N-(α-Pyridyl)-2-thioquinaldinamide as a New Sulphur Reagent for Photometric Determination of Copper(II)

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N-(α-Pyridyl)-2-thioquinaldinamide has been used for the spectrophotometric determination of Cu(II) in trace amounts in alkaline medium. The violet coloured copper complex formed in aqueous ethanol medium at pH 10.5 to 11.0 has an absorption maximum at 520 nm. The complex is found to be stable for 24h at room temperature. It obeys Beer's law in the range 0.6-16 ppm of Cu(II) with an optimum range of 3 to 12 ppm. The molar absorptivity is $5.2 \times 10^3$ I mol$^{-1}$ cm$^{-1}$. Alloy steel samples have been analysed for trace analysis of copper.

The present note describes the synthesis and use of N-(α-Pyridyl)-2-thioquinaldinamide as a spectrophotometric reagent for the determination of trace amounts of copper(II).

Copper(II) solution was prepared by dissolving pure electrolytic grade Cu wire in aqua-regia and then sulphuric acid and standardized by iodometric titration method. N-(α-Pyridyl)-2-thioquinaldinamide was synthesized by reported method and dissolved in ethanol to get 0.10% reagent solution.

Procedure

An aliquot containing 0.6 to 16 ppm of copper(II) was taken in a 25 ml standard flask. A few drops of 2 M KOH or 2N ammonia solution were added to adjust the pH of the solution to 10.5 - 11.0. Then 5 ml of 1% alcoholic reagent solution was added followed by requisite amount of ethanol so that the total volume contained 50% ethanol. The volume was made up and contents were mixed thoroughly for 2-3 min; the absorbance was measured after 5-7 min. A reagent blank was prepared under identical conditions. The absorbance of the complex (violet) was measured against reagent blank at 520 nm. Copper(II) complex showed absorption maximum at 520-530 nm at pH 10.5.

The complex showed constant absorbance for 2.5 - 7.0 ml of 1% reagent. A 5 ml solution was always used. The absorbance was constant upto 4 M KOH and 1-5 N NH$_3$ solution and it was always measured at pH 10.5-11.0.

The complex obeyed Beer's law from 0.6 to 16 ppm of Cu(II), the optimum range$^3$ being 3-12 ppm at 520 nm. The molar absorptivity was $5.2 \times 10^3$ 1 mol$^{-1}$ cm$^{-1}$. The photometric error was only 2.7% following Ayres' equation.

Effect of diverse ions

Copper(II) (6 ppm) was determined in the presence of many diverse ions following the adopted procedure. A 0.005 absorbance unit was set as the tolerance limit for the blank solution.

More than 300-fold excess of Mo(VI), W(VI), dioxouranium(VI), VO(III), Ti(IV), Al(III), In(III) did not interfere in the determination. Fe(III), Bi(III), As(III), Pb(II), Cd(II), Sn(II) and Hg(II) did not interfere. No interference due to Fe(III), Bi(III), As(III), Mn(II), Pb(II), Cd(II), Sn(II) and Hg(II) was observed in the presence of 5 ml of 10% TEA. 40 ppm of Ag(I) did not interfere. Except EDTA and CN$^-$, with 40 ppm as tolerance limit, most of the anions did not interfere when present in more than 300-fold excess.

Determination of copper in alloy steel

Steel (0.5 g) was dissolved in a 50 ml of 3M sulphuric acid and digested on a hot plate with repeated additions of the acid. The solution was treated with a few drops of conc. nitric acid for complete digestion. The clear solution so obtained was evaporated to a thick mass and then cooled, diluted with 50 ml water, filtered and washed with dilute acid. The filtrate and washings were cooled and transferred quantitatively into a 100 ml volumetric flask and volume made up to the mark. Aliquot portion (5-10 ml) was taken and to it 5 ml of 1% reagent and 5 ml of 10% TEA. HCl solution were added and pH was adjusted to 10.5-11.0. The solution was transferred into a volumetric flask, the volume made up to the mark with requisite amount of ethanol and contents were mixed thoroughly. The blank solution was prepared similarly and absorbance measured at 520 nm. The copper was determined and found to be 0.31%, 0.09%, 0.07% Cu with a deviation of ± 0.01% (certified : 0.32%, 0.10% and 0.08% Cu in BAS steel).

References