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The Radiochemistry of Copper

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of copper is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of copper which might be included in a revised version of the monograph.

The Radiochemistry of Copper

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF COPPER

Sidgwick, N. V., The Chemical Elements and Their Compounds, Vol. I, Oxford Press, London (1950), pp. 103-196.

Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. III, Longmans, Green and Co., London, (1923), pp. 1-294.

Charlot, G. and Bejier, D. (translated by Murray, R. C.) Quantitative Inorganic Analysis, Methuen and Co., London; John Wiley and Sons, Inc., New York, 1957, pp. 413-423.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., Applied Inorganic Analysis, 2nd ed., John Wiley and Sons, Inc., New York, Ch. 11, (1953).

Rodden, C. J., Analytical Chemistry of the Manhattan Project, McGraw-Hill Book Co., New York, (1950), Ch. 15, pp. 404-110.

Remy, H., Treatise on Inorganic Chemistry (translated by Anderson, J. S.), Elsevier Publishing Co., Amsterdam, (1956), Vol. II., Ch. 8.

II. LIST OF RADIOISOTOPES OF COPPER[a]

Isotope	Half-Life	Type of Decay	Method of Production
Cu^{60}	24 min.	β^+(93%), EC(7%)	$Ni^{60}(p,n)$ $Ni^{60}(d,2n)$ $Ni^{58}(\alpha,pn)$
Cu^{61}	3.3 hrs.	β^+(68%) EC(32%)	$Ni^{61}(p,n)$ $Cu^{63}(\gamma,2n)$ $Ni^{60}(d,n)$ $Ni^{58}(\alpha,p)$ Spallation of As with 190-Mev deuterons
Cu^{62}	9.7 min.	β^+	$Co^{59}(\alpha,n)$ $Ni^{62}(p,n)$ $Cu^{63}(n,2n)$ $Cu^{63}(\gamma,n)$
Cu^{64}	12.8 hrs.	EC(42%), β^-(39%), β^+(19%)	$Cu^{63}(n,\gamma)$ $Ni^{64}(p,n)$ $Cu^{65}(\gamma,n)$ $Zn^{64}(n,p)$
Cu^{66}	5.1 min.	β^-	$Zn^{66}(n,p)$ $Cu^{65}(n,\gamma)$ $Ga^{69}(n,\alpha)$
Cu^{67}	58.5 hrs.	β^-	$Zn^{68}(\gamma,p)$ $Zn^{67}(d,2p)$ Fission of U with protons Fission of As, Bi and Pb with deuterons
Cu^{68}	32 sec.	β^-	$Zn^{68}(n,p)$ $Ga^{71}(n,\alpha)$

[a] For detailed decay data and references to the data in this table, see Table of Isotopes, Strominger, D., Hollander, J. M., and Seaborg, G. T., Rev. of Mod. Phys., 30, No. 2, Pt. II, (1958).

III. REVIEW OF THOSE FEATURES OF COPPER CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. General

Copper is a metal with a characteristic reddish color. Very thin layers of the metal appear greeninsh-blue when viewed by transmitted light.

The most commercially important and abundant mineral is chalcopyrite, $CuFeS_2$. Double sulfides of copper with other metals, as well as cuprous sulfide, are also important minerals. Although the pure metal is used extensively in such articles as tubing and decorative building materials, it is used even more widely in alloys such as brass and bronze alloys and as a constituent in coinage alloys.

Many sources are available which discuss the physical and chemical properties of copper.(1-3) Mantell(2) lists the following physical properties for copper metal:

Density at 20°C, g/cc	8.96
Melting point, °C	1083
Boiling point, °C	2595
Thermal expansion, 1 x 10^{-6}/°C	16.5
Specific heat at 20°C, cal/g °C	0.092
Heat of fusion, cal/g	50.6
Thermal conductivity, cal/sec cm^2 °C cm	0.941
Electrical resistivity, μ ohm-cm at 20°C	1.673
Temperature coefficient of resistivity x 10^{-4} per °C	68.0

There are two naturally occurring stable isotopes of copper, Cu-63 and Cu-65. The abundances of Cu-63 and Cu-65 are 69.1% and 30.9% respectively, resulting in the atomic weight 63.54. Copper-64 (12.8h) is the most important radioisotope from the standpoint of radiochemistry since it can be produced in large quantities with high specific activities in nuclear reactors by the reaction $Cu^{63}(n,\gamma)Cu^{64}$. Copper-64 is produced in this manner and offered for sale by the Oak Ridge National Laboratory. Copper-66 can be similarly produced from copper-65, but the short half-life of copper-66 (5.1 min.) has caused it to have limited usefulness. Copper-67 has a half-life of 58.5 hours which is the longest lived radioisotope of copper known. Copper-67 can be produced by a number of reactions, such as the fission of bismuth, lead or uranium with high energy deuterons or protons.

The electronic ground state of the valence electrons of copper is represented by $3\ d^{10}\ 4\ s^{1}$. Copper, as well as silver and gold, has been compared with the alkali metals; because both groups have a single valence electron in an s orbital, causing these to have some similar properties. However, the fact that copper, silver, and gold have completed d orbitals underlying their s orbital electrons causes them to be significantly different chemically from the alkali metals. Copper exhibits a dipositive, as well as a unipositive, oxidation state. Copper in the unipositive state is always highly insoluble or strongly complexed. Many of the copper(II) compounds are very soluble, especially those in which the anion forms a strong acid.

Latimer(8) gives the following electromotive force values relating the various species of copper in acid and basic solutions:

a) Acid Solution

$$\underbrace{\mathrm{Cu} \xrightarrow{-0.521} \mathrm{Cu}^{+} \xrightarrow{-0.153} \mathrm{Cu}^{++}}_{-0.337} \xrightarrow{-1.8} \mathrm{CuO}^{+}$$

b) Basic Solution

$$\mathrm{Cu} \xrightarrow{0.358} \mathrm{Cu_2O} \xrightarrow{0.08} \mathrm{Cu(OH)_2}$$

At equilibrium in an aqueous solution in the presence of copper metal, the expression $(\mathrm{Cu}^{++})/(\mathrm{Cu}^{+})^{2} = K$ is applicable. At 20°C the value of K is approximately 10^{6}. Thus, appreciable quantities of copper(I) ions cannot exist in solution which limits unipositive copper to insoluble compounds and complexes. Copper has noble characteristics similar to silver, gold and the platinum metals, although to a lesser degree. This nobility is reflected in a negative oxidation potential in acid solutions resulting in the inability of non-oxidizing acids to dissolve copper. However, oxidizing acids will dissolve copper, with the most common examples being nitric and perchloric acids. Hot concentrated sulfuric acid will function as an oxidizing acid and dissolve copper to form copper(II) sulfate. Warm dilute sulfuric and dilute hydrochloric acids will in the presence of oxygen dissolve copper.

2. Soluble compounds of Copper

Many copper(II) compounds are soluble in aqueous solutions. Among the copper(II) compounds which are soluble and stable in water are the perchlorate, chlorate, nitrate, chloride, bromide, acetate, sulfate, bromate, lactate, and salicylate. Copper(II) fluoride is slightly soluble in cold water but decomposes in hot water to form the basic fluoride Cu(OH)F. The formate and laurate are also slightly soluble in cold water but are decomposed by hot water. Copper(II) iodide decomposes to copper(I) iodide in water.

3. Insoluble Compounds of Copper

All copper(I) compounds are insoluble in water. Some copper(I) compounds such as the acetate and formate are readily hydrolyzed in water to cuprous oxide. Some copper(I) compounds which are stable but insoluble in water are the halides, cyanide, thiocyanate, and sulfide. There is some doubt about the stability and existence of copper(I) fluoride(3,4) although Remy(1) stated that it is insoluble in water. The copper(I) ion is strongly complexed by a number of coordinating groups such as halide, thiocyanate, and cyanide ions as well as ammonia so that copper(I) compounds will dissolve easily in solutions containing an excess of these ions or ammonia. Table I gives a list of some of the insoluble compounds of univalent copper and a list of other media in which they are soluble.

