CANADA

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ELSIE M. PENNER & W. R. INMAN

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

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DETERMINATION OF COPPER IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS WITH BATHOCUPROÏNE*

ELSIE M. PENNER and W. R. INMAN
Department of Mines and Technical Surveys, Ottawa, Ontario, Canada

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Summary—A spectrophotometric method for determining 0·0005-0·125% of copper in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of copper to the univalent state with ascorbic acid, the yellow complex formed by copper[I] and bathocuproïne (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is extracted into n-amyl alcohol and the absorbance of the resulting extract is determined at 476 mμ. Other impurities present in the four high-purity metals described do not interfere in the proposed method.

INTRODUCTION

AN analytical project involving the determination of impurities in high-purity niobium, tantalum, molybdenum and tungsten metals is currently being conducted at the Mines Branch laboratories. As part of this project, the present investigation was undertaken to develop a suitable spectrophotometric procedure for determining trace amounts of copper that would be applicable to all four metals.

Several spectrophotometric procedures have previously been applied to the determination of small amounts of copper in matrices of the above metals,[1-7] but none of these methods were directly applicable to all four metals under consideration without some modifications.

Recently, Penner and Inman[8] reported a method for the determination of iron in the above metals. It was considered that the dissolution procedure and solution preparation described in this method would be easily adaptable to a procedure for copper in which the copper was extracted as a coloured complex with an organic solvent. Bathocuproïne was chosen as the chromogenic reagent in this investigation because of its sensitivity, reported specificity, and the solubility of its copper[I] complex in various organic solvents.[9,10,11] It is the most sensitive of the three cuproïne reagents; its copper[I] derivative has a molar extinction coefficient of 14,160 compared to 6,220 for cuproïne and 7,950 for neocuproïne.[10] Smith and Wilkins[9] first investigated its analytical potential and applied it to the determination of copper in iron.

This paper describes the successful use of bathocuproïne in determining copper in high-purity niobium, tantalum, molybdenum and tungsten metals. Moderate amounts (5 mg) of cobalt, cadmium, chromium, nickel, manganese and zinc do not interfere in this method.

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EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model DU.
pH meter: Leeds and Northrup.
Centrifuge: Clinical type.
Teflon (tetrafluoro-ethylene) beakers, 250 ml: Dynalab Corp., Rochester, N.Y.

Reagents

Water: De-ionised by passing distilled water through a column of Dowex 50W-X8 resin.

Standard copper solution: Dissolve 0·1000 g of pure copper in 10 ml of 1:1 nitric acid. Add 5 ml of concentrated perchloric acid and evaporate to fumes of perchloric acid. Cool, dilute to 500 ml with water and store in a polyethylene bottle. Dilute 5 ml of this stock solution to 200 ml with water. Prepare fresh as needed (1 ml of this diluted solution = 5 μg of copper).

Bathocuproïne, 0·002M solution: Dissolve 0·360 g of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (G. Frederick Smith Chemical Co.) in 500 ml of ethyl alcohol and store in a polyethylene bottle.

Ammonium tartrate, 25%, copper-free solution:* Dissolve 125 g of ammonium tartrate and 1 g of hydroxylamine hydrochloride in approximately 350 ml of water. Add 20 ml of bathocuproïne solution, allow to stand for 1 hr, then extract three times with 15-ml portions of a 3:1 mixture of chloroform and n-amyl alcohol. Extract the copper-free solution three times with chloroform to remove excess n-amyl alcohol. Filter, dilute to 500 ml with water and store in a polyethylene bottle.

*Boric acid, 5%, copper-free solution**: Dissolve 50 g of boric acid in approximately 800 ml of hot water. Cool, dissolve 1 g of hydroxylamine hydrochloride in this solution, then add 30 ml of bathocuproïne solution and allow to stand for 1 hr. Extract with chloroform and n-amyl alcohol as described for the ammonium tartrate solution. Filter, dilute to 1 litre with water and store in a polyethylene bottle.

