Bull. Chem. Soc. Jpn., 56, 1624—1626 (1983)

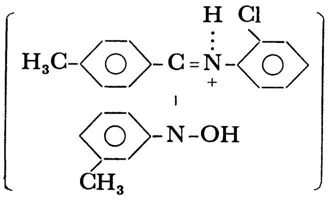
Gravimetric Determination of Copper(II) Using N^1-Hydroxy-N^1-(*m*-tolyl)-N^2-(*o*-chlorophenyl)-*p*-toluamidine Hydrochloride

Hemlata Mohabey, Pramod Kumar Sharma,* and Rajendra Kumar Mishra
Department of Chemistry, Ravishankar University, Raipur, 492 010, India

(Received August 13, 1982)

A simple, rapid, and accurate method has been developed for the gravimetric determination of Copper(II) using a new reagent N^1-hydroxy-N^1-(*m*-tolyl)-N^2-(*o*-chlorophenyl)-*p*-toluamidine hydrochloride (HTCPTH). The proposed reagent reacts quantitatively with copper at 3.3—11.0 pH giving a buff coloured precipitate. The precipitated complex can be easily filtered, dried and directly weighed as $(C_{21}H_{18}N_2OCl)_2Cu$. The complex is thermally stable as is evident from DTA and TGA studies up to 210 °C and insoluble in many organic solvents. Most of the common ions including Ni(II), Co(II), Cr(III), Mn(II), *etc.* do not interfere. The interference due to iron(III) can be eliminated by masking it with tartaric acid. The method has been successfully applied for the determination of copper in some British Chemical Standards alloys.

N^1-Hydroxy-N^1,N^2-diarylbenzamidines have been found to be potential analytical reagents for the determination of various transition elements.[1-3] This communication describes the use of a new *N*-hydroxyamidine, N^1-hydroxy-N^1-(*m*-tolyl)-N^2-(*o*-chlorophenyl)-*p*-toluamidine hydrochloride(I) for the gravimetric determination of copper(II).



1

The reagent reacts with copper(II) giving a buff coloured precipitate at 2.2—11.5 pH but the reaction is quantitative only at pH 3.3—11.0. The complex is stable towards heat and dilute mineral acids and no weight loss is observed upto 210 °C. The coprecipitated reagent can be completely removed by washing with hot 50% aqueous ethanol as the complex is insoluble in it. The conversion factor (metal/metal complex is very small (0.0833) and therefore small quantities of copper can be accurately determined. The method is free from interference of many foreign ions and is comparable to established methods.[4-9]

Experimental

Reagents and Chemicals. All the chemicals used were of A. R. grade.

Copper stock solution was prepared by dissolving the British Drug House, AnalaR copper metal in dilute nitric acid and the solution boiled to expel nitrogen oxides. The solution was standardized gravimetrically using salicylaldehyde oxime.[10]

The reagent, HTCPTH was prepared by condensing *N*-(*o*-chlorophenyl)-*p*-toluimidoyl chloride and *N*-(*m*-tolyl) hydroxylamine in equimolar amounts in ether as mentioned earlier.[1] A 1% solution of the reagent in ethanol was used for precipitation purposes. The pH of the solution was adjusted to 3.3 to 11.0 with acetic acid and ammonia.

Apparatus. A single pan semimicrobalance SAHM-68 (VEB-Analytic DDR) was used for weighing. The pH of the solution was measured with a Systronic pH meter type −322.

Recommended Procedure. An aliquot of copper solution containing 10—15 mg of copper was diluted to 150 ml. The pH of the solution was adjusted to 3.3 to 11.0 and heated to about 60 °C. To this added 1% reagent solution (20—30 ml per 12.8 mg copper) dropwise with constant stirring. The buff coloured precipitate was digested on water bath for 20 min and filtered through a preweighed G-3 sintered crucible. The complex was washed with hot water followed by 60% ethanol till the washings gave no red-purple colour with iron(III) chloride. It was dried at 120 °C to constant weight and weighed as $Cu(C_{21}H_{18}N_2OCl)_2$ (Found: C, 65.98; H, 4.66; N, 7.28; Cu, 8.30%. Calcd for: C, 66.09; H, 4.72; N, 7.34; Cu, 8.33%).

Properties of the Complex: The copper complex is insoluble in water and sparingly soluble in ethanol, acetone, carbon tetrachloride, chloroform and many other organic solvents. The complex can be dried to constant weight at 110—180 °C with out decomposition. The melting point of the complex is 208 °C and it blackens at this temperature. Though there was change in colour at the melting point of the complex, weight loss was observed only at 220 °C during thermogravimetric studies of the complex.

Precision. The standard deviation of ten independent determinations with 12.8 mg copper is 0.0066 while the relative standard deviation is 0.051%.

Effect of Foreign Ions. Following the procedure described above a known amount of copper (12.8 mg) was accurately determined at pH 3.5—5.5 in presence of many foreign ions. Vanadium(V), iron(II), and iron(III) form coloured complexes with the proposed reagent under the recommended procedure. These ions could be masked with tartaric acid (2 g) and thus the interference due to these ions was eliminated. It is evident from Table 1 that copper can be separated from almost all common ions like Pb(II), Co(II), Ni(II), Bi(III), Sn(IV), V(V), Fe(III), *etc.* and hence the method is suitable for analysis of copper alloys.