Some of the copper(II) compounds which are insoluble in water include the oxide, hydroxide, sulfide, carbonate, iodiate, arsenide, citrate, cyanide, hexacyanoferrate(III), hexacyanoferrate(II), oleate, stearate, and orthophosphate. Such compounds as the oxide, hydroxide, carbonate, arsenide and cyanide are soluble in relatively dilute acid solutions. The sulfide. oleate, and stearate can be dissolved in hot concentrated nitric acid. Again, ammonia, due to its ability to complex dipositive copper ions will dissolve all insoluble copper compounds. Table I also lists some of the insoluble copper(II) compounds along with a list of solvents for them. Dipositive copper ions react with a number of organic complexing and chelating agents to form insoluble compounds, but these will be treated later in the sections dealing with complexes and separations and determinations. If one wishes quantitative data for the solubility product constants of insoluble copper compounds reference can be made to the very excellent compilation of stability constants by Bjerrum and others.(5)

4. Complexes of Copper

Probably the most important aspect of complex formation from the analytical or radioanalytical chemist's standpoint is the role played by neutral complexes and complex ions in metal ion separations. Complex formation between metal ions and appropriate complexing agents allows separation reactions and/or processes to be carried out selectively. An example in the case of copper is the separation of copper(II) from Fe(III), Al(III), Bi(III) by precipitating $Fe(OH)_3$, $Al(OH)_3$ and $Bi(OH)_3$ leaving the soluble $Cu(NH_3)_4^{+2}$ in solution when excess ammonia is added.(7) Complexing agents are classified as monodentate, bidentate, tridentate, etc., if each complexing ion or molecule contains one, two, three, etc., electron donating groups respectively. Polydentate refers to complexing agents which contain more than one electron donating group; such complexes are also termed chelates. In many instances it is not known whether a particular complex exists as a monodentate complex or chelate as in the case of monobasic metal dithizonates.(6)

Table II gives a list of stability constants for some of the more familar complexes of copper and simple inorganic complexing agents. The values for the stability constants given in Table II were taken from the compilation by Bjerrum.(5) No attempt has been made to compile a comprehensive list of copper complexes. Should one desire additional information or data for copper complexes there are a number of sources available to

Table I

Solubility Characteristics of Copper Compounds*

Reagent	Compound	Solubility in Water	Solvents in Which Compounds are Soluble
		<u>Copper(I) Compounds</u>	
Cl	CuCl	Very Slightly Soluble (~0.1 g/l)	aq. NH_3, halide soln's.
Br^-	CuBr	Insoluble	aq. NH_3, halide soln's.
I^-	CuI	Insoluble	aq. NH_3, halide soln's.
CNS^-	CuCNS	Insoluble	aq. NH_3, halide soln's.
$S^=$	Cu_2S	Insoluble	Conc. HNO_3, aq. NH_3, CN^-, CNS^-
$CO_3^=$	Cu_2CO_3	Insoluble	aq. NH_3
	Cu_2O	Insoluble	aq. NH_3, conc. acids
CN^-	CuCN	Insoluble	Conc. Acids, aq. NH_3
		<u>Copper(II) Compounds</u>	
	CuO	Insoluble	aq. soln's. of NH_3, CN^-, acids
$S^=$	CuS	Insoluble	HNO_3, KCN, Conc. HCl, H_2SO_4
OH^-	$Cu(OH)_2$	Insoluble	Acids
$CO_3^=$	$CuCO_3 \cdot Cu(OH)_2$	Insoluble	Acids
IO_3^-	$Cu(IO_3)_2$	Insoluble (~0.1 g/l)	Dil. HNO_3, H_2SO_4
CN^-	$Cu(CN)_2$	Insoluble	Soln's. of KCN, NH_3, pyridine
$Fe(CN)_6^{-3}$	$Cu_3[Fe(CN)_6]_2$	Insoluble	aq. NH_3
$Fe(CN)_6^{-4}$	$Cu_2\ Fe(CN)_6$	Insoluble	aq. NH_3
PO_4^{-3}	$Cu_3(PO_4)_2$	Insoluble	acids, NH_4OH

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*Information in this table was taken from the <u>Handbook of Chemistry and Physics</u>, Chemical Rubber Publishing Co., Cleveland, Ohio, 39th ed. Edited by Hodgman, C. D., Weast, R. C. and Selby, S. M. pp. 520-526 (1957-1958).

Table II

Complex Ions of Copper[a]

Complexing Agent	Reaction	Ionic Strength	β[b]
	Copper(I) Ions		
Cl^-	$Cu^+ + 2Cl^- \rightleftharpoons CuCl_2^-$	0	7×10^4
	$Cu + 3Cl^- \rightleftharpoons CuCl_3$	0	6×10^5
Br^-	$Cu^+ + 2Br^- \rightleftharpoons CuBr_2^-$	0	8×10^5
I^-	$Cu^+ + 2I^- \rightleftharpoons CuI_2^-$	0	7×10^8
SCN^-	$Cu^+ + 2SCN^- \rightleftharpoons Cu(SCN)_2^-$	Variable	1×10^{12}
	$Cu^+ + 3SCN^- \rightleftharpoons Cu(SCN)_3^{-2}$	Variable	8×10^9
	$Cu^+ + 4SCN^- \rightleftharpoons Cu(SCN)_4^{-3}$	Variable	1×10^{10}
	$Cu^+ + 5SCN^- \rightleftharpoons Cu(SCN)_5^{-4}$	Variable	4×10^9
	$Cu^+ + 6SCN^- \rightleftharpoons Cu(SCN)_6^{-5}$	Variable	2×10^9
CN^-	$Cu^+ + 2CN^- \rightleftharpoons Cu(CN)_2^-$	0	1×10^{24}
	$Cu^+ + 3CN^- \rightleftharpoons Cu(CN)_3^{-2}$	0	3×10^{28}
	$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{-3}$	0	1×10^{28}
NH_3	$Cu^+ + NH_3 \rightleftharpoons CuNH_3^+$	2 $\underline{M}$ NH_4NO_3	8×10^5
	$Cu^+ + 2NH_3 \rightleftharpoons Cu(NH_3)_2^+$	2 $\underline{M}$ NH_4NO_3	7×10^{10}
	Copper(II) Ions		
NH_3	$Cu^{+2} + NH_3 \rightleftharpoons CuNH_3^{+2}$	0	2×10^4
	$Cu^{+2} + 2NH_3 \rightleftharpoons Cu(NH_3)_2^{+2}$	0	7×10^7
	$Cu^{+2} + 3NH_3 \rightleftharpoons Cu(NH_3)_3^{+2}$	0	8×10^{10}
	$Cu^{+2} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{+2}$	0	1×10^{13}
SCN^-	$Cu^{+2} + 3SCN^- \rightleftharpoons Cu(SCN)_3^{-1}$	Variable	1×10^5
	$Cu^{+2} + 4SCN^- \rightleftharpoons Cu(SCN)_4^{-2}$	Variable	3×10^6

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[a] The values for the stability constants were taken from the compilation by Bjerrum and others (see reference 5). Bjerrum's compilation lists the constants associated with the various equilibria of metal complexes which were available up to the middle of 1957. In most cases more than one value was available for a particular constant. The values listed in the above table were chosen by the following criteria:

Table II (Cont.)

(1) The values which were most recently determined and which had been corrected to an ionic strength of zero.

(2) If no corrections were made to zero ionic strength, then the most recently determined values were listed and the media indicated. In some cases, constants have not been determined as in the case for copper(I) halide compounds viz.,

$$K_1 = \beta_1 = \frac{(CuX)}{(Cu^+)(X^-)},$$

although the solubility product constants are known. If the concentration of copper(I) halide molecules were known, one could calculate K_1.

[b] The cumulative gross constants have been listed, and the notation of Bjerrum and others (see reference 5) has been followed.

Table III

Stability Constants for Copper Chelates[a]

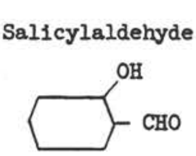
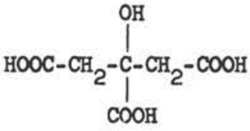
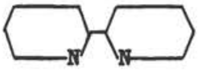
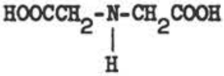
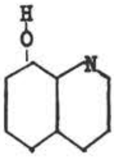
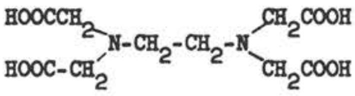
Chelating Agent	log K	Ionic Strength
Oxalic Acid HOOC-COOH	1.14 (K_1)	0.2 M
	3.85 (K_2)	0.2 M
	8.29 (K_1K_2)	0.01 M Na_2CO_3
Malonic Acid $HOOC-CH_2-COOH$	2.69 (K_1)	0.2
	5.24 (K_2)	0.2
	5.29 (K_1)	0.00 1M
Salicylaldehyde	9.5 (K_1)	~ 0.1
	7.4 (K_1)	~ 0.1
	13.3 (K_1K_2)	~ 0.1
Citric Acid	3.08 (K_1)	0.1
 $HOOC-CH_2-C(OH)(COOH)-CH_2-COOH$	4.39 (K_2)	0.1
	5.5 (K_3)	0.1
	14.2 (K)	0.1
Ethylenediamine	6.98 (K_1)	1.0

Table III (Cont.)

Chelating Agent	log K	Ionic Strength
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$	9.98 (K_2)	1.0
	10.7 (K_1)	1.0
	20 (K_1K_2)	1.0
Bipiridyl	4.4 (K_1)	0.3
	17.8 ($K_1K_2K_3$)	0.1
Aminodiacetic Acid	2.54 (K_2)	0.1
 $HOOCCH_2\text{-}\underset{\displaystyle H}{\underset{\vert}{N}}\text{-}CH_2COOH$	9.13 (K_3)	0.1
	10.3	0.1
	6.53 (K_1)	
8 - Hydroxyquinoline	5.02 (K_1)	--
	9.81 (K_2)	--
	15.0 (K_1)	--
	29.0 (K_1K_2)	
Ethylenediamine tetraacetic acid	2.0 (K_1)	0.1
	2.7 (K_2)	0.1
	6.2 (K_3)	0.1
	10.3 (K_4)	0.1
	18.3	0.1

[a] Data for this table were taken from Martell, A. E., and Calvin, M., Chemistry of the Metal Chelate Compounds, Prentice-Hall, Inc., 1952, pp. 5121-558.

lead one to the literature.(5,8) Table III lists some of the various types of chelates of copper. The examples listed which were taken from Martell and Calvin(9) are not a complete list, but are representative for the various types of chelating agents, e.g. amines, carboxylic acids, etc.

