n-PENTYL-2-PYRIDYL KETOXIME AS A SELECTIVE COLORIMETRIC REAGENT FOR COPPER

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Several pyridine-2-oximes have found application as colorimetric reagents for copper and iron. Examples include pyridine-2-aldoxime[1,2], 6-methylpyridine-2-aldoxime[3], methyl-2-pyridyl ketoxime[4], and phenyl-2-pyridyl ketoxime[5]. In most of the foregoing cases the determinations are subject to interference from a fairly large number of commonly occurring ions. In the present work *n*-pentyl-2-pyridyl ketoxime has been shown to have a sensitivity for copper which is lower than that of the aforementioned reagents, but to possess a much higher degree of selectivity toward this element.

EXPERIMENTAL

Materials and equipment

Standard copper solution. A 0.01 *M* solution was prepared by dissolving 0.6354 g of electrolytic copper (Matheson, Coleman and Bell, Norwood, Ohio) in 10 ml of concentrated nitric acid and diluting with water to the mark in a 1-l volumetric flask.

Hydroxylammonium chloride. A 10% solution was prepared by dissolving 100 g of hydroxylammonium chloride in 900 ml of water.

n-*Pentyl-2-pyridyl ketoxime hydrochloride.* The corresponding ketone was prepared from 1-bromopentane and 2-cyanopyridine and was oximated with hydroxylammonium chloride.

Fifty ml of anhydrous ether, 6.76 g (0.28 moles) of magnesium metal and a few crystals of iodine were introduced into a 1-l, 3-neck round-bottom flask fitted with a stirrer and a condenser. Fifteen ml of a solution of 31.4 ml of 1-bromopentane in 50 ml of anhydrous ether were introduced into the flask, and when the reaction started the remainder of the 1-bromopentane was added dropwise with constant stirring at a rate sufficient to keep the reaction at reflux temperature. An ice bath was used to help control the temperature. When the addition of 1-bromopentane was complete the reaction mixture was stirred for one hour while cooling to room temperature. A solution of 24.5 ml (0.25 moles) of 2-cyanopyridine in 200 ml of anhydrous ether was dropped into the cooled Grignard reagent with constant stirring over a 2-h period and the reaction mixture was stirred for 8 h at room temperature. A cold solution of 50 g of ammonium chloride in 200 ml of water and 50 ml of concentrated hydrochloric acid was added to the reaction, and the mixture was stirred for 5 h. The ether layer was separated and retained. The aqueous layer was refluxed for 2 h, cooled, made just alkaline with sodium hydroxide, and extracted with 4 150-ml portions of ether. All of the ether fractions were combined and distilled. The colorless fraction distilling at 118–119° at a pressure of 11 mm Hg was collected. The *n*-pentyl-2-pyridyl ketone becomes yellow when exposed to light, and must be stored in a dark bottle.

Two ml of *n*-pentyl-2-pyridyl ketone, 6 ml of 5 *M* hydroxylammonium chloride, and 6 ml of 5 *M* sodium acetate were combined with 10 ml of 95% ethanol and heated gently for 2 h. The *n*-pentyl-2-pyridyl ketoxime floated to the surface of the mixture, a red color indicating that it was contaminated with iron. The reaction mixture was extracted once with 20 ml of ether. The ether layer was retained and dried over anhydrous magnesium sulfate. The magnesium sulfate was separated by filtration and a steady stream of dry hydrogen chloride was bubbled through the ether solution precipitating *n*-pentyl-2-pyridyl ketoxime hydrochloride. The crude product was dried under vacuum and then shaken with 20 ml of ether saturated with hydrogen chloride. The precipitate was filtered off and dried at room temperature under vacuum. Melting point: 149–151°.

A 0.01 *M* solution of *n*-pentyl-2-pyridyl ketoxime hydrochloride was prepared by dissolving 0.573 g in 250 ml of water.

All spectrophotometric data were obtained on a Beckman Model DU spectrophotometer using matched 1-cm silica cells.

All pH measurements were made on a Beckman Model 76 pH meter.

Preliminary investigations

n-Pentyl-2-pyridyl ketoxime hydrochloride is a white crystalline solid, soluble in water and insoluble in ether, carbon tetrachloride, and benzene. It is hygroscopic and must be stored in a desiccator. Aqueous solutions are colorless and are stable under ordinary laboratory conditions for at least a month.

The reactions of *n*-pentyl-2-pyridyl ketoxime with metal ions are very similar to those of the lower homologues of the series. These reactions are summarized in Table I.

