Determination of Copper with *m*-(Mercaptoacetamido) phenol as a Gravimetric Reagent

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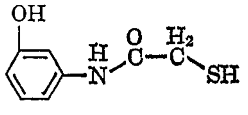
▶ *m*-(Mercaptoacetamido)phenol is a new reagent for the gravimetric determination of copper(II) at pH 2.0 to 6.0. Determinations, however, have been carried out only at pH 2.0 to 3.5, where commonly associated metals do not interfere. The structure of the copper-reagent complex is discussed. The reagent is reasonably soluble in aqueous and alcoholic media. It competes favorably with other reagents for this purpose.

THIOGLYCOLLANILIDES were introduced as useful analytical reagents by Bersin (*5*) and Berg and Roebling (*4*). The special affinity of these compounds for cobalt(II) has led to the gravimetric determination of cobalt (*4, 5, 17*). Ubeda and Capitan (*26*), however, effected the gravimetric and indirect iodometric determination of silver(I), copper(II), and mercury(II), using a few such compounds. Similarly, thionalide has been utilized for the titrimetric determination of certain metals (*12*). Swain, Misra, and Guha Sircar (*25*) drew attention to the precipitation of copper(II), silver(I), mercury(II), and lead(II) by various thioglycollanilides. But the compounds they used had the shortcoming of low solubility in water. In this communication the authors introduce a new thioglycollanilide, *m*-(mercaptoacetamido)-phenol, a condensation product of thioglycollic acid and *m*-aminophenol. It has sufficient solubility in aqueous medium and is appreciably specific for copper at low pH.



It precipitates copper a greenish yellow granular inner complex at a pH as low as 2.0, where only the cations of the noble metals, silver(I), tin(II, IV), mercury(II), and cerium(IV) are precipitated. Modified procedures, however, have been used for estimating copper in the presence of the last four.

The reagent reacts quantitatively with iodine (*12*) and thus can be standardized by titrating against iodine. A comparatively concentrated solution of the reagent for this purpose can be prepared in 20% alcohol. The compound is stable in the solid state, but its aqueous solution is slowly oxidized in air (*12*).

The copper complex is freely soluble in acetone, slightly soluble in alcohol, and insoluble in chloroform and other nonpolar solvents. When heated above room temperature, it shrinks to a brown mass.

EXPERIMENTAL

Preparation of Reagent. Different procedures (*2, 3, 17, 26*) for the preparation of thioglycollanilides have been mentioned in the literature. In the preparation of the present compound, however, a modification of Van Allan's method (*27*) was used.

In that method, the reactants are refluxed at ca. 100° C. in an atmosphere of benzene for about 9 hours. We, however, refluxed them (11.0 grams of *m*-aminophenol and 6.5 ml. of 80% thioglycollic acid) for about 3 hours at 120° to 130° C. Aerial oxidation was prevented by keeping a layer of toluene on the surface of the reactants. The melt was then cooled and allowed to solidify. The crude product was ground with 20% hydrochloric acid to remove the unreacted amine. The granular, cream-colored product so obtained (yield about 6 grams) was crystallized from absolute alcohol twice; colorless needles (m.p. 160–61° C.) were obtained. Analysis: Found: S, 17.73%; N, 7.58%. $C_8H_9O_2SN$ requires: S, 17.48%; N, 7.31%. Solubility in water at 30° C., 0.1012% (w./v.); at 90° C., 2.8660% (w./v.).

Reagent Solution. For copper determination, a 1.0% solution of the reagent in warm 20% alcohol was prepared. Fresh solutions were used.

Standard Copper Solution. About 5.0 grams of analytical reagent grade copper sulfate pentahydrate was dissolved in 1 liter of distilled water. Copper was determined gravimetrically by the thiocyanate method. An aliquot was then suitably diluted to give a 0.1% solution of the metal.

Solutions of Diverse Ions. Solutions of diverse ions were prepared by dissolving suitable soluble salts of E. Merck or British Drug House quality to give 1.0% of the desired ion in solution.

