SHORT COMMUNICATIONS

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH 2-HYDROXY-1-ACETONAPHTHONEOXIME

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SEVERAL oximes[1-3] are used for the extraction and photometric determination of copper(II). 2-Hydroxy-1-acetonaphthoneoxime [2-HANO] has been used[4] for the gravimetric determination of copper(II) and also for the amperometric determination[5] of copper, nickel and palladium. A survey of literature shows that extraction studies have not carried out with this reagent. The present paper communicates the results obtained in the rapid extraction spectrophotometric determination of copper(II) with 2-HANO in methyl iso-butylketone [MIBK]. The proposed method is simple and rapid. The high tolerance limit of zinc makes the method useful for the determination of copper in brass. The method was also extended for the determination of copper in chalcopyrites.

A stock solution of copper(II) was prepared and standardised by volumetric method[6]. The reagent was prepared by the literature method[7]. A 0.02 M reagent in MIBK was used for all studies.

Potassium hydrogenphthalate, sodium hydroxide and ammonium chloride, ammonium hydroxide solutions were used to prepare buffer solutions of different ranges. All other chemicals used were of A. R. Grade.

Recommended procedure: An aliquot of the solution containing 10–60 μg of copper was taken in a 50 ml separating funnel. To this 10 ml of buffer solution followed by 10 ml of 0.02 M reagent in MIBK were added and shaken vigorously for 3 min, allowed to settle for 5 min. The organic layer is separated dried over anhydrous sodium sulphate and the absorbance was measured at 370 nm against the reagent blank.

Absorption spectra: The absorption spectrum of the coloured complex formed between copper(II) and 2-HANO extracted into methyl isobutylketone at pH 8 against reagent blank as the reference shows maximum absorbance at 370 nm. The reagent has negligible absorbance at this wavelength.

Effect of pH: The extraction of Cu(II)-2-HANO system was studied over the pH range 4–10. The extraction of complex commences at pH 5.5 and is quantitative between pH 7–8.5. After this the extraction decreases. So all studies were carried out at pH 8 only.

Validity of Beer's law: The absorbance of different amounts of Cu(II) extracted at pH 8.0 was measured against the reagent blank. The system obeys Beer's law over the concentration range of 20–60 μg in 10 ml solution.

Effect of reagent concentration: From the studies of varying volume and concentration of reagent for extraction of Cu(II) it was found that a ten-fold excess of reagent is sufficient. Among the various solvents tried (*n*-butanol, *n*-amyl acetate, chloroform, carbon tetrachloride and methyl iso-butylketone) only MIBK has been found suitable.

Stability, sensitivity and period of equilibrium of complex: The absorbance is constant only upto 48 hr. The molar absorptivity of the complex is 5.1×10^3 l mol^{-1} cm^{-1}. The Sandell sensitivity is 0.0125 μg cm^{-2}. From the results of variation in period of shaking it was found that 3 min of shaking the contents with solvent is sufficient.

Effect of diverse ions: Several foreign ions were examined for their effect on extraction of copper(II). The error of $\pm 2\%$ in recovery of copper(II) was taken as interference. The tolerance limit of some of the ions in the extraction of copper (45 μg) at pH 8 is as follows. Nickel and iron (10 μg) interfere strongly. Fe^{3+} can be eliminated by the addition of sodium fluoride. Sodium, potassium, calcium, barium, strontium, zinc, nitrate, chloride, acetate, sulphate and chlorate upto 10000 μg did not interfere. Chromium, molybdenum, uranium tungsten, lead, manganese, cadmium, phosphate, tartarate upto 5000 μg did not interfere. Cerium, thorium, vanadium, iodate upto 1000 μg and aluminium, bismuth, thiosulphate upto 500 μg did not interfere. 100 μg each of EDTA and oxalate did not interfere.

Comparison with other oxime reagents: The reagent 2-HANO is compared with some well-known oximes. It

was found that 2-HANO is also a sensitive reagent for copper(II).

Reagent	Molar absorptivity l. mol^{-1} cm^{-1} ($\times 10^3$)
Orthohydroxy acetophenone oxime[8]	3.4
n-Pentyl-2-pyridylketoxime[1]	2.7
Phenyl 2-(6-methylpyridyl) ketoneoxime[1]	10.8
6-Methyl-2-pyridinecarboxamide-oxime[1]	7.2
Salicylaldoxime (*n*-amyl acetate)[1]	7.2
2-Hydroxy-1-acetonaphthone-oxime	5.1
2,4-Dihydroxyvalerophenone-oxime	0.16

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SYNTHESIS AND PHYSIOLOGICAL EVALUATION OF A THIAZOLIDINEDIONE AND ITS AZODERIVATIVES FROM NINHYDRIN

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NINHYDRIN has been used to synthesise a variety of heterocyclics[1-3] and to estimate amino acids. Quinoxaline derivatives are known to possess insecticidal and acaricidal activity[4]. Several thiazolidinediones are reported to exhibit a good spectrum of biological activity[5-8]. These reports prompted us to undertake the synthesis of a 2,4-thiazolidinedione 2-azine (III) containing 11*H*-indeno[1, 2-*b*] quinoxalin-11-one moiety and its aryl azoderivatives (IV) starting from II.

The starting materials 11*H*-indeno[1, 2-*b*] quinoxalin-11-one (I) and 11*H*-indeno[1, 2-*b*] quinoxalin-11-one thiosemicarbazone were prepared according to our earlier procedure[9].

11*H*-indeno[1, 2-*b*]quinoxalin-11-one thiosemicarbazone (II) on interaction with either chloroacetyl chloride or chloroacetic acid in the presence of anyhydrous ethanol and dry pyridine gave the cycloproduct 2,4-thiazolidine dione 2-azine (III) containing 11*H*-indeno[1, 2-*b*]quinoxalin-11-one which on further reaction with diazolised substituted sulphanilamides furnished the corresponding p-[(2,4-dioxo-5-thiazolidinyl)azo]benzene sulphonamide 2-azine containing 11*H*-indeno[1, 2-*b*]quinoxalin-11-one (IV). The products (III & IV) obtained have been confirmed by analytical and spectral (IR, PMR and mass) data.

2,4-Thiazolidinedione 2-azine containing 11H-indeno [1,2-b]-quinoxalin-11-one (III):

A mixture containing II (0.01 mol) and chloroacetyl chloride or chloroacetic acid (0.01 mol) in anhydrous ethanol (10 ml) and dry pyridine (10 ml) was refluxed for 6 hr and poured into crushed ice with constant stirring. The product separated was filtered, dried and purified from DMF, m.p. 250°C, yield 70%. (Found: C, 61.88; H, 2.98; N, 20.10; $C_{18}H_{11}N_5OS$ requires C, 62.62; H, 3.18; N, 20.29%). IR (nujol, νcm^{-1}) 3400 (-NH-), 1710 (amide C=O), 1600 (νCN); PMR (δ, pyridine-d_5), 7.5-8 (8H, m, aromatic), 2.20 (2H, s, -s-CH_2-), 8.55 (s, 1H, -NH-); mass: m/z 345 (M^+,