TABLE I

REACTIONS OF *n*-PENTYL-2-PYRIDYL KETOXIME WITH VARIOUS CATIONS

Cation	*Color*	
	pH 2.0–6.0	*pH 6.0–10.0*
Iron(II)	Orange	Purple-red
Iron(III)	Pale orange	Pale red
Copper(I)	Pale green[a]	Yellow-green[b]
Copper(II)	Green	Green
Cobalt(II)	Yellow[a]	Yellow
Manganese(II)	Pale yellow	Pale yellow

[a] Solid forms
[b] Hydroxide forms at approximately pH 7

Reaction with copper

When a 5-fold excess of *n*-pentyl-2-pyridyl ketoxime is added to a solution containing copper(I) a soluble green product is formed. On standing for a few minutes a green precipitate settles out. This material was separated, dried at 110°, and analyzed. Calculated for $Cu(C_{11}H_{16}N_2O)Cl \cdot 1/2\ H_2O$: C = 43.98%, H = 5.71%, Cl = 11.82%. Found: C = 43.87%, H = 5.77%, Cl = 12.01%. The copper compound precipitates from aqueous solutions above pH 1.5. At about pH 7 the compound decomposes, leaving a residue of hydrous copper oxide. The copper(I)–oxime compound is soluble in chloroform and in isoamyl alcohol and can be extracted into these solvents from aqueous suspensions. This extractability is exploited in the spectrophotometric procedure for copper described below. In isoamyl alcohol the copper(I)–oxime compound conforms to Beer's law in concentrations up to $5.6 \cdot 10^{-4}$ *M* and has a molar absorptivity of 2650 at 360 mμ.

Procedure

Weigh out a sample containing less than 1 mg of copper and dissolve in nitric or sulfuric acid or in aqua regia. By the addition of sodium hydroxide adjust the pH to between 2.5 and 3.0. Add 20 ml of 10% hydroxylammonium chloride, 5 ml of 0.01 *M* oxime, and extract once with 15 ml of isoamyl alcohol. Allow the layers to separate and reject the aqueous phase. Transfer the organic layer to a 25-ml volumetric flask and dilute to the mark with isoamyl alcohol. At the end of 1 h, determine the absorbance of the solution at 360 mμ.

Influence of foreign ions

The effect of foreign ions on the determination of copper by the foregoing method was examined. The metals chosen were those which form colored complexes with the ligand and those usually associated with copper. The results are summarized in Table II. Cobalt(II) forms a solid yellow compound with the ligand which is also extracted into isoamyl alcohol and interferes with the determination of copper by this method.

TABLE II

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF COPPER WITH *n*-PENTYL-2-PYRIDYL KETOXIME

Foreign ion	*Mole ratio foreign ion to copper*	*mg Copper*	
		Added	*Found*
Iron(II)	4 : 1	0.635	0.635
Arsenic(III)	5 : 1	0.635	0.635
Cobalt(II)	5 : 1	0.635	[a]
Nickel(II)	4 : 1	0.635	0.634
Antimony(III)	5 : 1	0.635	0.641

[a] Complete interference

RESULTS AND DISCUSSION

To test the reliability of this method a copper determination was run on National Bureau of Standards Sample No. 53d, a lead-base bearing metal. In addition to lead and copper it contained antimony, arsenic, tin, bismuth, and nickel. Samples weighing 0.2 g were weighed into 150-ml beakers, treated with 15 ml of concentrated sulfuric acid, and heated for 1.5 h. The mixture was cooled, diluted with 50 ml of water and the resulting lead sulfate was filtered off using a porous bottom crucible. The above procedure was then followed. The results of the analyses are given in Table III.

TABLE III

DETERMINATION OF COPPER IN NATIONAL BUREAU OF STANDARDS SAMPLE NO. 53d

Sample weight (g)	*Weight copper (mg)*		*Per cent copper*
0.2002	0.533		0.266
0.1434	0.381		0.266
0.2258	0.600		0.266
		Average	0.266
		NBS value	0.268

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SUMMARY

n-Pentyl-2-pyridyl ketoxime hydrochloride has been prepared and examined as a colorimetric reagent for copper. It is less sensitive than some reagents, but shows a remarkable selectivity toward copper. The copper(I)-oxime compound can be extracted into isoamyl alcohol or into chloroform. In isoamyl alcohol the colored compound conforms to Beer's law in concentrations up to $5.6 \cdot 10^{-4}$ *M* and has a molar absorptivity of 2650 at 360 mμ. A procedure for the colorimetric determination of copper is given and its reliability is shown.

RÉSUMÉ

Les auteurs ont effectué une étude sur la préparation et l'utilisation du chlorhydrate de *n*-pentyl-2-pyridylcétoxime, comme réactif colorimétrique du cuivre. Sa sensibilité est inférieure à celle de certains réactifs, mais sa sélectivité est remarquable. Le composé obtenu peut être extrait dans l'alcool isoamylique ou dans le chloroforme. Une méthode est proposée pour le dosage colorimétrique du cuivre.

ZUSAMMENFASSUNG

n-Pentyl-2-pyridylketoxim-hydrochlorid wurde hergestellt und als kolorimetrisches Reagens auf Kupfer geprüft. Es erwies sich als unempfindlicher, aber selektiver als andere Reagentien. Die Kupfer(I)-Oxim-Verbindung kann mit Isoamylalkohol oder Chloroform extrahiert werden. Für die gefärbte Verbindung ist in Isoamylalkohol das Beersche-Gesetz bis zu einer Konzentration von $5.6 \cdot 10^{-4}$ *M* gültig. Die molare Absorption beträgt 2650 bei 360 mμ.

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