HCl (1*N*), 10% (w./v.) sodium acetate, 10% (w./v.) sodium potassium tartrate, and 5.0% (w./v.) sodium fluoride were prepared from reagent grade samples.

Universal pH paper (E. Merck) and a Cambridge bench type pH meter were used to determine the pH of the solutions.

Determination of Copper. Copper solution (20 ml.) was taken in a 400-ml. beaker and diluted to about 150 ml. Sodium acetate (10.0 ml.) and the required amount of 1*N* HCl were introduced to bring the pH to between 2.0 and 3.5. The contents were heated to 80° to 90° C. and the reagent was added while the solution was kept thoroughly stirred. The greenish yellow precipitate was coagulated by heating on a steam bath for 15 to 20 minutes and filtered through a sintered crucible (No. G3). The precipitate was washed three to four times with 10.0-ml. portions of hot 5% alcohol, then heated at about 125° C. for 2 hours, and weighed. The weight of the complex multiplied by the factor 0.2588 gives the weight of copper. The results are recorded in Table I.

Copper Determinations in Presence of Diverse Ions. When copper was determined in the presence of diverse ions, the solution of these ions was introduced before the pH of the medium was adjusted. Alkali and alkaline earth metals, ammonium, Fe(II), Fe(III), Cr(III), Mn(II), Zn(II), UO_2(II), VO(II), Tl(III), Th(IV), Zr(IV), Al(III), Cd(II), Co(II), Ni(II), and tungstate do not interfere with the determination in the pH range of 2.0 to 3.5. Molybdate, however, gives a deep blue color at this pH (*13, 14*) and, hence, in this case copper was determined between pH 5.0 and 6.0. Lead(II), bismuth(III), antimony(III), and arsenic(III) form precipitates with the reagent, but these are soluble on heating. Hence, when these elements were present, the copper complex was filtered while hot. While determining Cu(II) in the presence of Fe(III), Bi(III), and Sb(III), the pH was adjusted by using sodium potassium tartrate. Stannic interference was removed by the addition of ca. 10.0 ml. of 5.0% sodium fluoride solution. Tin(II) and cerium(IV) were removed as hydroxides by raising the pH with sodium acetate and boiling. Copper(II) was then determined in the filtrate after adjusting the pH. In the case of mercury(II), a freshly prepared solution of stannous chloride was added to a gray tinge. The excess stannous was removed as above, along with the precipitate of mercurous chloride. Silver(I) was removed as chloride with 1*N* HCl. The required amount of sodium acetate was then added to the filtrate and copper was determined. The concentration limits of Pb(II), Bi(III), Sb(III), and As(III) are listed in Table I. In case of other ions, however, the limiting concentration has been studied only up to five times the amount of copper(II).

RESULTS AND DISCUSSION

Various organic analytical reagents are reported for the gravimetric determination of copper(II). Salicylaldoxime (*10*), which forms a greenish yellow complex with copper(II) in acetic acid medium, decomposes in the reaction medium above 80° C. and contaminates the complex with unremovable products. The presence of zinc(II), cobalt(II), and nickel(II) impairs the determination (*23*). α-Benzoinoxime (*11*) produces a green complex with copper(II) in ammonical medium, but large quantities of ammonium salts prevent precipitation (*11*). Further, the excess of the reagent cannot be removed completely (*1*) and thus the complex has to be ignited, which is a practical drawback. The reagent is not only photosensitive but also gives unreliable results for copper(II) in the presence of iron(III) and zinc(II) (*22*). Quinaldinic acid (*15, 19, 20*) is also a popular reagent for this purpose, but so far as has been reported, it possesses comparatively less sensitivity, specificity, and solubility at the low pH at which it is used (*16*). 8-Quinolinol (*6*) is not specific for this purpose. Rubeanic acid (*18, 21*) is reported to be a very sensitive reagent which can precipitate copper(II) from slightly acidic solution. Its complex, however, is not of definite composition because of adsorbed impurities and, hence, it must be ignited.