Both unipositive and dipositive copper ions show highly pronounced tendencies to react with complexing agents. Both ions form more stable complexes with complexing agents having C or N as the electron donating atom(1) than those having O or F as the electron donating atom. Thus, ammonia and cyanide solutions will dissolve many copper compounds which are insoluble in water. The ammonia and thiocyanate complexes of copper(I) are slightly more stable than those of copper(II).

5. Separation and Determination of Copper

Copper can be separated from other metals by the methods of precipitation,(7,10,11) solvent extraction,(10,12,13,14) ion exchange,(15,16) electrolysis,(7,70) electrical transference,(17) and vaporization.(18,19,20) The methods of precipitation, solvent extraction, ion exchange, and electrical transference are for the purposes of the analytical chemist more suited to the separation of moderate or trace amounts of copper. Larger amounts of copper can be separated in many cases by the easy and rapid method of electrolysis. The radiochemistry of copper has not been studied as extensively as many of the other elements. As Sandell(10) points out, the methods available for the determination of copper are in general quite satisfactory and leave little to be desired. The existence of suitable methods for determining copper, as well as the absence of long-lived isotopes of copper, probably account for the scarcity of radiochemical studies of copper. Sandell(10) also makes the observation that the separation of copper before its determination is not now so important as formerly, due to the availability of many color reagents which are more or less specific. However, some elements interfere with many of the color determinations of copper and other activities interfere with the radiochemical determination of copper so that in many instances separations of copper are required.

5a. Separation by Precipitation

Reports dealing with the separation of copper from other elements by the method of precipitation are very numerous. A number of reviews(7,10,11,24) are available to lead one to this voluminous literature. The most commonly used precipitants for copper are the sulfide and thiocyanate. Copper falls in the so-called sulfide group of elements. It can be separated from elements other than this group by precipitating with hydrogen sulfide in an acid media (0.1 - 3 N in acid). The elements Cu, Hg, Pb, Bi, Cd, As, Sb, and Sn are normally thought of as comprising the sulfide group of elements, although Mo, Se, Te, Ge, Au, Pt, Pd, Rh, Os, Ru, and Ir, have been classified as being in this group. In many respects, such as the distinct acid characters of Se and Te, these latter elements have a chemistry quite different from the more common sulfide group elements. Separation of copper from As, Sb, Sn, and Hg is effected by dissolving the sulfides of these elements in sodium polysulfide. Copper can then be removed from the other precipitated sulfides by dissolving it in a cyanide solution. Copper dissolves as the complex cyanide leaving the sulfides of Bi, Cd, and Pb intact. Copper is removed from tin and germanium by precipitating CuS from a solution containing oxalic acid. The source of the sulfide ion is usually an external one of hydrogen sulfide gas, although hydrogen sulfide can be generated internally by the hydrolysis of thioacetamide. Much work has been done with sulfide precipitations using thioacetamide as the source of sulfide.(23,30)

Thiocyanate precipitation has been used to separate copper from Co, Ni, Mn, Zn, As, Sn, Bi, and Sb.(24,26) Precipitation of cuprous thiocyanate has been employed quite extensively in radiochemical procedures in which copper has been separated from a limited number of other activities (see Procedures 1, 2, 3, 4, 5, 8, 9, Section VII). Cuprous thiocyanate ($K_{sp} = 2 \times 10^{-13}$) precipitates from a slightly acid solution of cupric ion to which has been added sulfur dioxide or sulfite salt and sodium thiocyanate. Oxidants interfere with this reaction if they are not reduced by the sulfite. The nitrate ion can be eliminated by first adding sulfuric acid and boiling until SO_3 fumes come off before commencing the precipitation. Only a very slight excess of thiocyanate should be used in order to prevent the formation of soluble thiocyanate complexes of copper. The precipitates of Sb(III), Bi(III), and Sn(IV) thiocyanates can be prevented from forming by adding 2-3 g of tartaric acid. When copper is reduced by hydroxylamine hydrochloride in an ammonical, acetic acid, or tartatic acid solution and acetylene gas is bubbled through the solution, copper acetylide is precipitated.(29) Only silver, mercury, gold, palladium, and osmium are precipitated and thus interfere under these conditions. Iron, aluminum, and bismuth must be held in solution by ammonium tartarate to prevent their precipitation.

Some other precipitants which have been used for separating copper from other elements are salicylaldoxime(27,29) α-nitroso-β-naphthol,(25) and α-benzoinoxime.(27) It has been reported that gold and palladium are the only interfering elements when copper is precipitated with salicyaldoxime.(28) Salicyaldoxime has been used in the radiochemical determination of copper in biological materials(27) (see Procedure 9, Section VII). Many organic reagents react with copper to form precipitates or species which will extract into organic solvents.(10,31) However, in most cases, the products formed with copper and organic reagents have been used as specific color tests for copper and have not been investigated from the standpoint of separating copper from other metals.

5b. Separation by Solvent Extraction

The extraction of copper dithizonate from an aqueous solution into an organic solvent has been used in at least one radiochemical separation (see Procedure 6, Section VII). For non-radiochemical separations copper dithizonate extractions have been very popular and in many cases are to be preferred to sulfide or thiocyanate precipitations. Primary copper dithizonate has an extraction constant equal to 1.1×10^{10} when extractions are made from 1.0 M HCl into carbon tetrachloride; for chloroform extractions an extraction constant of 3×10^{6} has been given.(10) Thus, copper may be extracted practically completely from 1.0 M HCl into carbon tetrachloride which contains 0.01 per cent dithizone. Dithizone reacts with at least 19 elements, viz. Mn(II), Fe(II), Co(II), Pd(II), Pt(II), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(I) and (II), In(III), Tl(I) and (II), Sn(II), Pb(II), Bi(III), Te(IV), and Po(II). Of these elements only palladium, gold, silver, mercury, and bismuth interfere in the extraction of copper from 0.1-1.0 M acid solutions. Mercury, silver, and bismuth can be prevented from extracting by adding halide ions to the aqueous phase.

Some other organic reagents which have been used to separate copper from other metals by solvent extraction include acetylacetone,(31-36) diquinolyl,(32) thenoyltrifluoroacetone,(37) 8-hydroxyquinoline (oxine),(38-40) diethylammonium diethyldithiocarbamate,(14,41) and cupferron.(42) Sandell(10) has directed attention to a number of organic reagents which may be used to extract copper into non-aqueous solvents. Acetylacetone has been used to separate copper from zinc by extracting the copper acetylacetonate into acetylacetone from an aqueous solution at a pH of 2.(33-35) The same authors suggested a similar procedure for the separation of copper from nickel. It has also been concluded from data obtained for individual extractions of copper and lead with acetylacetone that copper could be separated from lead.(34) Maddock and Meinke(42) have employed cupferron to extract copper cupferronate into carbon tetrachloride in a radiochemical procedure for copper (see Procedure 10, Section VII). A recent article(43) dealing with the solvent extraction and determination of copper with organic reagents recommend the reagents bathocuproine (2,9-dimethyl-, 4,7-diphenyl-, 1,10-phenanthroline), diethylammonium salt of diethyldithiocarbomatic acid, and zinc dibenzyldithiocarbomate. However, most of the reagents which have been used for copper have had colorimetric determinations as their objectives and not activity separations for radiochemical procedures.

5c. Separation by Ion Exchange and Chromatography

In their reference work on chromatography Lederer and Lederer(72) give an excellent review of the chromatographic separations of inorganic substances which have been studied with paper and ion exchange columns. McOmie and Pollard(73) in 1953, presented a very complete summary of the work which had been done on the separation of cations by paper chromatography. Some recent reviews of the status of chromatography are the ones by Strain(74) which include 462 references and Kraus and Nelson(75) which list 158 references. The review of ion exchange by Kunin(76) contains 111 references which deal with the separations of inorganic materials by ion exchange. These reviews give adequate reference material to lead one to the fields of chromatography and ion exchange.

