

**TREATISE
ON
ANALYTICAL
CHEMISTRY**

**PART II
ANALYTICAL CHEMISTRY
OF THE ELEMENTS
VOLUME 3**

TREATISE ON ANALYTICAL CHEMISTRY

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PART II
~~ANALYTICAL~~ CHEMISTRY
~~OF THE~~ ELEMENTS
VOLUME 3

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Part II
Section A

COPPER

BY W. CHARLES COOPER, *Canadian Copper Refiners Ltd., Montreal East, Quebec, Canada*

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I. INTRODUCTION

Copper is one of the oldest metals known to man and is probably the first metal to be employed by him for useful purposes. The indications are that the metallurgy of copper likely originated at the site of the earliest civilization in the valleys of the Tigris and Euphrates rivers. Copper objects believed to date prior to 4000 B.C. have been found in Mesopotamia and in Egypt, and there is evidence that the pre-Dynastic Egyptians, prior to 3200 B.C., employed copper carbonate as a pigment and fashioned the metal into axes, adzes, and boring tools (17).

The word "copper" is derived from the Latin "cuprum," which in turn is a corruption of "aes cyprium," a term used by the Romans to describe the metal obtained from Cyprus, where copper deposits were worked as long ago as 3000 B.C.

A. OCCURRENCE

Copper is found in the native state and in the combined form as the sulfide, oxide, and carbonate. The principal ores of copper are chalcopyrite, CuFeS_2 , chalcocite, Cu_2S , and bornite, Cu_5FeS_4 .

B. PRODUCTION

The recovery of copper from sulfide ores is effected by a series of concentrating, smelting, and refining operations (6,11). The ore, which has been properly crushed and classified, is introduced as a pulp or slurry to flotation cells in which the copper sulfide is collected as a copper concentrate and separated from the bulk of the waste material or gangue. Since the concentrates contain, besides copper sulfide, iron sulfide as well as a certain amount of gangue, subsequent treatment in the reverberatory smelting furnace is designed to eliminate sulfur as the dioxide and to slag off the iron, silicates, and other impurities. Because of its affinity for sulfur, copper appears as Cu_2S along with FeS in the copper matte from the reverberatory furnace. This matte is blown in a converter to produce blister copper, which is then cast in the form of anodes for electrolytic refining. Electrolytic refining makes possible the elimination of the great

majority of impurities in the blister or anode copper as well as the recovery of silver, gold, selenium, and tellurium, which appear in the slimes which settle out during electrolysis. The copper cathodes are cast into various shapes so that the copper can be fabricated into wire, rod, tube, or sheet or used to produce copper alloys.

II. PROPERTIES

A. PHYSICAL PROPERTIES

Copper is a metal with a characteristic red or salmon pink color which is second only to silver in its electrical and thermal conductivity. The electrical resistivity of the International Annealed Copper Standard is 0.15328 ohm/m.-g. (meter-gram) at 20°C. The conductivity and working properties of copper are affected by the presence of impurities, the principal of which in regular refined copper is oxygen. The physical properties of copper and the effect of impurities have been discussed in detail (11).

Natural copper is a mixture of two isotopes, ^{63}Cu and ^{65}Cu . The existence of other isotopes with mass numbers 60, 61, 62, 64, 66, and 67 is known. The only isotope suitable for radioactive tracer work is ^{64}Cu , which has a half life of 12.8 hours (11).

Copper has a melting point of 1083°C. and a boiling point of 2595°C. (11). The density of the metal varies with its composition and mode of preparation, a value of 8.9592 g./cc. having been reported for pure copper (114).

B. ELECTROCHEMICAL PROPERTIES

Standard electrode potentials of analytical interest are presented in Table I. Polarographic data are given in Table VII, Section VI-C.

TABLE I
Standard Electrode Potential Data for Copper (64)

Reaction	E° , v.
$\text{Cu}(\text{NH}_3)_4^{+2} + 2e = \text{Cu} + 4\text{NH}_3$	-0.05
$\text{Cu}^{+2} + e = \text{Cu}^+$	0.167
$\text{CuCl}_2^- + e = \text{Cu} + 2\text{Cl}^-$	0.19
$\text{Cu}^{+2} + 2e = \text{Cu}$	0.3448
$\text{Cu}^+ + e = \text{Cu}$	0.522
$\text{Cu}^{+2} + 2\text{I}^- + e = \text{CuI}_2^-$	0.690
$\text{Cu}^{+2} + \text{I}^- + e = \text{CuI}$	0.877

C. OPTICAL PROPERTIES

Copper solutions can be excited in an oxyacetylene flame, and the copper luminosity is such that the measurement of the intensity of the sensitive line 3247.5 Å. or 3273.9 Å. permits the accurate estimation of the element (21). Copper imparts a green color to an oxidizing flame and a blue color to a reducing flame.