m-(Mercaptoacetamido)phenol is superior to these compounds in ease of preparation, solubility in aqueous medium, and keeping qualities in the solid form. The copper complex of the reagent can be safely digested for a fairly long time on the steam bath. Commonly occurring metals do not interfere with the determination of copper at pH 2.0 to 3.5. Since the reagent is appreciably soluble in boiling water, an excess remains in the reaction medium. Furthermore, copper(II) can be precipitated at low pH; hence, the complex is granular and easily filterable. The composition of the complex is definite and thus it is directly weighable.

Structure of Copper-Reagent Complex. The weight of the copper complex shows that the copper atom is attached to only one molecule of the reagent. It appears, therefore, that the copper in the complex is present in the cuprous state. This is also evident from the fact that the mercapto group can reduce Cu(II) to Cu(I) (*12*) and that a solution of Cu(II), completely reduced by sulfite, forms a similar greenish yellow precipitate (*24*). The complex formed by Cu(II), on dissolution in hydrochloric acid, gave the test for Cu(I) with thiocyanate. The cuprous state in the complex is stabilized by coordination (*8, 12*). To satisfy the four coordination number of Cu(I) (*7*), two water molecules might have been attached to one molecule of the complex (*9*). This is supported by the fact that the complex shrinks greatly on heating. The complete reaction can be represented (*12*) as

$$2R - S^- + 2Cu(II) \rightarrow$$
$$2Cu(I) + R{-}S{-}S{-}R \text{ (reduction)}$$

$$R{-}S^- + Cu(I) + 2H_2O \rightarrow$$
$$(R{-}S)Cu \cdot 2H_2O \text{ (chelation)}$$

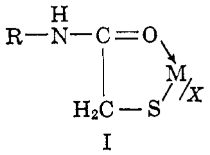
Table I. Determination of Copper(II) in Presence of Diverse Ions

[20 mg. of copper(II) taken for each determination]

Diverse ion	Added as	Limiting concn., mg.	Wt. of Cu complex, mg.	Cu found, mg.	Error, mg.
...	...	...	77.3	20.01	+0.01
...	...	...	77.2	19.98	−0.02
...	...	...	77.3	20.01	+0.01
Na(I), K(I), NH_4(I)	Chloride	100	77.4	20.03	+0.03
Ca(II)[a], Ba(II),[a] Sr(II)[a]	Nitrate	100	77.2	19.98	−0.02
Mg(II), Be(II)	Nitrate	100	77.4	20.03	+0.03
Fe(II)	Mohr's salt	100	77.3	20.01	+0.01
Fe(III)	Ferric alum	100	77.5	20.06	+0.06
Cr(III)	Acetate	100	77.4	20.03	+0.03
Al(III)	Acetate	100	77.3	20.01	+0.01
Co(II)	Acetate	100	77.6	20.08	+0.08
Ni(II)	Nitrate	100	77.5	20.06	+0.06
Zn(II)	Chloride	100	77.4	20.03	+0.03
Mn(II)	Chloride	100	77.1	19.95	−0.05
Ag(I)	Nitrate	100	77.3	20.01	+0.01
Pb(II)[a]	Nitrate	30	77.5	20.06	+0.06
Bi(III)	Nitrate	10	77.4	20.03	+0.03
Hg(II)	Nitrate	100	77.1	19.95	−0.05
Sn(IV)	Chloride	100	77.2	19.98	−0.02
Sn(II)	Chloride	100	77.1	19.95	−0.05
As(III)	Chloride	30	77.4	20.03	+0.03
Sb(III)	Chloride	15	77.5	20.06	+0.06
Cd(II)	Nitrate	100	77.3	20.01	+0.01
UO_2(II)	Nitrate	100	77.4	20.03	+0.03
VO(II)	Sulfate	100	77.4	20.03	+0.03
Ce(IV)	Sulfate	100	77.0	19.93	−0.07
Th(IV)	Nitrate	100	77.2	19.98	−0.02
Tl(III)	Sulfate	100	77.4	20.03	+0.03
Zr(IV)	Nitrate	100	77.1	19.95	−0.05
Tungstate	Sodium	100	77.3	20.01	+0.01
Molybdate	Ammonium	100	77.4	20.03	+0.03

[a] Standard copper acetate solution used.

