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SPECTROPHOTOMETRIC DETERMINATION OF NANOGRAM LEVEL OF COPPER(II) BY ITS CATALYTIC EFFECT

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A new simple, sensitive and selective catalytic method for the determination of nanogram level of copper(II) is proposed. N,N-Dimethyl-p-phenylenediamine reacts with N,N-dimethylaniline to form Bindschedler's Green leuco base (BGL) and in the presence of hydrogen peroxide, copper(II) catalyzes the oxidation of BGL to a colored compound (λ_{max}=725 nm).

The application of catalytic reactions to analytical chemistry, especially to the trace analysis is progressed recently.1,2) There are two main problems in catalytic analysis: one is the further increase in sensitivity and the other is the improvement of selectivity. For the determination of copper, various catalytic methods have already been reported.3-7) However, most of them are not selective, although the sensitivity is relatively high. Therefore, the development of more sensitive and more selective catalytic methods for the determination of copper is still expected.

The present work shows the analytical application of the catalytic effect of copper(II) on the hydrogen peroxide oxidation of Bindschedler's Green leuco base (BGL),8) which is formed by the reaction of N,N-dimethyl-p-phenylenediamine (DPD) and N,N-dimethylaniline (DA). In case of using the commercially available BGL, high reagent blanks were found probably because of the oxidation and/or the decomposition products of BGL formed during its storage. On the other hand, when DPD and DA as the reactants were used in place of BGL, the blank values were found to be kept low because the oxidation product of BGL were avoided. Formed BGL is oxidized by copper(II) to the colored product (λ_{max}=725 nm). The reduced copper(I) is oxidized again by hydrogen peroxide to copper(II) in the same way as described previously.9,10) Thus the oxidation of BGL proceeds catalytically with a minute amount of copper(II), and the method allowed the determination of nanogram level of copper(II).

DA was purified by vacuum distillation. All other chemicals used were analytical grade ones and deionized distilled water was used to prepare the solutions of the reagents. The recommended procedure is as follows: To 20 - 25 ml of a sample solution containing not more than 100 ng of copper(II) in a beaker, 5 ml of 2.0×10^{-2} M DA solution and 2 ml of 1.2×10^{-3} M DPD solution were added and the pH of the solution was adjusted to ca. 7.2 by adding 2 ml of 0.5 M sodium dihydrogen phosphate, 4 ml of 1 M ammonia and finally 0.1 M hydrochloric acid using pH meter. The solution was transfered to a 50-ml volumetric flask, and diluted to ca. 48 ml with water. The mixed solution was kept at 30°C in a thermostat to attain thermal equilibrium (about 10 min). Subsequently, 1 ml of hydrogen peroxide (3 M) was added and the solution was diluted to the mark with water of 30°C. Then the content was mixed to initiate the reaction, and exactly after 10 min, 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 725 nm was measured preferably within 20 min using a 10-mm glass cell against a distilled water reference. The above recommended procedure was developed on the basis of the following study.

The oxidation product with and without copper(II) shows the absorption maximum at 725 nm (Fig. 1). The absorption spectrum is identical with that of the oxidation product of the commercial BGL.

The effect of pH on the color development by the catalytic reaction was examined at the reaction time of 10 min at 30°C. The results are shown in Fig. 2. The color development was at a maximum and almost constant in the pH range of 7.0 - 7.4.

The reaction proceeds faster at higher temperatures. However, increase in temperature also increased the blank absorbance, particularly above 35°C.

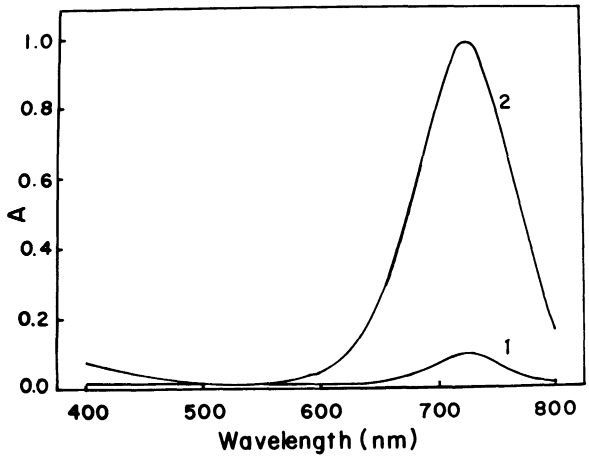

Fig. 1. Absorption spectra of the product. 1. reagent blank. 2. 100 ng of copper(II). Treated as in the proposed procedure.