An ion exchange resin consists of a three-dimensional hydrocarbon network to which is attached a large number of ionizable groups. The resin is called a cation exchange resin if the ionizable groups are strongly or weakly acidic (reacts with cations) and an anion exchange resin if the groups are weakly or strongly basic (reacts with anions). The most common cation exchange resins contain the sulfate group as the acidic group and are usually produced by sulfonating phenolic resins and resins containing divinylbenzene as part of the polymer structure. Amberlite IR-100 is an example of the sulfonated phenolic type resin. The Dowex resins are examples of the sulfonated resin containing divinylbenzene. Dowex 50 and 50W are sulfonated cation exchange rations. Lederer and Lederer(72) classify and summarize many of the properties for a number of cation and anion exchange resins which are commercially available. The cation exchange resin Zeo-Karb which is sulfonated coal has been tried for the separation of Ag-Cu,(77) Cu-Mn,(78) and Ni, Cu, Zn(79) mixtures with poor separation. Amberlite IR-100 H (acid form) has been used to separate Cu-Ag and Cu-Cd mixtures as classroom experiments.(80,81) Apparently very little work has been done toward actually separating copper from multicomponent cation mixtures by cation exchange. Koch's(82) work with Dowex 50 in which he investigated the separation of Cd, Zn, Cu, Co, Ni, Ca, Sr, and Ba represents one of the best examples of cation exchange separations. Koch(82) eluted the cations from the resin with 3.1 M HCl. The elution curves which Koch obtained for these cations is shown in Figure 1. It can be seen from these curves that good separation of copper from all of the other cations of this group is obtainable. Koch(82) also investigated the separation of Hg, Cd, Zn and Cu with Dowex 50 using 0.4 M HCl as eluent. These elution curves are shown in Figure 2. It can be seen from Figure 2 that copper can be easily and rapidly separated from Hg and Cd by this method. Bonner and Smith(83) have reported a selectivity scale for the monovalent and divalent cations on Dowex 50. This selectivity scale is based upon the arbitrary index that the affinity of Li for Dowex 50 is 1. The selectivity values appear in Table IV. These selectivity coefficients are derived with the aid of the Gibbs-Duhem equation applied to the equilibria involved as developed by Argersinger and others(84) and Bonner, Argersinger and Davidson.(85) Strelow(86) has studied the exchange of 43 cations with sulfonated polystyrene A.G 50W-X8 which is processed from Dowex 50 by the Bio-Rad Laboratories of Berkeley, California. Strelow(86) objects to the selectivity scale used by Bonner and Smith,(83) because it does not take into account the influence of the aqueous phase. Strelow(86) says that more specific information about the elution of a cation is given by the equilibrium distribution coefficient, Kd, where

$$Kd = \frac{\text{amount of ion on resin x Vol. of water phase, ml}}{\text{amount of ion in water phase x wt of dry resin}} \qquad (1)$$

This coefficient changes with composition and concentrations in the water phase, the nature of the resin, and the cation to resin ratio in the system.

Strelow's(86) values for Kd for 43 cations are shown in Table V. Strelow(86) found that experimental elution maxima compared favorably for all cations except rare earths to elution maxima which were calculated by

$$\bar{v} = Kd \times (\text{mass of dry resin}) \qquad (2)$$

where $\bar{v}$ stands for the volume of the eluting agent, in ml., which has to be passed through the column to elute the maximum of the elution peak.

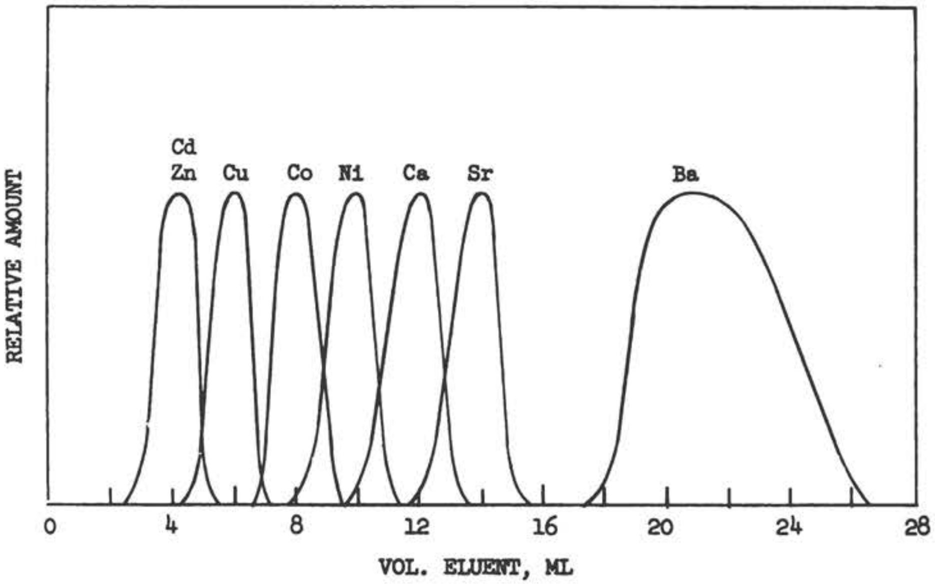


Figure 1. Elution curves for some of the divalent metal ions; 3.1 M HCl used as eluent; ion exchange resin, Dowex 50, 200-400 mesh. (Taken from UCRL-2531.(82))

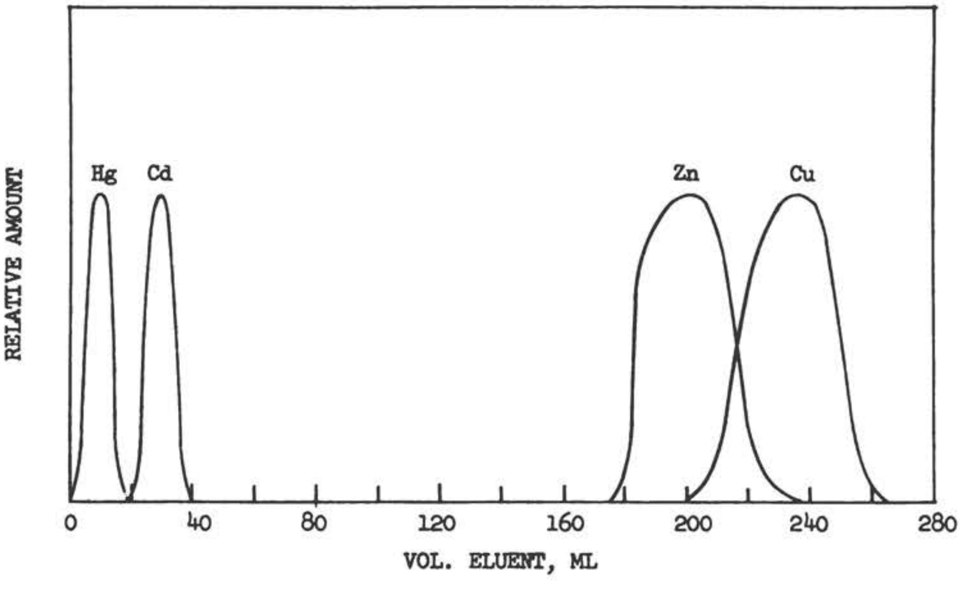


Figure 2. Elution curves for some of the divalent metal ions; 3.1 M HCl used as eluent; ion exchange resin, Dowex 50, 200-400 mesh. (Taken from UCRL-2531.(82))

Table IV

Selectivity Scales for Monovalent and Divalent Ions on Dowex 50[a]

	4% DVB[b]	8% DVB[b]	16% DVB[b]
Li	1.00	1.00	1.00
H	1.32	1.27	1.47
Na	1.58	1.98	2.37
NH_4	1.90	2.55	3.34
K	2.27	2.90	4.50
Rb	2.46	3.16	4.62
Cs	2.67	3.25	4.66
Ag	4.73	8.51	22.9
Tl	6.71	12.4	28.5
UO_2	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Zn	3.13	3.47	3.78
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Cd	3.37	3.88	4.95
Ni	3.45	3.93	4.06
Ca	4.15	5.16	7.27
Sr	4.70	6.51	10.1
Pb	6.56	9.91	18.0
Ba	7.47	11.5	20.8

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[a] Values of selectivity coefficients taken from Bonner, O. D. and Smith, L. L., J. Phys. Chem., 61, 326 (1957).

[b] DVB = divinylbenzene.

Table V

Equilibrium Distribution Coefficients, K_d, for 43 Cations in Hydrochloric Acid Using the Cation Exchange Sulfonated Polystyrene Resin[a]

HCl Ion	0.1 N	0.2 N	0.5 N	1.0 N	2.0 N	3.0 N	4.0 N
ZrO^{+2}	$> 10^5$	$> 10^5$	$\sim 10^5$	7250	489	61	14.5
Th^{+4}	$> 10^5$	$> 10^5$	$\sim 10^5$	2049	239	114	67
La^{+3}	$> 10^5$	10^5	2480	265.1	48	18.8	10.4
Ce^{+3}	$> 10^5$	10^5	2460	264.8	48	18.8	10.5
Y^{+3}	$> 10^5$	$> 10^4$	1460	144.6	29.7	13.6	8.6
Ba^{+2}	$> 10^4$	2930	590	126.9	36	18.5	11.9
Hg^{+} [b]	$> 10^4$	7600	640	94.2	33	19.2	13.6
Al^{+3}	8200	1900	318	60.8	12.5	4.7	2.8
Sr^{+2}	4700	1070	217	60.2	17.8	10.0	7.5
Ga^{+3}	$> 10^4$	3036	260	42.58	7.75	3.2	0.36
Ca^{+2}	3200	790	151	42.29	12.2	7.3	5.0
Pb^{+2} [b]	$> 10^4$	1420	183	35.66	9.8	6.8	4.5
Fe^{+3}	9000	3400	225	35.45	5.2	3.6	2.0
Cr^{+3}	1130	262	73	26.69[c]	7.9	4.8	2.7
Tl^{+} [b]	173	91	41	22.32	9.9	5.8	3.3
Ni^{+2}	1600	450	70	21.85	7.2	4.7	3.1
Co^{+2}	1650	460	72	21.29	6.7	4.2	3.0
Mg^{+2}	1720	530	88	20.99	6.2	3.5	3.5
Mn^{+2}	2230	610	84	20.17	6.0	3.9	2.5
Fe^{+2}	1820	370	66	19.77	4.1	2.7	1.8
Cs^{+1}	182	99	44	19.41	10.4	--	--
UO_2^{+2}	5460	860	102	19.20	7.3	4.9	3.3
Ag^{+} [b]	156	83	35	18.08	7.9	5.4	4.0

Table V (Cont.)