Ascorbic acid, 10%, copper-free solution: Dissolve 10 g of ascorbic acid (Analytical Reagent, British Drug Houses Ltd.) in approximately 60 ml of water. Add 5 ml of bathocuproïne solution and allow to stand for 5 min. Extract twice with 8-ml portions of a 3:1 mixture of chloroform and n-amyl alcohol, then three times with chloroform to remove excess n-amyl alcohol. Filter and dilute to 100 ml with water. Prepare a fresh solution every second day.

n-Amyl alcohol: Analytical Reagent, obtained from Mallinckrodt Chemical Works.

Chloroform: Analytical Reagent, obtained from Fisher Scientific Co.

Procedure

Calibration curve: Pipette 20 ml of 25% ammonium tartrate solution, 40 ml of 5% boric acid solution and 20 ml of 10% ascorbic acid solution into a 250-ml beaker. Using a pH meter, adjust the resulting "base" solution to pH 5·5 with concentrated ammonia solution and dilute to volume with water in a 200-ml volumetric flask. Add a 20-ml aliquot of this solution to each of six 60-ml separatory funnels that are marked at 25 ml, then, by burette, add to the last five funnels 1, 2, 3, 4 and 5 ml, respectively, of standard copper solution (*i.e.*, 1 ml = 5 μg of copper). The first funnel contains the blank. Dilute the contents of each funnel to the 25-ml mark with water and swirl to mix. (Because n-amyl alcohol is soluble to a certain extent in water, *i.e.* 2·19% by weight at 25°, the total volume should be kept relatively constant). Add to each funnel 2 ml of 0·002*M* bathocuproine solution, mix and allow to stand for 10 min, then add, by pipette, 10 ml of n-amyl alcohol, stopper and shake for 2 min. Allow 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the n-amyl alcohol extracts into 15-ml centrifuge tubes and centrifuge for 30 sec. Determine the absorbance of each extract against the blank as the reference solution, using 2-cm cells, in a Beckman DU spectrophotometer, at a wavelength of 476 mμ. Plot μg of copper *vs.* absorbance.

Procedure for Niobium, Tantalum, Molybdenum and Tungsten Metals: In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker, add 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon watch glass. Through the lip of the beaker add concentrated nitric acid slowly, 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. (For molybdenum metal and a separate reagent blank, add at this point, 2 ml of concentrated hydrochloric acid and heat until the dark brown colouration disappears and the solution becomes pale yellow.) Add 3 ml of formic acid to destroy excess nitric acid and heat

* The use of hydroxylamine hydrochloride rather than ascorbic acid is recommended as reducing agent in the preparation of the solution because ascorbic acid produces a dark yellow colouration in 1 week.

gently until the evolution of brown oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water and evaporate to approximately 5 ml. Add 10 ml of water and 10 ml of 25% ammonium tartrate solution, and heat gently without boiling for 5 to 10 min, at which point the solution should be clear. Add 20 ml of 5% boric acid solution and allow to stand for 20 min. (If the copper determination cannot be completed the same day, allow to stand overnight at this point.) Add 10 ml of 10% ascorbic acid solution, mix, then using a pH meter adjust the pH to 5·5 with concentrated ammonia solution. Transfer to a 100-ml volumetric flask and dilute to volume. (At this point, slightly low results, *i.e.*, 0·002% at the 0·1-% level, are obtained if the samples are allowed to stand for more than 2 hr before the extraction and subsequent determination of the copper.) Transfer a suitable aliquot (4–20 ml) of both sample and blank solutions, depending on the copper content of the sample, to 60-ml separatory funnels. Dilute to the 25-ml mark with water and proceed with the copper extraction as described for the calibration curve. Measure the absorbance of the sample against the reagent blank and determine the copper content of the aliquot by reference to the calibration curve. When 20-ml aliquots of sample solution are taken:

1 μg of copper = 0·001%.

RESULTS

Extraction of the coloured complex

Although the copper[I]-bathocuproïne complex can be extracted into various organic solvents,[9,10,11] n-amyl alcohol was chosen for the present work because of its ready availability.

In preliminary experiments with pure copper solutions, up to 50 μg of copper contained in 25 ml of solution could be extracted quantitatively in a single stage with 10 ml of n-amyl alcohol. Larger amounts (100 μg) could also be extracted with approximately 99·5% efficiency, but this was not feasible in the present investigation because of the high optical density of the resulting extract.