Determination of Copper in Alloys. An accurately weighed amount of alloy containing 10—15 mg of copper in 25 ml aliquot of the final solution was dissolved in 40% nitric acid. The solution was evaporated to near dryness to remove the oxides of nitrogen. It was diluted to 100 ml and the precipitated tin and antimony oxides were filtered and washed with hot dilute acetic acid and the solution diluted to 250 ml. Copper was determined by the recommended procedure. It is evident from the results summarised in Table 2, that the amount of copper in its alloys could be determined accurately and precisely.

Thermal Analysis of Copper Complex. Thermogravimetric and differential thermal analysis were carried out to evaluate the thermal stability of the copper complex of HTCPTH. The TGA and DTA curves were obtained using

TABLE 1. DETERMINATION OF COPPER IN PRESENCE OF FOREIGN IONS

Copper taken: 12.8 mg, pH: 4.0±0.1.

Ion	Amount of diverse ion added (mg)	Wt of copper complex	Copper found (mg)	Error (%)
Fe(III)	25	153.76	12.81	+0.07
Co(II)	100	153.54	12.79	−0.07
Ni(II)	60	154.06	12.83	+0.23
Mn(II)	50	153.46	12.78	+0.16
Cr(III)	100	153.70	12.80	0.00
W(VI)	25	153.58	12.79	−0.07
Sb(III)	100	153.88	12.82	+0.16
Bi(III)	50	153.77	12.81	+0.07
Ti(IV)	25	153.70	12.80	0.00
Zr(IV)	50	153.60	12.79	−0.07
Al(III)	100	153.66	12.80	0.00
La(III)	100	153.90	12.82	+0.16
Th(IV)	50	153.71	12.80	0.00
U(VI)	50	154.02	12.83	+0.23
Se(VI)	60	153.72	12.80	0.00
Hg(II)	50	153.22	12.76	−0.31
Zn(II)	150	153.72	12.80	0.00
Cd(II)	100	153.65	12.80	0.00
Ca(II)	100	153.70	12.80	0.00
Ba(II)	50	153.58	12.79	−0.07
Na(I)	200	153.78	12.81	+0.07
Vanadate	25	153.70	12.80	0.00
Tartrate	3000	153.46	12.78	−0.16
Citrate	2000	153.60	12.79	−0.07
Chloride	150	153.90	12.82	+0.16
Bromide	150	153.68	12.80	0.00

TABLE 2. DETERMINATION OF COPPER IN BCS ALLOYS[a)]

Sample No. and name	Copper found (%)	Certified value (%)	Standard deviation (%)
5 f Brass	70.76, 70.81, 70.78 70.77, 70.79 average value: 70.78	70.80	0.0187
6 f Gun metal	87.86, 87.88, 87.84 87.85, 87.87 average value: 87.86	87.90	0.0158
8C White metal	4.09, 4.12, 4.09 4.06, 4.09 average value: 4.09	4.10	0.0217

a) BCS: British Chemical Standards.

an automatic unit HOM-BUDAPEST Devitograph (Type-OD-102). The TGA curve (Fig. 1) shows that there is no weight loss upto 220 °C thereby indicating that the chelate is nonhydrated in nature. At 220 °C the complex starts to decompose and 5% weight loss is observed between 220 to 240 °C. Accelerated weight loss takes place in the region 240—760 °C. At about 760 °C nearly 90% weight loss is observed. Here oxide level beings giving a horizontal straight line. It is evident from thermogravimetric analysis that the thermal stability 220 °C of copper–HTCPTH complex is higher than copper–salicylaldehyde oxime[11)] *i.e.* 140 °C.

The DTA curve of the complex consists of a pronounced exothermic peak at about 210 °C which may be due to possible phase transition from solid to liquid (melting). Melting may be accompanied by the loss of organic part of the compound as nearly 5% weight loss takes place at 220 °C (melting with decomposition). The other broad and prominent exothermic peak at about 550 °C may be due to another phase transition in the complex due to loss of ligand molecules as accelerated weight loss is observed in the range 240—760 °C. A small but noticiable endothermic peak is noticed at about 400 °C. There must be some new decomposition products at this temperature as is obvious from weight loss curve. Metal 8-quinolinolates[12)] and 2-quinolinecarboxylates[13)] also show endothermic decomposition peaks.