HCl / Ion	0.1 *N*	0.2 *N*	0.5 *N*	1.0 *N*	2.0 *N*	3.0 *N*	4.0 *N*
Cu^{+2}	1510	420	65	17.50	4.3	2.8	1.8
Hg^{+2} [b]	4700	1090	121	16.85	5.9	3.9	2.8
Zn^{+2}	1850	510	64	16.03	3.7	2.4	1.6
Rb^{+}	120	72	33	15.43	8.1	--	--
K^{+}	106	64	29	13.87	7.4	--	--
Be^{+2}	255	117	42	13.33	5.2	3.3	2.4
Ti^{+4}	$> 10^4$	297	39	11.86	3.7	2.4	1.7
V^{+4}		230	44	7.20	--	--	--
Na^{+}	52	28.3	12	5.59	3.6	--	--
Li^{+}	33	18.9	8.1	3.83	2.5	--	--
Sn^{+4}	~ 10	45	6.2	1.60	1.2	--	--
Cd^{+2}	510	84	6.5	1.54	1.0	0.6	--
V^{+5}	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Mo^{+5}	10.9	4.5	0.3	0.81	0.2	0.4	0.3
Se^{+4}	1.1	0.6	0.8	0.63	1.0	--	0.7
Bi^{+3}	Ppt.	Ppt.	< 1.0	1.0	1.0	1.0	1.0
As^{+3}	1.4	1.6	2.2	3.81	2.2	--	--
Sb^{+3}	Ppt.	Ppt.	Ppt.	Ppt.	2.8	--	--
Pt^{+4}	--	--	--	1.4	--	--	--
Au^{+3}	0.5	0.1	0.4	0.84	1.0	0.7	0.2
Hg^{+2}	1.6	0.9	0.5	0.28	0.3	0.2	0.2

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[a] Taken from Strelow, F. W. E., Anal. Chem. 32, 1185 (1960) (reference 86).

[b] Done in nitric acid.

[c] More than one cationic species present.

Equation 2 is valid only when the total amount of cation is less than about 3% of the total column capacity.(87) Strelow(86) discusses the effect of various factors on the value of Kd and how values of Kd effect elution curves but does not discuss any separations.

Riches(102) suggested the separation of the cations Cd^{++}, Cu^{++}, Mn^{++}, Ni^{++}, and Zn^{++} from plant material containing 0.1 N $(NH_4)_3PO_4$ using Amberlite 100. The cations are then eluted from the resin with 1 N HCl.

Anion exchange separations of copper from other metal ions may possibly be more useful than cationic exchange separations due to the fact that copper ions readily form anionic complexes. Anionic exchange is also favored because a high ionic strength can be maintained to keep the ion in the anionic form and because usually small amounts of reagent in the eluting media is required. The anion exchange resins most often used and preferred are the quarternary ammonium salts of polystyrene divinylbenzene. Dowex-1 and -2 and Amberlite IRA-400, -401, -410, and -411 are examples of such resins. The most important recent contributions to the separation of the transition elements is a series of papers by Kraus and others(16,87,88,89,90) in which Dowex-1 was used. Kraus and Nelson(91) reported their extensive work in which the exchange behavior of almost all the elements on Dowex-2 was investigated. The elution curves of Kraus and Moore(16) for the separation of the transition elements Ni^{++}, Mn^{++}, Co^{++}, Cu^{++}, Fe^{+++}, and Zn^{++} by eluting from Dowex-1 with various concentrations of HCl are shown in Figure 3. It is seen that good separation of all these cations from each other was obtained. Kraus and Moore(16) also give the elution constants of all these elements as a function of the molarity of HCl. A complete separation of Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++}, and Zn^{++} was also discussed by Atteberry and others.(92) Anion exchange studies with Dowex-1 were also reported by Herber and Irving(93) using bromide complexes instead of chloride complexes. Separations of Co^{++}, Cu^{++}, Zn^{++}, Ga^{+++}, and Ni^{++} were obtained with carrier-free and macro amounts behaving

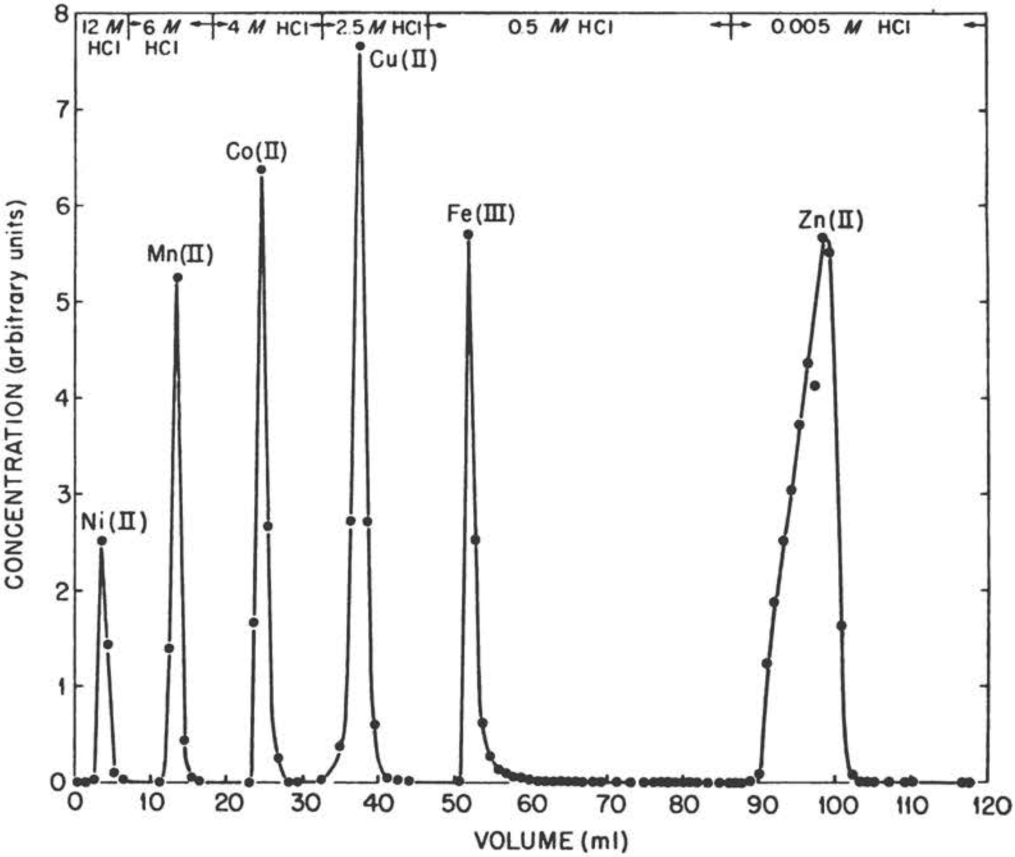


Figure 3. Separation of Transition Elements Mn to Zn. (Dowex-1 Column; 26 cm x 0.29 cm., flowrate = 0.5 cm/min.). Taken from Kraus, K. A. and Moore, G. E., J. Am. Chem. Soc., 75, 1460 (1953).

identically. Pratt and Bradford(95) used Dowex-1 to separate Cu^{++} and Zn^{++} from soil samples before determining these cations with zincon reagent. The qualitative anion exchange behavior of a large number of elements on Dowex-2 was reported by Hicks and others.(113)

An alumina column has been used(94) to separate the following combinations of ions: Cu^{++}, Cd^{++}; Cd^{++}, Pd^{++}; Zn^{++},(8) Cd^{++}, Fe^{+++}; and Sb^{+++}, Zn^{++}. Many separations of metal ion combinations have been studied by paper chromatography. Instead of outlining this very voluminous literature, mention will be made of the summaries of this subject which are presented by Lederer and Lederer(72) and McOmie and Pollard.(73)

5d. Separation by Electrolysis, Electrical Transference and Volatilization

Electrolytic separation of copper from other metals can be applied to systems in which the copper is present in larger than trace amounts. Lingane(70) has reviewed this field adequately, and a few of the results which he lists for copper analysis will be included here. Lingane(70,71) devised a method applicable to the determination of copper in copper alloys containing antimony, arsenic, lead, tin, nickel, zinc, and practically all other common metals. The alloy was dissolved in a mixture of hydrochloric acid and nitric acid and a solution containing sodium tartrate and urea was added. The solution was diluted and hydrazine dihydrochloride was added to act as an anodic depolarizer. The electrolysis was carried out with platinum electrodes with the cathode having a potential of -0.36 ± 0.02 v *versus* a saturated calomel electrode. Such analyses were carried out on U. S. National Bureau of Standards copper-base and tin-base alloys giving results which compared favorably in precision and accuracy with the results of the more laborious methods on which the Bureau's analytical data were based. The tin-based alloy contained, according to the Bureau's analysis, the following metals:

Metal	%
Cu	3.19
Sn	87.45
Sb	7.39
Pb	1.81
Bi	0.027
Ag	0.030
As	0.051
Fe	0.029

Copper was separated from all of these metals except silver and bismuth, and analyses showed 3.18% copper to be present. Lingane(70) also describes how copper can be separated from bismuth by electrolysis.