Reduction of copper

In the method previously described for determining iron in high-purity niobium, tantalum, molybdenum and tungsten metals with bathophenanthroline,[8] reduction of iron was achieved with a mixture of ascorbic acid and hydroxylamine hydrochloride. Colour fading was observed in the n-amyl alcohol extract of the iron[II]-bathophenanthroline complex when ascorbic acid alone was employed as reductant. This was attributed to insufficient ascorbic acid being extracted into the organic phase to prevent air oxidation of the complex.

In the present investigation, tests performed with ascorbic acid alone showed that reduction of copper in sample solutions of each of the four metals, prepared according to the described procedure, and to which standard additions of copper had been made, was rapid and complete. The colour of the extract was stable for at least 3 days.

These results indicate that the copper[I]-bathocuproïne complex is less subject to atmospheric oxidation than the corresponding iron[II]-bathophenanthroline complex.

Effect of pH

A search of the literature did not reveal references to methods for determining copper with bathocuproïne in which the optimum pH range for the complete formation of the complex has been defined. Therefore, in order to determine this range, the following procedure was used with a series of "base" solutions (described under *Calibration Curve*) of increasing pH.

A known amount of pre-reduced copper (ascorbic acid) was added to a 20-ml aliquot of each of the above "base" solutions and the resulting "test" solutions were each diluted to 25 ml with water. (Reduction of the copper prior to addition to the aliquot of "base" solution ensures that all of the

copper will be present in the reduced form at the given pH). Then, 2 ml of 0·002*M* bathocuproïne solution were added and, after a 10-min interval to allow for colour development, the copper complex was extracted with 10 ml of n-amyl alcohol. The absorbance of each extract was measured in a 2-cm cell against its corresponding blank, prepared by carrying a second 20-ml aliquot of each "base" solution (without added copper) through the same procedure.

Because the dilution of a 20-ml aliquot of "base" solution to 25 ml with water prior to the addition of bathocuproïne solution and extraction of the copper complex is accompanied by a small variation in pH, the initial pH adjustment of each "base" solution was, therefore, only an approximation, and the exact pH at which the copper complex was formed in the "test" solutions was determined by measuring the pH of the aqueous phase after the copper complex was extracted. (The pH of the "test" solution is not altered by the extraction step and therefore the measured pH is that of the solution prior to extraction.) The results of these tests (Table I) show that colour development is complete in the pH range 1·45 to 6·25.

TABLE I.—EFFECT OF pH ON THE FORMATION OF THE COPPER[I]-BATHOCUPROÏNE COMPLEX

pH of aqueous phase	Optical density of extract
0·85	0·539
1·45	0·562
2·45	0·570
4·05	0·569
4·75	0·566
5·35	0·567
5·70	0·563
6·25	0·559
6·60	0·501
7·75	0·265

Copper present: 15 μg.

During the above tests it was observed that the rate of colour formation at pH 0·85 was quite slow; therefore, if a longer time interval was allowed after the bathocuproïne addition, complete colour development would probably be obtained at this pH.

Experiments to determine the effect of pH on the formation of the copper complex in solutions of the high-purity metals were performed with molybdenum solutions only, because it was considered that the optimum conditions for determining copper in molybdenum metal would also be applicable to the other three metals. In these experiments, synthetic molybdenum samples containing 0·10% of added copper were prepared as described under *Procedure* and the final pH of these solutions was varied from 0·5 to 7·0. The results of these tests showed that complete colour development, indicated by total recovery of the added copper, was obtained over the same pH range described above for test solutions.

Because the method for iron[9] required a final sample solution pH of approximately 5·5, this pH was also chosen for the present work; copper and iron could then be determined on aliquots of the same sample solution. Tests carried out at pH 5·5 on synthetic niobium, tantalum and tungsten samples also indicated complete formation of the copper-bathocuproïne complex.

