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A NEW CATALYTIC DETERMINATION OF COPPER(II) BY MEANS OF THE OXIDATIVE COUPLING REACTION OF p-HYDRAZINOBENZENESULFONIC ACID WITH m-PHENYLENEDIAMINE

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A new sensitive catalytic method for the determination of copper(II) is proposed. In the presence of hydrogen peroxide, copper(II) catalyzes the oxidation of p-hydrazinobenzenesulfonic acid to p-sulfobenzenediazonium ion, which is coupled with m-phenylenediamine to form a yellow azo dye (λ_{max}= 454 nm). By means of this catalytic reaction, nanogram amounts of copper(II) can be determined easily.

Arylhydrazines are known to be oxidized and coupled with aromatic compounds to produce intensely colored azo dyes.[1] The catalytic action of selenium(IV) on the oxidation of p-hydrazinobenzenesulfonic acid(HBS) by chlorate has already been used for the determination of trace amounts of selenium.[2,3] The present authors found that in the presence of hydrogen peroxide copper(II) catalyzed the oxidation of HBS to p-sulfobenzenediazonium ion, which then was converted to a yellow azo dye (λ_{max} = 454 nm) by coupling with m-phenylenediamine(PD). In this paper, a new catalytic method for the determination of nanogram amounts of copper(II) based on this reaction is described.

HBS and m-phenylenediamine dihydrochloride(PD) were used without further purification. All other chemicals used were of analytical grade and deionized - distilled water was used to prepare the solutions. The recommended procedure is as follows: To 25 ml of a sample solution containing not more than 100 ng of copper(II) in a beaker, 4 ml of 0.4 mol dm^{-3} sodium fluoride, 3 ml of 2.0 mol dm^{-3} sodium acetate as a buffer and 3 ml of 6.0×10^{-2} mol dm^{-3} were added. The pH of the solution was adjusted to 4.4 - 4.5 by adding 1 mol dm^{-3} hydrochloric acid using pH meter. The solution was transferred to a 50-ml volumetric flask and kept at 35°C in a thermostat for 10 min. Subsequently, a mixture of 1 ml of 5.0 mol dm^{-3} hydrogen peroxide and 2 ml of 2.0×10^{-2} mol dm^{-3} HBS in a test tube immersed in the thermostat was pipetted into the solution of the flask to initiate the reaction. Finally the solution was diluted to the mark with water of 35°C. Exactly 20 min after the initiation of the reaction, about 4 ml of the reaction mixture was pipetted into a 10-mm glass cell and the absorbance was measured at 454 nm preferably within

30 sec, against a distilled water reference. The net absorbance was obtained by substracting a blank absorbance.

The absorption spectrum of the azo dye formed during the catalytic reaction with copper(II) was identical with that of the previous finding,[3)] and the absorption maximum found at 454 nm. The reaction proceeded faster at higher temperatures, but with increase in temperature, the blank absorbances also increased, particularly above 45°C. Taking into account this situation, a reaction temperature between 35°C and 45°C was selected for the recommended procedure. For the practical purposes, a reaction time of 20 min at 35°C was satisfactory. The maximum and constant color development was obtained in the pH range of 4.3 - 4.7, decreasing quite rapidly on both sides of this range. Thus, the reaction was carried out in the pH range of 4.4 - 4.5.

The effect of PD concentration on the color development was examined at a constant concentration of 8.0×10^{-4} mol dm^{-3} HBS. The results are shown in Fig. 1. The absorbance remains almost constant over the range of $2.4 \times 10^{-3} - 5.4 \times 10^{-3}$ mol dm^{-3} diamine. Fig. 2 shows that the absorbance increases with increase in the concentration of hydrogen peroxide. A hydrogen peroxide concentration of 0.1 mol dm^{-3} was chosen for the sake of high sensitivity and reproducibility.