Garrison and others(17) have modified the electrical transference methods of Kendall and West(101) to obtain rapid separations of carrier-free radioisotopes from other activities and from milligram amounts of non-isotopic carriers. Their apparatus consisted of a stack of filter papers moistened with electrolyte and placed between two platinum electrodes. By this technique carrier-free radio-arsenic was separated from milligram amounts of copper hydroxide carrier. The arsenic remained stationary on the paper while the cupric ions migrated to the cathode.

In the analysis of brass, zinc and lead can be separated from the copper and tin by volitalizing the zinc and lead at 1200°C.(18) A silica test tube can be used for the distillation apparatus. Bismuth can also be separated from copper in alloys with copper by distilling the bismuth.(19) It was found by Erbacher and others(20) that trace amounts of copper could be distilled from the mixture of chlorides of zinc, magnesium and copper under conditions at which copper chloride is not normally thought to be volatile.

6. Determination by Neutron Activation Analysis

Due to its advantages of sensitivity, lack of contamination problems and selectivity and its increasingly wide-spread use, some comments about neutron activation analysis as it has been applied to the determination of copper are in order. The principles and techniques of this method may be obtained from a number of sources.(44-50) The usual procedure followed is to activate the "unknown" sample along with a comparator sample in an intense flux of neutrons such as exists in a nuclear reactor and compare the activities produced of the element to be determined. For many determinations, it is necessary to chemically separate from the sample the radioactivity desired from any interfering activities. With the aid of a gamma scintillation spectrometer, it is often possible to resolve the gamma radiation energies of those elements present which emit gamma rays and thereby avoid, to a greater or lesser extent, the problems of chemical separation.

The amount of radioactivity, A, produced in a sample in a time, t, after the beginning of the activation is given by the equation

$$A = N f \sigma_{ac} S \tag{3}$$

when A is the radioactivity in disintegrations per second; N is the number of nuclei in the sample; f is the neutron flux, as number of neutrons per square centimeter per second; σ as the atomic cross section (in barns) for the neutron reaction leading to the formation of the radionuclide; and S the "saturation factor," or $1-e^{-\lambda t}$, or the ratio of the amount of radioactivity produced in time, t, to the amount produced in an infinite time. The decay constant, λ, is characteristic of the radioelement of interest and is equal to $0.693/T_{1/2}$, there $T_{1/2}$ is the half-life of the radioelement. Equation (3) can be rewritten to estimate the sensitivity of the method. Providing the rate of radioactivation is constant during the time of irradiation, this relation can be expressed as

$$W = \frac{A\, M}{6.02 \times 10^{23}\, f\, \sigma_{ac}\, S} \tag{4}$$

where W = the weight of the element required to correspond to a selected value of the activity, A, appropriate to the measurement of the radioactivity, and

M = the chemical atomic weight of the element being determined.

Thus, it is seen that the sensitivity of the method depends upon the number of atoms of the target nuclide in the sample, the magnitude of the activation cross-section for the nuclear reaction, the intensity of the flux of neutrons irradiating the sample, and the length of irradiation. Also, the half-life of the radionuclide produced and the nature of radiations emitted must be favorable for the measurement, although these do not control the inherent sensitivity of the method.

The neutron activation method for the determination of copper usually makes use of the reaction $Cu^{63}(n,\gamma)Cu^{64}$. The isotopic activation cross-section for this reaction is 4.3 ± 0.2 barns.(51) Copper-64 decays by electron capture (42% of decays resulting in electron capture), beta emission (39%), and positron emission (19%). A gamma radiation with an energy of 1.34 Mev is also emitted. A gamma-ray spectrum of copper-64 shows, in addition to the 1.34 Mev photopeak, a photopeak at 0.511 Mev due to the annihilation of the positron emitted. Figure 4 shows the gamma-ray spectrum of copper-64 obtained using a 3" x 3" thallium activated sodium iodide scintillation crystal. Leddicotte et al.,(48) have made use of copper-64 in the neutron activation analysis of copper in metals, oil, ash, animal tissue, lithium, aluminum alloys, and sugar cane.

A sensitivity for copper was found to be 0.01 ppm based on the production of 40 disintegrations per second at a neutron flux equal to 5×10^{11} n/cm^{-2}/sec^{-1} and an irradiation time necessary to produce saturation of the copper-64 activity. Radiochemical separations of the copper were made on all of the samples except aluminum alloys before determinations were made of the copper activity. In the case of the aluminum alloys, it was possible to employ a gamma scintillation spectrometer to determine the gamma activity (positron annihilation spectrum) of the copper-64 in the presence of some other activities.(48) Brooksbank, Leddicotte, and Dean (see Procedure 2, Section VII) report in detail their work dealing with the neutron activation analysis of aluminum alloys.(22)

Morrison(50) reported a sensitivity of detection for trace copper analysis by neutron activation method of 0.001 micrograms. Morrison's results were based upon a neutron flux of 3.4×10^{12} n/cm^{-2}/sec^{-1} with an irradiation time of three days. Morrison reported in considerable detail about the determination of copper in an aluminum alloy whereby the analysis was effected nondestructively using a gamma spectrometer. Iredale(21) has also published a report dealing with the nondestructive analysis of copper in aluminum by the method of neutron activation analysis. A number of other investigators have used the neutron activation method to determine copper in aluminum and aluminum alloys. Albert, Caron

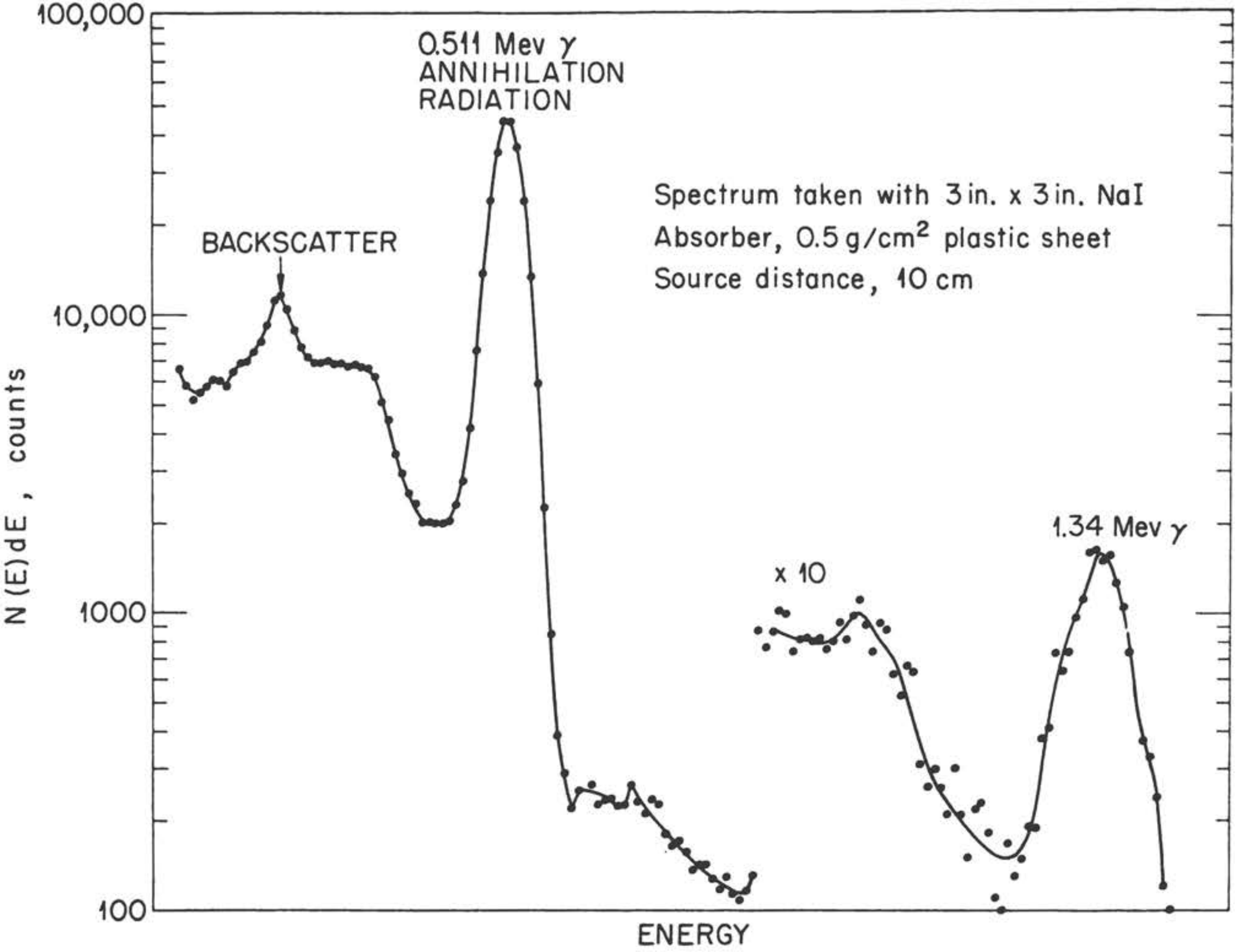


Fig. 4 Gamma-ray spectrum of Cu^{64}, half-life = 12.8 hr.

