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A NEW METHOD FOR THE DETERMINATION OF COPPER(II) BY THE CATALYTIC OXIDATION OF VARIAMINE BLUE B BASE ANALOGUE

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A new sensitive and selective catalytic method for the determination of copper(II) is proposed. p-Anisidine reacts with N,N-dimethylaniline to form variamine blue B leuco base analogue. Copper(II) catalyzes the hydrogen peroxide oxidation of the analogue to a blue compound (λ_{max}= 740 nm). By the use of this reaction, as little as 10^{-8} M copper(II) can be determined easily.

Various catalytic methods for the determination of copper have been reported.$^{1-5)}$ However, most of them are not selective, although the sensitivity is relatively high. Thus, the development of more sensitive and selective catalytic methods for copper is still expected. Recently, the authors have presented a sensitive catalytic method for iron by hydrogen peroxide oxidation of variamine blue B leuco base analogue, N-(p-methoxyphenyl)-N',N'-dimethyl-p-phenylenediamine (MDP), which was formed by the reaction of p-anisidine with N,N-dimethylaniline (DMA).$^{6)}$ It was also found that the same reaction was catalyzed by a trace amount of copper(II). In this paper, a new method for the determination of nanogram level of copper(II) based on its catalytic effect on the same reaction is described. When the commercially available variamine blue B base was used, high reagent blanks were found probably because of the oxidation products of this compound formed during its storage. On the other hand, by using the reactants separately and replacing aniline with DMA, the blank values were found to be kept low as described previously.$^{6)}$

p-Anisidine and DMA were purified by vacuum sublimation and vacuum distillation, respectively. All chemicals used were of analytical grade and deionized - distilled water was used to prepare the solution. The recommended procedure is as follows: To 20 ml of a sample solution containing not more than 500 ng of copper (II) in a beaker, 2 ml of 0.5 M sodium fluoride, 8 ml of 2.5×10^{-2} M anisidine, 5 ml of 8.0×10^{-2} M DMA, 1 ml of 1.5 M acetic acid and 5 ml of 2.0 M ammonia as an activator were added. The pH was adjusted to 3.9 - 4.0 with 2 M and 0.1 M hydrochloric acid using pH meter. The mixture was transfered to a 50-ml volumetric flask as a reaction vessel and diluted to *ca*. 48 ml with water. The mixed solution was kept at 60°C in a thermostat to attain thermal equilibrium. Then, 1 ml of 5 M hydrogen peroxide was added, and the solution was diluted to the mark with water of 60°C and mixed well to initiate the reaction. Exactly 10 min after the initiation of the reaction, about 5 ml of the reaction mixture in a thermostat was pipetted into a dry test tube immersed in an ice water bath to quench the reaction. Then the absorbance at 740 nm in a 10-mm glass cell was measured preferably within 20 min against a distilled water reference. The net absorbance was obtained by subtracting a blank absorbance to compensate for any changes in color of the reagents on storage and in amounts of impurity of the reagents.

MDP is probably oxidized to a blue compound, N,N-dimethyl-N'-(p-methoxyphenyl)-1,4-quinonediiminonium ion(DMQ) by trace amounts of copper(II) in the presence of hydrogen peroxide. The blue compound, DMQ, had an absorption maximum at 740 nm in the proposed conditions.[7)]

The reaction temperature of 60°C was selected and a reaction time of 10 min was chosen for the sake of high sensitivity and reproducibility. The absorbance of the reaction mixture remained unchanged for at least at 30 min so long as the mixture was kept in an ice water bath, while it tended to increase slowly when the mixture was left at room temperature after having been cooled in ice water. Thus, the reaction mixture should be kept in an ice water bath until the absorbance was measured. The effect of pH on the color development for the catalytic reaction was examined for a constant reaction time of 10 min at 60°C. The results are shown in Fig. 1. The color development was maximal and almost constant in the pH range of 3.8 - 4.2.

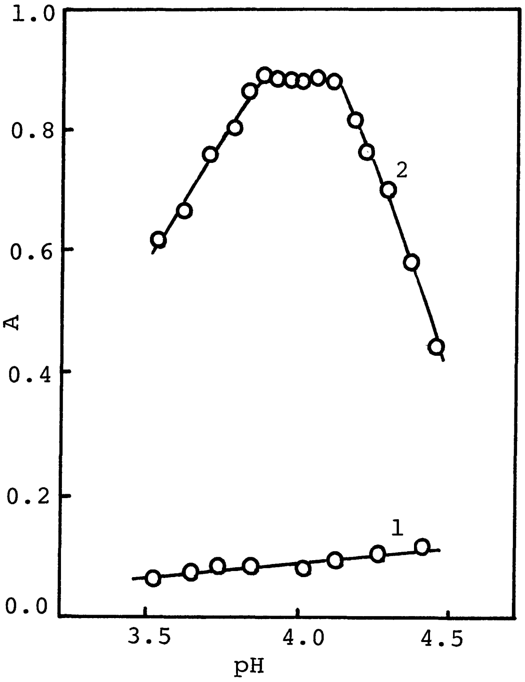

Fig.1. Effect of pH
1: reagent blank 2: 500 ng of copper(II)
Other conditions as in the procedure.