Effect of diverse metal ions

The reported specificity of bathocuproïne for copper was investigated by testing separately the effect of 5-mg quantities of the various impurities (cobalt, cadmium, nickel, manganese and zinc) that occur in small amounts in samples of the four high-purity metals on a known amount (15 μg) of copper. The effect of chromium[III] [added as $CrK(SO_4)_2.12H_2O$] was also tested, because this cation was found to interfere in the determination of copper with the related neocuproïne reagent (2,9-dimethyl-1,10-phenanthroline).[12]

The results of these tests showed that none of the ions tested interfered in the copper determination. Iron also does not interfere when complexed with citrate or tartrate.[9,10]

Application to synthetic niobium, tantalum, molybdenum and tungsten samples for copper contents up to approximately 0·1%

In order to determine its accuracy, the proposed method was applied to the analysis of a series of synthetic samples in which the added copper varied from 0·005 to 0·10%. The standard copper solution was added after the formic acid treatment. The results obtained are given in Table II.

TABLE II.—RECOVERY OF COPPER BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Cu present, %	Cu found, %	Sample	Total Cu present, %	Cu found, %
Nb + 0·005% Cu	0·0054	0·0055	Ta + 0·005% Cu	0·0051	0·0050
Nb + 0·010% Cu	0·0104	0·0103	Ta + 0·010% Cu	0·0101	0·0098
Nb + 0·025% Cu	0·0254	0·0253	Ta + 0·025% Cu	0·0251	0·0249
Nb + 0·050% Cu	0·0504	0·0502	Ta + 0·050% Cu	0·0501	0·0502
Nb + 0·100% Cu	0·1004	0·0993	Ta + 0·100% Cu	0·1001	0·1004
Mo + 0·005% Cu	0·0052	0·0052	W + 0·005% Cu	0·0050	0·0050
Mo + 0·010% Cu	0·0102	0·0102	W + 0·010% Cu	0·0100	0·0098
Mo + 0·025% Cu	0·0252	0·0254	W + 0·025% Cu	0·0250	0·0249
Mo + 0·050% Cu	0·0502	0·0505	W + 0·050% Cu	0·0500	0·0499
Mo + 0·100% Cu	0·1002	0·1009	W + 0·100% Cu	0·1000	0·1001

Duplicate determinations of copper in the above Nb, Ta, Mo and W metals by the proposed method gave average results of 0·0004, 0·0001, 0·0002% and none detected, respectively.

DISCUSSION

Table II shows that the results obtained by the proposed bathocuproïne method agree favourably with the total calculated percentage of copper present in the range of values up to approximately 0·1%.

In the proposed procedure, the formation and subsequent extraction of the copper[I]-bathocuproïne complex takes place under essentially the same conditions previously described for the formation and extraction of the iron-bathophenanthroline complex.[8] Therefore, both copper and iron can be determined in the same sample using separate aliquots of sample solution prepared as described in the method for iron, provided that de-ionised water and both copper- and iron-free reagents are used throughout the procedure.

The method presented in this paper is suitable for samples containing between 0·0005 and 0·125% of copper, but copper contents below 0·0005% can be determined

fairly accurately because the reagent blank contains approximately 1 μg or less of copper. Materials containing more than 0·125% of copper can also be successfully analysed by reducing the initial sample weight. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Eine spektralphotometrische Methode zur Bestimmung von 0·0005 bis 0·125% Kupfer in hochgereinigtem Nb, Ta, Mo und W wird beschrieben. Nach Lösen der Probe wird Kupfer reduziert (Ascorbinsäure) und mittels Bathocuproin (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolin) in der Form eines gelben Komplexes in n-Amylalkohol ausgeschüttelt. Der Extrakt wird bei 476 mμ photometriert. Andere Verunreinigungen in den oben erwähnten Metallen stören bei der Methode nicht.

Résumé—Description d'une méthode de dosage du cuivre en concentration de l'ordre de 0·0005 à 0·125% dans des échantillons de niobium, tantale, molybdène et tungstène très purs. On dissout l'échantillon et l'on réduit le cuivre à l'état cuivreux au moyen de l'acide ascorbique; le complexe jaune formé par le cuivre cuivreux et la bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phénanthroline) est extrait par l'alcool n-amylique et l'on détermine l'absorption de cet extrait à 476 μ. Les autres impuretés présentes dans les échantillons des métaux purs cités, ne gênent pas le dosage.

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