The effect of sodium acetate concentration was also examined as shown in Fig. 3. A constant absorbance was obtained at the concentration of the acetate higher

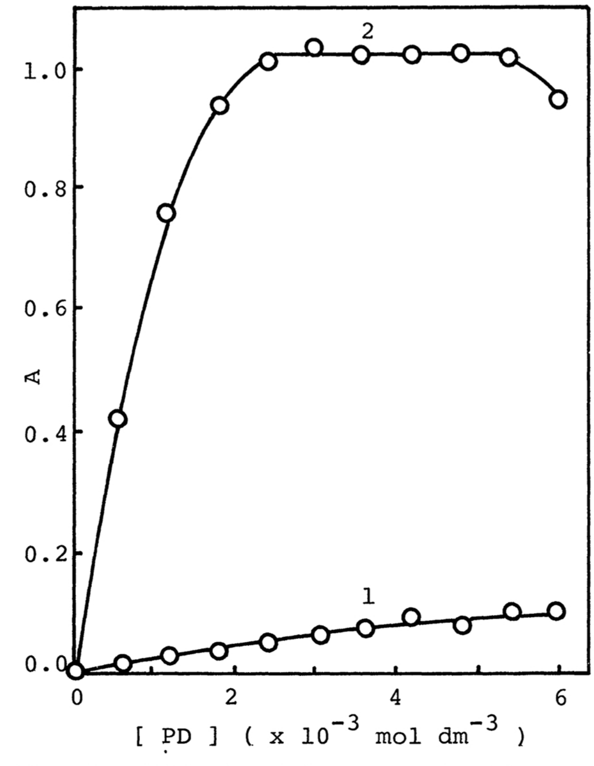

Fig. 1. Effect of PD concentration
1: reagent blank 2: 100 ng of copper(II)
Other conditions as in the procedure.

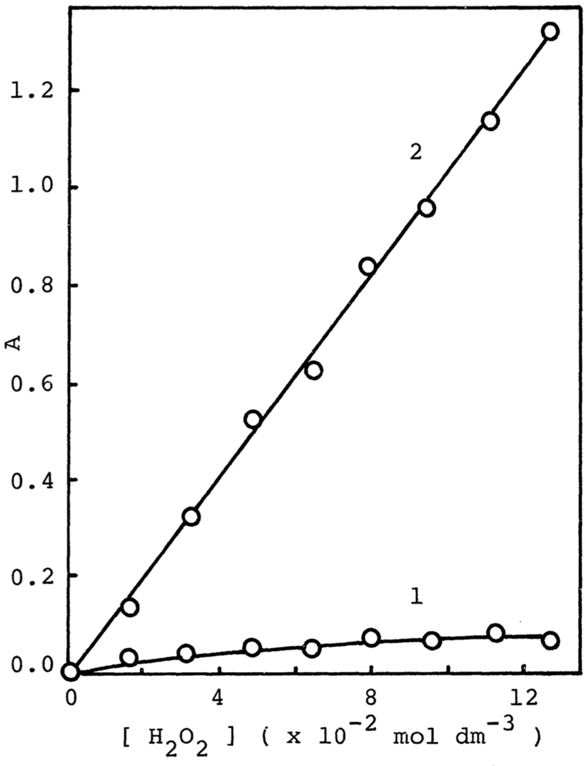

Fig. 2. Effect of hydrogen peroxide concentration
1: reagent blank 2: 100 ng of copper(II)
Other conditions as in the procedure.

than 6 x 10^{-2} mol dm^{-3}. A concentration of the acetate was selected as 0.12 mol dm^{-3} in the procedure.

The following ions and compounds caused no interference with the determination of 50 ng of copper(II) at least up to the specified amount: 100 µg of Al(III), Ba(II), Ca(II), Ce(III), Mg(II), Sr(II), Br^-, I^-, ClO_4^-, PO_4^{3-}; 10 µg of Ag(I), As(III), Pb(II), Bi(III), Cd(II), Hg(II), Mn(II), Mo(VI), Ni(II), Se(IV), Sn(II), Sn(IV), V(V), W(VI); 10 mg of sodium chloride, sodium nitrate, potassium chloride, ammonium chloride. Positive interferences were observed for iron(III), cerium(IV) and chromium(III,VI). These ions seem to act as catalysts in the color development. The interference of iron(III) can be effectively eliminated by sodium fluoride as shown in Fig. 4. It should be emphasized that selenium(IV) two hundred times as much as copper(II) does not interfere with the determination of copper(II), since the optimum pH range of the reaction for the selenium(IV) determination is quite different from that for copper(II).