and Chaudron(52) determined copper and sodium in very high purity aluminum in which copper was present to the extent of 2-10 ppm. An irradiation time of 60 hours was employed. Jervis and Mackintosh(53) in their report on the analysis of reactor-grade aluminum by neutron activation analysis gave results for thirteen elements which were present in trace amounts in the aluminum. The copper content ranged from 0.15 ppm in zone-refined aluminum to 53.0 ppm in the grade (Grade 15) having the highest copper content. For copper analyses irradiations were made for 10-20 hours in a flux of 7×10^{13} $n/cm^{-2}/sec^{-1}$. Yakovlev et al,(54) used this method to determine copper in aluminum and aluminum oxide in which the copper content varied from 8-10 ppm. Copper has also been determined in a variety of other materials including silicon,(54-57) biological materials,(29,48) cellulose acetate,(58) germanium,(54,59-61) iron,(62,63) magnesium,(64) marine sediments,(65,66) meteorites,(62) minerals,(67) zirconium alloys,(53), bismuth,(54) iron and nickel oxides,(54) gold,(54) selenium,(54) and water.(68)

Although the high neutron fluxes of nuclear reactors are needed to analyze for copper in concentrations below the <u>ppm</u> range, copper can be determined in the <u>ppm</u> range or above by the use of other neutron sources. Recently Guinn and Wagner(69) reported their results for the analysis of some 25 elements using a Van de Graaff accelerator photoneutron source giving a thermal neutron flux of approximately 7×10^{7} $n/cm^{-2}/sec^{-1}$. Their analyses were carried out with the aid of a gamma scintillation spectrometer and without chemical separations being employed. Copper was found to be experimentally detectable to 4 ppm.

IV. METHODS OF DISSOLUTION OF COPPER CONTAINING MATERIALS

1. <u>Copper and Copper Alloys</u>

Copper metal and its alloys can be dissolved by oxidizing acids such as nitric and perchloric acids especially when heated slightly. One should take the recommended precautions when heating with perchloric acid. Hot sulfuric will dissolve the alloys if air or oxidizing materials can get to the sample.

2. Copper Minerals

The dissolution of copper minerals is treated in a number of sources.(11,24) Copper minerals can usually be dissolved by attack with mineral acids. Hydrochloric acid is preferable as an initial solvent to dissolve oxidized minerals followed by nitric acid to dissolve sulfide minerals.(11) Further treatment with hydrofluoric acid or fusion with sodium carbonate or potassium pyrosulfate may be required to dissolve silicates or minerals not dissolved by acids. Whitehead(96) recommends a mixture of nitric and hydrochloric acids to dissolve difficultly soluble sulfide minerals followed by heating with sulfuric acid to copious fumes to convert to the sulfate. Copper has been extracted from soils by shaking the soils with a 0.01 M solution of ethylenediaminetetraacetic acid solution.(97) Copper bearing ores can be dissolved by mixing the powdered ore with a finely ground 1:1 mixture of NH_4Cl and NH_4NO_3, heating to 240-250°C for 5-7 min., and dissolving in water.(98) Minerals can also be dissolved by fusing with sodium peroxide and dissolving the fusion residue in acids.(99)

3. Biological and Organic Materials

Biological and organic samples can be brought into solution either by wet ashing with acids or by fusing with sodium peroxide (see Procedures 9 and 10, Section VII). Precautions such as the use of heavy plastic shields should be used for protection when fusion with sodium peroxide is being carried out. Biological materials can be reduced to an ash in a muffle furnace, and the ash can be dissolved in acids. Koirtyohann and Feldman(100) in analyzing tissue ash by a spectrometric method use a muffle furnace to ash the samples and conduct gases coming from the sample through a combustion tube or alternately through a Meeker burner to control odors coming from the sample.

V. SAFETY PRACTICES

In working with materials which are radioactive, one is vitally concerned with radiation and radioactive contamination safety in addition to the safety required in handling conventional noxious substances. Radioactivity presents both external and internal hazards to those working with radioactive materials. The external hazard results from the radiation in the form of x-rays, gamma rays or high energy beta rays which are emitted from many radionuclides. This type of hazard is associated with millicurie or higher amounts of radioactivity and is one which is usually posed to large parts of the body. The problem of external hazard is met by either shielding, working at a sufficient distance from the source of radiation, by the use of remote handling devices, or by combinations of these methods. The internal hazard results from the possibility of getting radioactive substances into the body by inhalation, ingestion, or through wounds. The internal hazard is particularly acute whenever one is working with a radionuclide which has a long half-life, because the radionuclide is eliminated slowly from the body and/or deposits selectively in small organs or bones in the body.

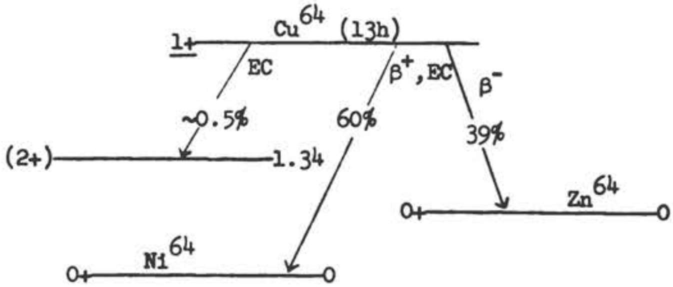
Since the half-lives of copper radioisotopes are relatively small and the radiations are of the beta-gamma type, safety practices required in handling these radionuclides are fairly easily met. Instead of describing in detail specific safety practices which would be used in working with radioisotopes of copper, references will be made to more general treatments of radiological safety covering safety practices for a large number of radionuclides. Official Government publications are excellent sources of information for radiological safety practices and procedures, and National Bureau of Standards Handbook's No's. 42 and 48(106,107) are recommended. Other sources of information such as the U. S. Atomic Energy Commission's General Handbook for Radiation Monitoring(108) and the Oak Ridge National Laboratory's Master Analytical Manual(109) discuss the problem of handling radioactive material. In addition, many textbooks such as Overman and Clark's Radioisotope Techniques(110) are to be recommended for their treatment of radiological safety procedures.

VI. COUNTING TECHNIQUES FOR RADIOISOTOPES OF COPPER

Copper-64 decays by the emission of beta particles, positrons and by electron capture.(103) Beta particles and positrons are emitted having energies of 0.57 Mev and 0.65 Mev respectively. About 0.5% of the electron capture decays result in the plus 2 state of Ni^{64} which goes to its ground state by the emission of a 1.34 Mev gamma ray. The decay scheme of Cu^{64} is shown in Figure 5. Copper-64 can be counted by a G-M end window counter or an internal flow-type counter. Scintillation methods can also be used to count Cu^{64}. Sodium iodide (thallium activated) scintillation crystals are the most often used scintillation detectors. Although the 1.34 Mev gamma mentioned above can be counted by scintillation methods, it is much less intense than the annihilation gamma resulting from the annihilation of the positrons emitted by Cu^{64}. It is in most cases preferable to employ a scintillation counter equipped with a differential pulse height analyzer and count a narrow range of gamma energies including the 0.511 Mev annihilation gamma rather than make gross gamma counts. In his catalog of gamma-ray spectra, Heath(104) gives the gamma-ray spectrum of copper-64 as it was obtained with a 20-channel gamma-ray scintillation spectrometer using a 3" x 3" sodium iodide scintillation crystal (thallium activated). Figure 4 shows the gamma-ray spectrum of copper-64 as it is obtained in this Laboratory with a 200-channel gamma-ray scintillation spectrometer. The detector was a 3" x 3" thallium activated sodium iodide crystal.

Copper-66 has a half-life of 5.1 minutes. Copper-66 decays by beta emission to Zn^{66}. Nine per cent of these decays result in Zn^{66} nuclei which are excited and go to the ground state by the emission of a 1.04 Mev gamma ray.(103) The decay scheme of Cu^{66} is shown in Figure 5. The short half-life of Cu^{66} prohibits its use unless one has available rapid

Copper-64 Decay Scheme



Copper-66 Decay Scheme

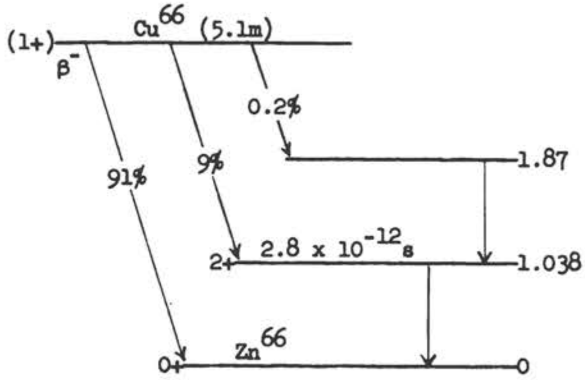


Figure 5. Decay Schemes of Copper-64 and Copper-66. Taken from Strominger, D., Hollander, J. M., and Seaborg, G. T., Rev. Modern. Phys. 30, 585-903 (1958).

methods for producing and processing the isotope. The most prominent beta particle emitted by Cu^{66} has an energy of 2.6 Mev. Thus, Cu^{66} is easily counted by both G-M and scintillation counters.