The complexes of thioglycollanilides with metals are generally represented (*12*) as



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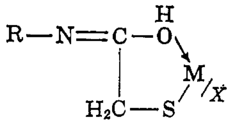

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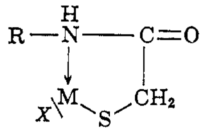
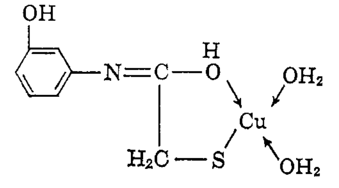


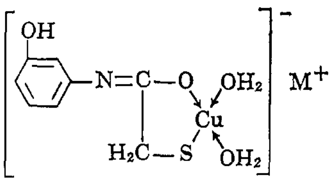
III

where *X* is the valency of metal M.

It is not always possible to select a particular formula for a particular cation. In the present case, however, the solubility of the complex in acetone and alcohol, and insolubility in chloroform and other nonpolar solvents, conform to formula II (*12*). The complete structure of the complex can, therefore, be written as:



This structure explains the solubility of the complex in alkalies. On dissolution in alkalies it probably becomes (*12*);



where M stands for Na, K, or NH_4.

The hydrogen of the hydroxyl group in the benzene ring might also be replaced by the alkali metal.

ACKNOWLEDGMENT

The senior author is grateful to U.G.C. (India) for the grant of a research fellowship.

LITERATURE CITED

(1) Azzalin, E., *Ann. Chim. Appl.* **15,** 373 (1923).
(2) Beckurts, H., Frerichs, H., *J. Prakt. Chem.* **66,** 174 (1902).
(3) Benary, Erich, *Ber.* **46,** 2105 (1913).
(4) Berg, Richard, Roebling, W., *Ibid.*, **68,** 403 (1935); *Z. Angew. Chem.* **48,** 430, 597 (1935).
(5) Bersin, Theodor, *Z. Anal. Chem.* **85,** 428 (1931).
(6) Calvet, J., *Compt. Rend.* **195,** 148 (1932).
(7) Emeleus, H. J., Anderson, J. S., "Modern Aspects of Inorganic Chemistry," pp. 49–50. Routledge and Kegan Paul, London, 1962.
(8) *Ibid.*, p. 205.
(9) *Ibid.*, p. 239.
(10) Ephraim, F., *Ber.* **63,** 1928 (1930).
(11) Feigl, F., *Ibid.*, **56B,** 2083 (1923).
(12) Feigl, F., "Chemistry of Specific, Selective, and Sensitive Reactions," pp. 227–39, Academic Press, New York, 1949.
(13) Gupta, H. K. L., Sogani, N. C., ANAL. CHEM. **31,** 918 (1959).
(14) Hemence, J. H., *Analyst* **65,** 152 (1940).
(15) Majumdar, A. K., *Ibid.*, **64,** 874 (1939).
(16) *Ibid.*, **68,** 242 (1943).
(17) Misra, R. N., Guha Sircar, S. S., *J. Indian Chem. Soc.* **32,** 127 (1955).
(18) Ray, P., *Z. Anal. Chem.* **79,** 94 (1929).
(19) Ray, P., Bose, M. K., *Ibid.*, **95,** 400 (1933).
(20) Ray, P., Gupta, J., *Mikrochem.* **17,** 14 (1935).
(21) Ray, P., Ray, R. M., *J. Indian Chem. Soc.* **3,** 118 (1926).
(22) Shik, I. R., *Zavodsk. Lab.* **9,** 542 (1940).
(23) *Ibid.*, **10,** 261 (1941).
(24) Spacu, G., Kuras, M., *Z. Anal. Chem.* **102,** 24, 190 (1936).
(25) Swain, R. C., Misra, R. M., Guha Sircar, S. S., *J. Indian Chem. Soc.* **33,** 329 (1956).
(26) Ubeda, F. D., Capitan, F., *Anales Real. Soc. Españ. Fís. Quím. (Madrid)* **45B,** 413 (1949).
(27) Van Allan, J. A., *J. Am. Chem. Soc.* **69,** 2914 (1946).