The reproducibility of this method is satisfactory with the relative standard deviations of 2.8% and 2.1% for five determinations of 50 and 100 ng of copper(II), respectively.

The above procedure was applied to the determination of copper in some river

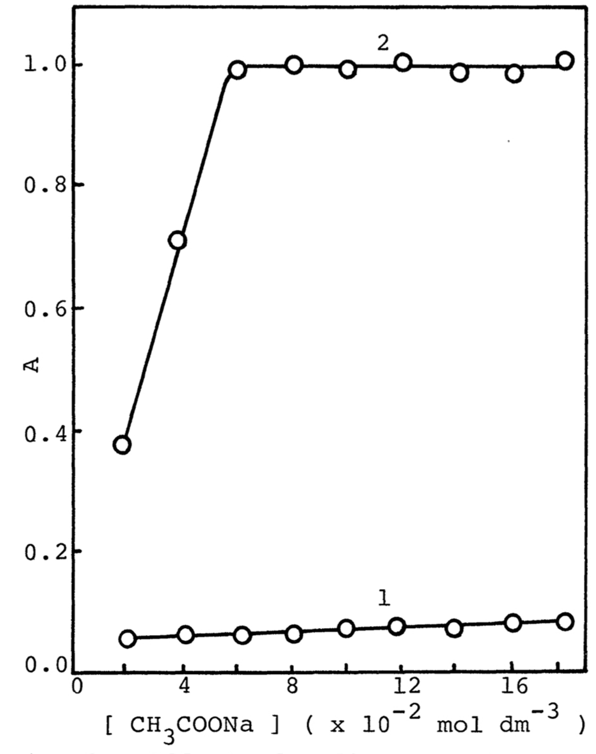

Fig. 3. Effect of sodium acetate concentration

1: reagent blank 2: 100 ng of copper(II)
Other conditions as in the procedure.

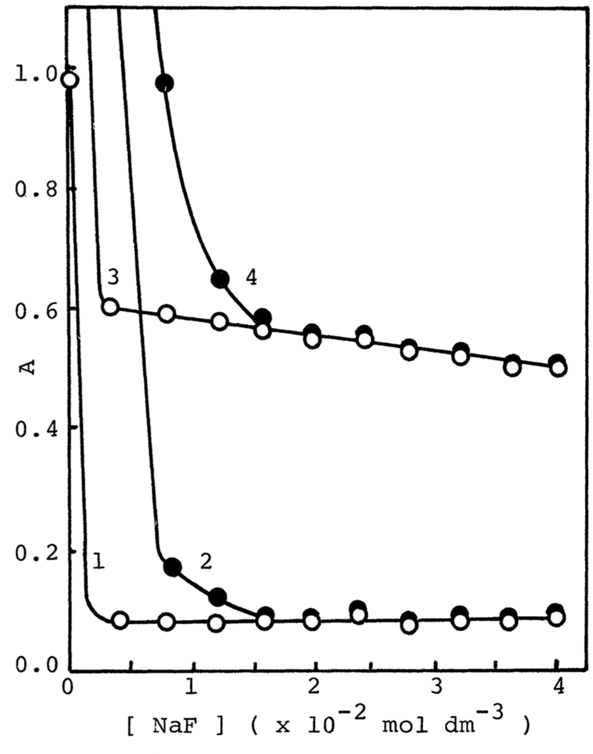

Fig. 4. Effect of sodium fluoride concentration

1: reagent blank 2: 10 µg of iron(III)
3: 50 ng of copper(II) 4: 50 ng of copper(II) and 10 µg of iron(III)
Other conditions as in the procedure.

water samples. The results (0.5 - 1.1 ppb) were in good agreement with those obtained by flameless atomic absorption spectrometry (0.5 - 1.1 ppb).

Detailed results will be published elsewhere.

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