The arc and spark excitation behavior of copper is favorable not only for the determination of copper itself but also for the estimation of numerous elements found in copper and copper alloys (see Sections VII-D and VII-E).

The sensitive lines of copper are given in Table II.

TABLE II
Sensitive Lines of Copper (50)

Wavelength	Excitation potential	Intensity ^a		Sensitivity ^b
		Arc	Spark	
5218.202	6.2	700		U3
5153.235	6.2	600		U4
5105.541	3.8	500		U5
3273.962	3.8	3000R	1500R	U2
3247.540	3.8	5000R	2000R	U1
2246.995	15.9	30	500	V3
2192.260	16.2	25	500	V2
2135.976	16.2	25	500	V1

^a R indicates self-reversal.

^b U1, U2, etc., represent order of decreasing sensitivity for neutral atoms, and V1, V2, etc., for singly ionized atoms.

D. CHEMICAL PROPERTIES

Copper is found in subgroup I of the periodic system along with silver and gold. The principal oxidation states of the element are +1 and +2, with the bivalent copper compounds being generally more stable. The existence of unstable trivalent copper is denoted by the oxide, Cu_2O_3 , and by the anions CuO_2^- , CuF_6^{-3} , $\text{Cu}(\text{IO}_6)_2^{-7}$, and $\text{Cu}(\text{TeO}_6)_2^{-9}$ (102).

Copper possesses a number of distinctive chemical properties which can be employed to advantage in its analysis:

1. In dilute acid solution copper is precipitated as the sulfide with hydrogen sulfide and thereby separated from the elements of the ammonium sulfide group, the alkaline earths, and the alkali metals. Copper(II) sulfide is but slightly soluble in ammonium sulfide.

2. Copper is sufficiently electronegative that it can be separated from numerous elements by electrodeposition onto a platinum cathode or into mercury (72).

3. Copper(II) oxidizes the iodide ion to free iodine, and the titration of the liberated iodine with thiosulfate permits the quantitative estimation of copper.

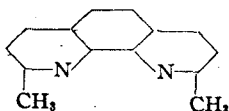
4. In ammoniacal solution copper forms intense blue colored complexes with ammonia molecules, the principal complex being $\text{Cu}(\text{NH}_3)_4^{+2}$.

5. Copper(II) reacts with ferrocyanide to give a reddish brown precipitate, $\text{Cu}_2\text{Fe}(\text{CN})_6$, which reaction serves as a sensitive test for copper.

6. Copper forms complexes with a number of organic reagents including α -benzoinoxime, salicylaldoxime, cupferron, quinaldinic acid, 8-hydroxyquinoline, 2,2'-biquinoline, dithizone, and sodium diethyldithiocarbamate. These complexes permit the gravimetric, volumetric, and/or photometric determination of copper (see Sections VI-A, VI-B, and VI-D).

The stability of copper complexes is reported to exceed that of the corresponding complexes of bivalent zinc, nickel, cobalt, iron, and manganese with the order of stability being almost independent of the nature of the ligand, whether NN, NO, or OO (57b).

Of the various copper specific reagents, the compound 2,2'-biquinoline (cuproine) is one of the most sensitive, having a molecular extinction coefficient of 6430 (55). Still more sensitive but more difficult to synthesize are 2,9-dimethylphenanthroline,



and 2,4,7,9-tetramethylphenanthroline, which have molecular extinction coefficients of 7950 and 8860, respectively.

Nelson and Gantz (90a) have given the order of the relative stabilities of copper(II) complexes with numerous anions, determined from transmittance curves, as follows: oxalate, thiocyanate, citrate, acetate, formate, tartrate, bromide, phosphate and sulfate, fluoride, and chloride and nitrate.

Reliable dissociation constant data are available for a limited number of organocopper complexes. The following data on certain of the more prominent copper chelates are of interest.

Dithizone

