahydrate, nickel (II) chloride hexahydrate, cobalt (II) sulfate heptahydrate, lead (II) acetate trihydrate and tin (II) chloride dehydrate were products of Merck (Darmstadt, Germany). Alizarin red S was obtained from Fluka (Buchs, Switzerland). The stock solution (1000 mg. L^{-1}) of Cu (II) was prepared by dissolving appropriate amount of Cu $(SO_4)_2$.$5H_2O$ in deionized water. 0.01 M phosphate buffer was used to adjust the pH of the solutions, wherever suitable.

Assay procedure

3 mL alizarin red S (10 ppm), 2 mL chloroform, 1mL buffer pH 8.5 and 3 mL of boric acid 0.01 M were transferred into a test tube. The contents were shaken for approximately 1 min. The two phases were allowed to separate complex of alizarin- boric acid was formed between two aqueous and organic phases. Then aliquot phases were decanted and complex was washed several times with deionized water till obtaining colorless solution. Aliquots of solution (3 mL) of Cu^{2+} 0.6 - 15 µg.mL^{-1} and 1 mL buffer (pH 7.5) were added into the test tube and shaken for 1 min. After separation of two phases, the absorbance of aqueous solution was measured at 240 nm against the reagent blank. The reagent blank was prepared exactly like the procedure described above, but in the absence of Cu^{2+}. A calibration graph was drowned or regression equation calculated.

RESULT AND DISCUSSION

Compounds that contain hydroxylic group can react with boronat. The interaction that may occur is the formation of a cyclic ester complex, as illustrated in Figure 2.These complexes can form with 1, 2 or 1, 3-diol- containing compounds when the hydroxyl groups are oriented in the proper geometry like alizarin red S.

Due to the simple stoichiometry of the occurred reaction dealing with the formation of boric acid with alizarin red S and also high stability and insolubility of obtained precipitate in aqueous media, we were interested in developing a new simple method for the quantitative determination of Cu (II).Therefore, boric acid at alkaline pH (8) was used as suitable reagent for the precipitation of alizarin red S in aqueous solution and formation of complex between two organic and aqueous solvent. Alizarin has been a well-known ligand for complexation of so many metal ions (Hosseini, 2006; Chamsaz, 2002; Farhadi and Maleki, 2002; Basavaiah, 1999; Amin, 2002; Shama and Amin, 2004; Alkan et al., 2003). So in presence of metal ions, the complex of alizarin red S and boric acid is dissociated and new complex between alizarin red S and metal ions formed and metal solution get red.

Determination of Cu (II) in aqueous solution

Our studies proved that the most sensitive pH for determination Cu (II) by alizarin red S is pH 7.5. So we choose this pH using buffer solution in aliquots of solution of Cu (II) in assay procedure. A linear correlation was found between absorbance and concentration of Cu (II) in the range of 0.6-15 µg.mL^{-1} (Figure 3). The equation representative calibration curve is:

$A= 0.0259 C + 0.048$
$R^2= 0.9688$

Where A and C correspond to absorbance and Cu (II) concentration in µg.mL^{-1}, respectively. The correlation

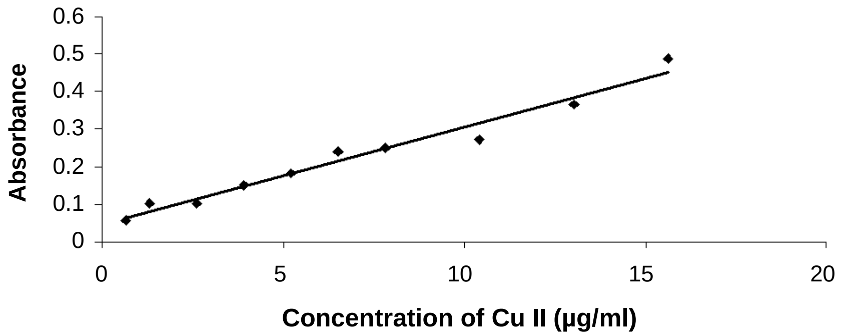

Figure 3. Calibration curve of Cu (II) at pH 7.5.

Table 1. Effect of foreign ions.

Sn^{2+}	Co^{2+}	Ni^{2+}	Ag^+	Hg_2^{2+}	Pb^{2+}	**metal ions**
419	407	404	405	414	410	max (nm)
0.0306	0.0291	0.0069	0.0436	0.0385	0.0134	absorbance

coefficient indicates excellent linearity. The molar absorptivity coefficient was found 2.8 × 10^3 L.mol^{-1}.cm^{-1}. The method has a detection limit of 0.5 µg.mL^{-1}.

Effect of foreign ions

The possible interference attributable to varies ions, which may be present as the major constituents of mineral samples or found in water samples, was examined by introducing them in to the (3 mL) solutions containing 10 µg.mL^{-1} of each ions and treating as described in the procedure. The results are given in Table 1. It was observed that all the ions were interfered even at low concentrations. This is due to formation of complex between alizarin red S and the mentioned ions.

Conclusions

The developed method offers a good sensitivity for the determination of Cu (II) in the range of 0.6 - 15 µg.mL^{-1} in water. The important feasibility of the method is its simplicity in treatment with the aqueous samples. Results were found not significantly different from AAS and had less standard deviation in this proposed method than in AAS technique.

This paper described a method for the determination of Cu (II) in pure form. In terms of simplicity and expense, the proposed method could be considered superior to the methods reported previously, especially with those based on instrumental analysis. It is clear that alizarin red-S is highly sensitive reagent for the determination of so many metal ions compared with other reagents. Although methods using are more selective compared with the proposed procedure, the latter is less time consuming (maximum time is 10 min), In addition it is applicable at room temperature and has no problem in view of the environmental pollution.

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