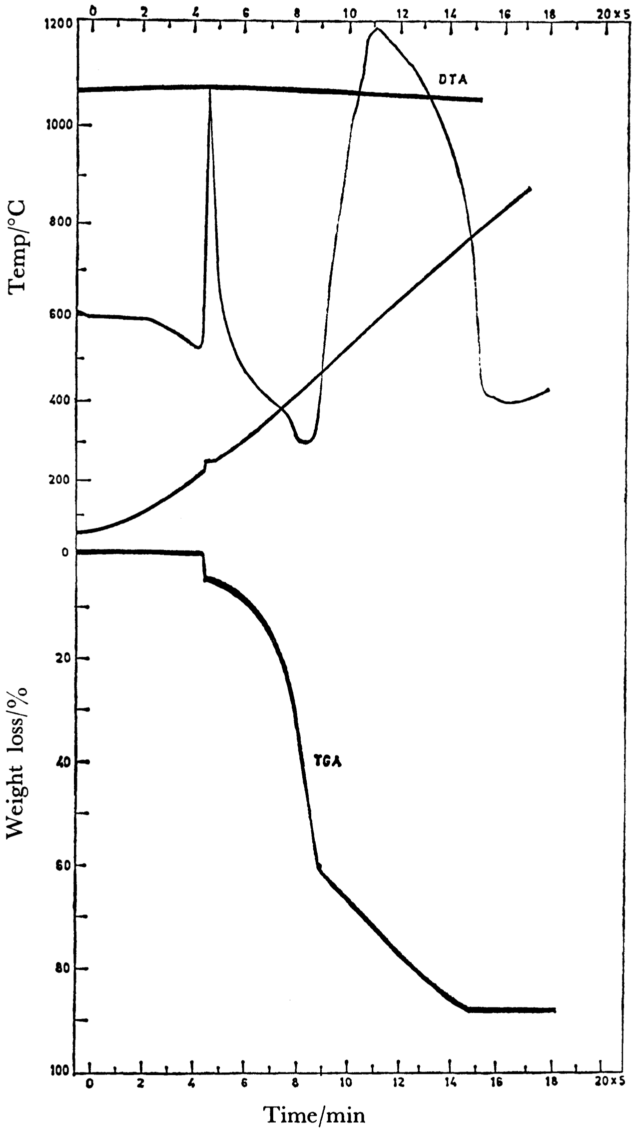


Fig. 1. DTA and TGA curves of copper complex of N^1-hydroxy-N^1-(*m*-tolyl)-N^2-(*o*-chlorophenyl)-*p*-toluamidine hydrochloride.

Hence the direct weight of copper complex after drying at 110—180 °C for gravimetric determination is justified.

Infrared Spectra. The ligand molecule consists of a broad band at 2550 cm^{-1} confirming the presence of protonated azomethine nitrogen in *N*-hydroxyamidine hydrochloride.[14)] The absence of any band in the region 2500—2730 cm^{-1} due to $\overset{+}{N}$–H stretching mode in the spectra of copper complex suggests that deprotonation of azomethine nitrogen occurs when copper complex is formed. The band due to $C=N^+$ stretching ($1610\ cm^{-1}$)[15,16] is displaced to lower frequency ($1570\ cm^{-1}$) on complex formation. This indicates the formation of C=N⋯⋯Cu coordinate linkage. The N–O stretching mode appears at $930\ cm^{-1}$ in the free ligand.[17,18] Replacement of proton of N–OH group by copper leads to displacement of N–O stretching mode to higher frequency and appears at $950\ cm^{-1}$ in the copper complex.

The authors are thankful to Head, Department of Chemistry, Ravishankar University, Raipur for providing Research facilities and to the Council of Scientific and Industrial Research, New Delhi for the award of a Fellowship to one of them (P.K.S.).

References

1) K. Satyanarayana and R. K. Mishra, *Anal. Chem.*, **46**, 1609 (1976).
2) H. Mohabey and R. K. Mishra, *J. Indian Chem. Soc.*, **57**, 142 (1980).
3) P. K. Sharma and R. K. Mishra, *Croat. Chem. Acta*, **53**, 87 (1980).
4) J. H. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 529 (1940).
5) P. Ray and J. Gupta, *Mikrochemie*, **17**, 14 (1935).
6) S. C. Shome, *Analyst*, **75**, 27 (1950).
7) N. C. Sogani and S. C. Bhattacharya, *Anal. Chem.*, **28**, 1616 (1956).
8) F. Feigl and A. Caldas, *Anal. Chim. Acta*, **8**, 339 (1953).
9) S. P. Gupta, O. P. Malik, and J. Singh, *J. Indian Chem. Soc.*, **52**, 656 (1975).
10) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," Longmann, Green, London (1964), p. 498.
11) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier, London (1953), p. 347.
12) R. G. Charles, *Anal. Chim. Acta*, **27**, 474 (1962).
13) G. Thomas and R. A. Paris, *Anal. Chim. Acta*, **25**, 159 (1961).
14) B. Witkop, *J. Am. Chem. Soc.*, **76**, 5597 (1954).
15) C. N. R. Rao, "Chemical Applications of Infra-red Spectroscopy," Academic Press, New York (1963), p. 267.
16) B. Witkop and T. W. Beiler, *J. Am. Chem. Soc.*, **76**, 5589 (1954).
17) P. A. Gigure and I. D. Liu, *Can. J. Chem.*, **30**, 498 (1952).
18) A. T. Pilipenko, E. A. Shpak, and L. L. Shevchenko, *Zh. Neorg. Khim.*, **121**, 463 (1967).