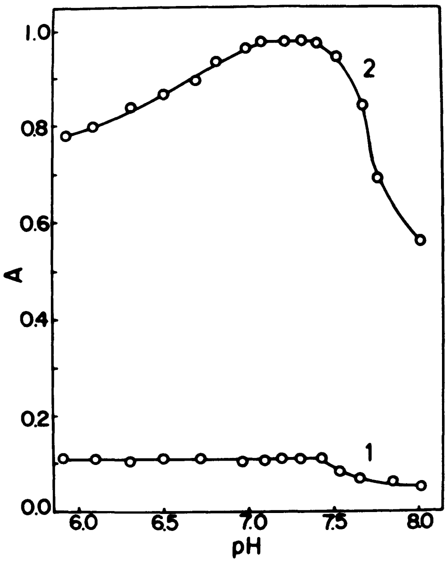

Fig. 2. Effect of pH on color development. 1. reagent blank. 2. 100 ng of copper(II). Other conditions as in the procedure.

Therefore the reaction temperature of 30°C was selected and a reaction time of 10 min was chosen for the sake of high sensitivity and reproducibility.

The absorption of the reaction mixture remained practically constant for at least 30 min when the mixture was cooled in an ice water bath, but it tended to increase slowly when it was rewarmed to room temperature after taking out from the ice water bath. Thus the reaction mixture should be kept in an ice water bath until the absorbance is measured.

The effect of the reagents concentrations on the color development was also examined. The reaction proceeded faster when the concentrations of DPD and DA were higher. However, the blank values also increased depending on the concentrations of the reagents. Consequently, the concentrations of DPD and DA were selected as 4.8×10^{-5} M and 2.0×10^{-3} M, respectively. As the absorbance remained constant when the hydrogen peroxide concentration was kept in the range of 4.4×10^{-2} - 8.4×10^{-2} M, its concentration was selected as 6.0×10^{-2} M.

The reaction rate for the catalytic reaction depends on the buffer used to control the pH. The rate of the color development increased depending on the increase of ammonia concentration, while it decreased depending on the increase the phosphate concentration. However, it is not fully understood at present why the rate should increase or decrease depending on buffer used. Detailed results will be reported elsewhere.

Typical working curve over the range 0 - 100 ng of copper(II) per 50 ml of the working solution for the proposed procedure is shown in Fig. 3. This method is sensitive and the reproducibility is satisfactory with a relative standard deviation of 1.2% for tenfold determinations of 50 ng of copper(II), although the working curve is not linear (Fig. 3).

The following ions and compounds caused no interference on the determination of 50 ng of copper(II) up to at least the concentrations indicated: 100 µg of Mg(II), Ca(II), Mn(II), As (III, V); 10 µg of Cd(II), Hg(II), Pb(II), Al(III), V(V), W(VI); 1 µg of Ni(II), Zn(II), Fe(III), Cr(III, VI), Mo(VI); 0.5 µg of Co(II); 10 mg of F^-, ClO_4^-; 1 mg of Br^-; 10 µg of I^-; 10 mg of sodium chloride, sodium nitrate, sodium sulfate, potassium nitrate and ammonium chloride. It should be emphasized that co-existing iron(III) twenty times as much as copper(II) dose not interfere on the determination of the latter, since the pH range of the reaction of iron(III) is different from that of copper(II).

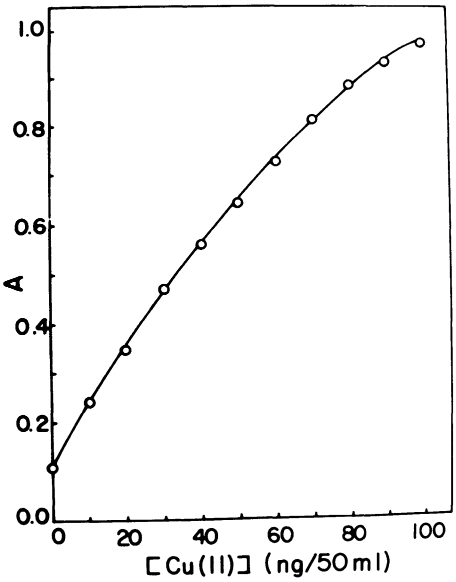

Fig. 3. Working curve for copper(II). Conditions as in the proposed procedure.

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