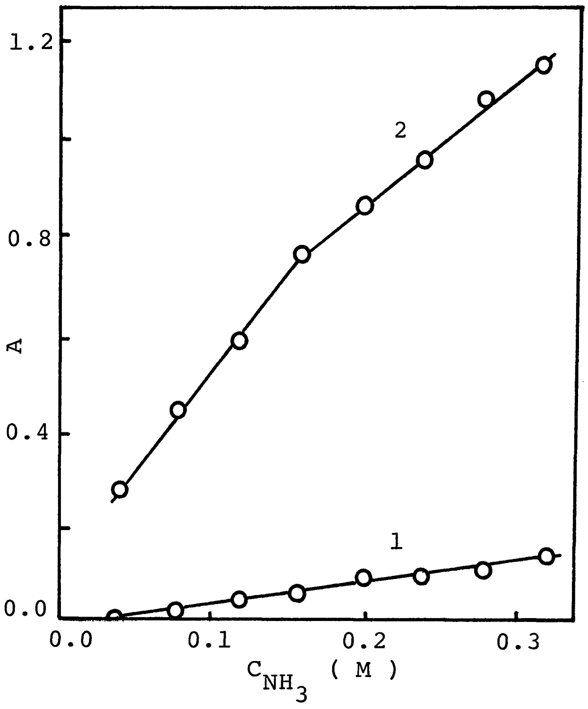

Fig.2. Effect of ammonia concentration on the color development
1: reagent blank 2: 500 ng of copper(II)
Other conditions as in the procedure.

The effect of DMA concentration was examined at a constant concentration of the anisidine. The color development was maximal and almost constant over the range of 7.2×10^{-3} M - 1.0×10^{-2} M DMA at the 4.0×10^{-3} M anisidine concentration, decreasing on both sides of this range. The rate of the color development tended to increase with increase in the concentration of ammonia as shown in Fig. 2. In this case, ammonia seems to act as an activator.[8)] The concentration of acetic acid higher than 4.0×10^{-2} M resulted in the decreased rate of the color development. Therefore, the concentration of acetic acid was fixed at 3.0×10^{-2} M. The effect of hydrgen peroxide concentration was also examined on the color development with and without copper(II) as shown in Fig. 3. The absorbance increased as the concentration of the hydrogen peroxide increased, but a constant absorbance was obtained at the concentration of the peroxide higher than 8.0×10^{-2} M and the blank absorbances were found to be kept low. In the proposed procedure, the concentration of hydrogen peroxide was selected as 0.1 M.

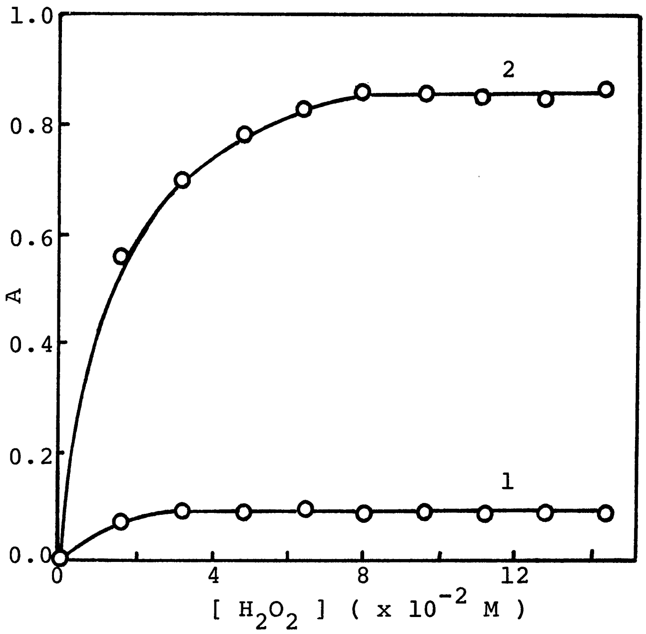

Fig.3. Effect of hydrogen peroxide concentration on the color development
1: reagent blank 2: 500 ng of copper(II)
Other conditions as in the procedure.

The following ions and compounds caused no interference on the determination of 200 ng of copper(II) at least up to the specified amounts: 100 µg of As(III), As(V), Ca(II), Cd(II), Co(II), Hg(II), Mg(II), Mn(II), Ni(II), Zn(II); 10 µg of Ag(I), Al(III), Ce(III), Ce(IV), Mo(VI), Pb(II), V(V), W(VI), Br^-, I^-; 10 mg of sodium chloride, sodium nitrate, sodium sulfate, potassium chloride. Positive interferences from iron(III) and chromium(III,VI) were observed. However, it should be emphasized that serious interference of iron(III) can be eliminated by sodium fluoride. Negative interferences were observed from tin(II) and tin(IV), possibly because of adsorption of the reactants on the hydrolyzed species of tin as described previously.[6)]

The reproducibility of this method is satisfactory with relative standard deviations of 2.3%, 1.7% and 1.2% for five determinations of 100, 200 and 500 ng of copper(II), respectively.

The method was evaluated using a tap water in comparison with flameless atomic absorption spectrometry. The results are shown in Table 1. Recovery of added copper (II) was found to be quantitative and the reproducibility was satisfactory.

Further study is underway for evaluating the method using samples such as river, sea and waste waters.

Table 1. Determination of copper in tap water.

Sample taken ml	Copper added ng	Copper found ng	Copper corrected for addition, ppb[a]
20	0	33	17
20	0	35	18
20	0	32	16
20	100	135	18
20	100	134	17
20	100	137	19

[a] The value obtained by flameless atomic absorption spectrometry was 20 ppb.

References and Note

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7) The absorption maximum of DMQ was found at 735 nm in the previous work(Ref. 6). The shift of the absorption maximum may be attributable to ammonia added as an activator in the system. However, it is not understood at present why the shift of the maximum occured in the presence of ammonia.
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