RECEIVED for review June 14, 1965. Accepted September 30, 1965.

Determination of Gold in Cyanide Waste Solutions by Solvent Extraction and Atomic Absorption Spectrometry

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► A method is presented for the determination of 0.01 to 0.5 p.p.m. of gold in cyanide waste solutions. The gold(I) cyanide is oxidized to gold(III) chloride and extracted from 3M HCl into methyl isobutyl ketone. The gold concentration is determined directly in the organic phase by atomic absorption spectrometry. By using a high ratio of aqueous to solvent phase and a solvent which provides a considerable enhancement of the gold absorbance in the flame, the sensitivity of the gold determination is increased by a factor of about 100. Methyl isobutyl ketone is the most favorable solvent because it has the highest distribution coefficient, produces a satisfactory flame, and has a reasonably low solubility in water and a reasonably high absorbance enhancement. Distribution coefficients and experimentally determined absorbance enhancement factors for a number of solvents are included. The method is many times faster than methods in current use for low gold concentrations and the reproducibility and accuracy of results are very good.

NO METHOD which is satisfactory in both speed and accuracy seems to have been described in the literature for the determination of very low concentrations of gold in cyanide waste solutions. The gold concentrations normally found are of the order of 0.01 to 0.1 p.p.m. Tucker (*9*) has presented a polarographic method for the determination of gold in these solutions, using volumes of 2 to 20 liters, and a preliminary ion exchange concentration step including a wet ashing of the resin. Although satisfactory in accuracy, this method is too lengthy for the analysis of large numbers of samples and especially for plant control. Atomic absorption spectrometry (*10*) is extremely well suited for the direct determination of low concentrations of certain elements in solution. Unfortunately, the detection limit for gold in aqueous solution is of the order of 1 p.p.m. (*7, 8*). A primary concentration step or other means for increasing the sensitivity of the method therefore has to be applied.

Berry (*3*) has shown that the presence of water-soluble organic solvents considerably enhances sensitivities for sodium and potassium in flame photometry. Dean (*5*) was the first to extract an element into a water-insoluble organic solvent and then determine it by spraying this solvent into the flame. Allan (*2*) reported a considerable gain in sensitivity in the determination of copper by atomic absorption spectrometry using a similar procedure. Methods for the determination of a small number of other elements using atomic absorption spectrometry with organic solvent enhancement of sensitivity have been described since (*1, 11, 12*), but no work seems to have been undertaken for the determination of gold.

By making use of the additive effects of two favorable factors—a high volume ratio of the phases in the extraction process, and a high sensitivity enhancement factor for the atomic absorption measurement caused by the presence of the organic solvent—it was hoped to increase the sensitivity of the method by a factor of 100. It thus remained to find an organic solvent which had a sufficiently high distribution coefficient for gold ($K_d \gtrsim = 1000$), a low solubility in water, and favorable flame characteristics.

EXPERIMENTAL

Apparatus and Reagents. A Zeiss P.M.Q.II spectrophotometer with a gold hollow cathode lamp as a light source was used for the atomic absorption measurements. An aluminum burner, similar to that described by Butler (*4*), was fitted with a flat water-cooled burner plate. A standard Zeiss atomizer operated at 20-p.s.i. air pressure was used for spraying the sample solutions. Because the ketone is flammable and causes the flame to become smoky and fuel-rich, a supplementary air supply was added which