The gamma-ray spectrum of copper-66 is shown in Figure 6. This spectrum was obtained with the 200-channel gamma-ray spectrometer previously mentioned by the method of complement-subtraction as described by Lee(114) and Bate and Leddicotte.(115) To obtain the spectrum of copper-66, a spectrum of copper metal of natural isotopic composition

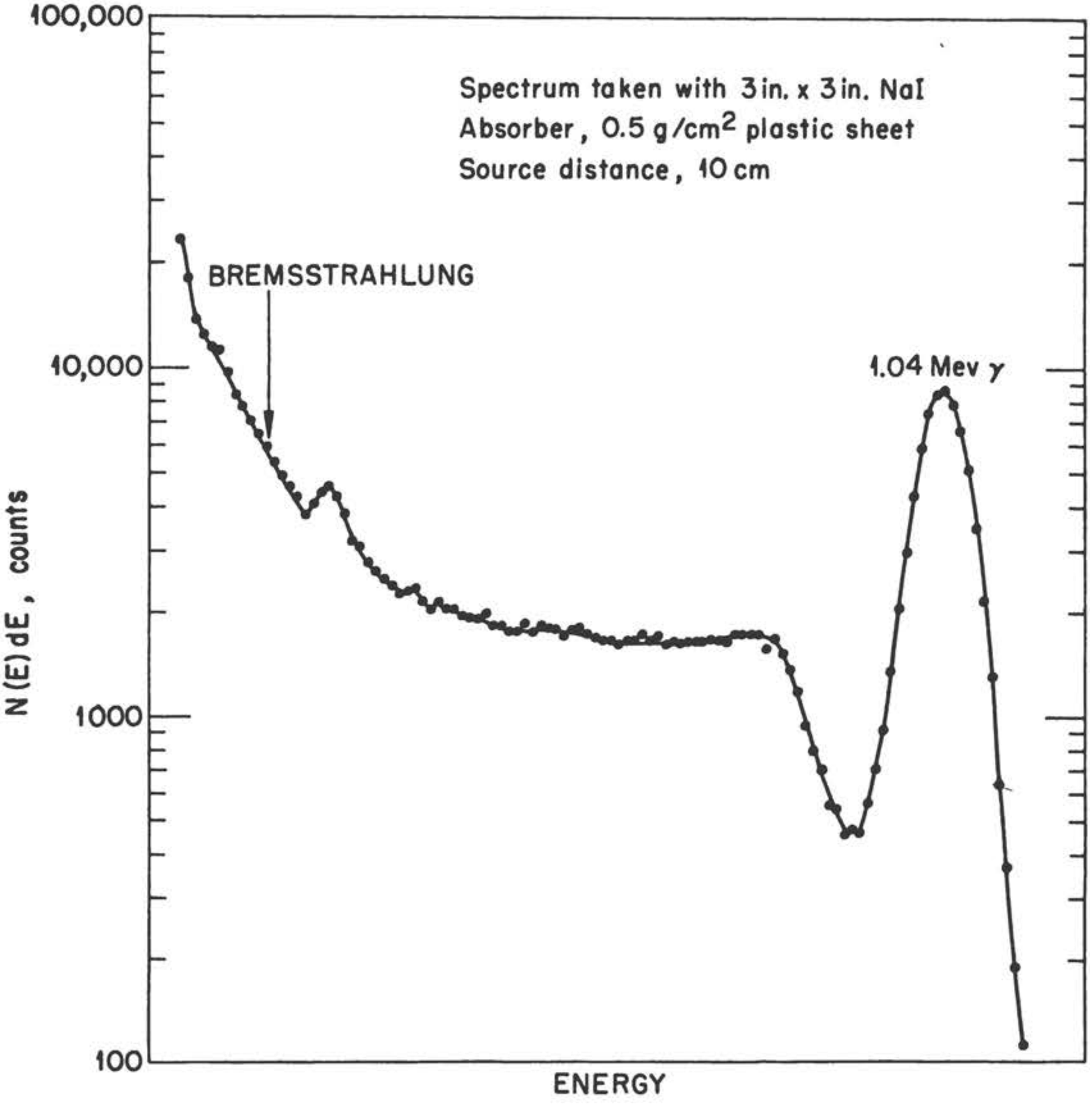


Fig. 6. Gamma-ray spectrum of Cu^{66}, half-life = 5.1 min.

which had been freshly activated with a thermal neutron flux of approximately 10^{13} n/cm^{-2}/sec^{-1} was recorded in the memory of the spectrometer. The spectrum was complemented, and the copper-64 component of the recorded spectrum was electronically subtracted using a copper-64 source in which the copper-66 had decayed. The extent of the subtraction was followed by watching the ocilloscope which is provided with the spectrometer. Subtraction was carried out until the 0.511 Mev photopeak of copper-64 was no longer visible on the screen. After subtraction of the copper-64 component, the resulting spectrum was printed out and plotted graphically as shown in Figure 6. The gamma-ray spectrum of copper-66 shown in Figure 6 closely resembles the one obtained by Heath(104) using a 20-channel gamma-ray spectrometer.

VII. COLLECTED RADIOCHEMICAL SEPARATION PROCEDURES FOR COPPER

The radiochemical procedures which are tabulated here are typical ones which have been developed and tested for the separation of copper from materials which in many cases contain a number of other radioactivities. Precipitation techniques, such as the precipitation of copper with hydrogen sulfide and sodium or potassium thiocyanate, have been the ones most thoroughly developed and tested. Thus, a number of the tabulated procedures are the ones using precipitation as the method of separation. It was felt it was justifiable to include a number of methods which use hydrogen sulfide as a precipitant from the standpoint that some differences such as type of sample, copper content, and method of producing the radiocopper existed. References have been made earlier in the section dealing with the neutron activation method for copper analysis to other sources which use techniques for separating copper activity from other activities which are similar to the methods herein tabulated.(52,65)

Carrier-free radioisotopes of copper-64 and copper-67 can be obtained by deuteron bombardment of zinc. This method of producing carrier-free radioisotopes of copper is given in Procedure 6. Copper-64 can also be easily produced by neutron bombardment of zinc-64, especially if the energy of the neutrons is epithermal. Due to the fact that carrier-free radioisotopes of copper can be easily produced by these methods, the Szilard-Chalmers method(111) for producing high specific activities of copper radioisotopes has met with little practical acceptance. However, some success has been obtained by the method.(112)

PROCEDURE 1

Source: Leddicotte, G. W., ORNL Master Analytical Manual, Method No. 5 11230 "Copper, Neutron Activation Analysis (Isotopic Carrier) Method."

Method: Precipitation

Element Separated: Copper

Target Material: Variety of Materials Containing Traces of Copper

Type of Bombardment: Neutron

Time for Separation: 2 - 3 hours

Equipment Required: Reactor neutron source and standard laboratory equipment

Yield: Greater than 50%

Degree of Purification: See Note 1

Advantages: High sensitivity with good decontamination

Procedure

(1) Irradiate unknown and comparator (0.025 to 0.030 g to nearest 0.1 mg) samples in a neutron flux of 5×10^{11} n/cm^{-2}/sec^{-1} for 16 hours. (See Note 2).

Comparator Sample (copper metal or suitable copper compound)

(2) Transfer comparator sample to 100 ml volumetric flask, dissolve in small measured volume of 6 N HNO_3, dilute to 100 ml with water, mix well.

(3) Pipet 1.00 ml aliquot of this solution into second 100 ml vol. flask, dilute to volume with water, mix well.

(4) Pipet 1.00 ml of this solution into a 50 ml centrifuge tube and 2.00 ml of standard copper carrier solution (see Note 3). Also, add 1 ml each of the holdback carriers (see Note 4). Dilute to 20 ml with water, mix well, and acidify to 1 M HCl.

Unknown Samples

(5) Transfer irradiated sample to 20 ml glass centrifuge tube, add 2.00 ml of standard copper carrier solution (see Note 3).

(6) Add 1 ml each of holdback carriers of cadmium, cobalt, iron, manganese, sodium, strontium, and zinc. Add dropwise enough nitric acid

to dissolve the sample. If necessary, heat the mixture to effect solutions.

(7) Dilute with water to 20 ml, acidify to 1 M HCl.

Separation

(8) To effect separation of copper from the solutions above, saturate solutions with H_2S, centrifuge mixture and discard supernatant liquid. Wash precipitate with two 10-ml portions of hot water. Centrifuge the mixture and discard the washes.

(9) Dissolve the CuS precipitate in 1 ml of conc. HNO_3. Dilute the solution to 10 ml with water and 1 ml of iron holdback carrier (See Note 4), mix well.

(10) Make solution basic with 6 M NH_4OH, centrifuge down the $Fe(OH)_3$ and transfer the supernatant solution to another 50-ml glass centrifuge tube. Discard the precipitates.

(11) Acidify the solution with conc. HCl to 0.5 M. Add solid sodium bisulfite powder to reduce Cu^{++} to Cu^+ (a change in color from blue to green results). Precipitate the Cu^+ as CuCNS by adding a slight excess of solid KCNS. Centrifuge the mixture and discard supernatant liquid. Wash the precipitate with 10 ml of H_2O. Centrifuge the mixture and discard supernatant liquid. Wash the precipitate with 10 ml of H_2O. Centrifuge the mixture and discard the wash liquid.

(12) Filter the CuCNS through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel; wash the precipitate three times with 5 ml portions each of H_2O and 95% ethyl alcohol. Dry the precipitate for 15 minutes in a drying oven at 110°C. Weigh the CuCNS precipitate and filter paper on an analytical balance. Record the net weight of the precipitate (carrier) or (unknown). Mount the precipitate and count its radioactivity.

(13) By comparing the final weights of the precipitates to the amounts of copper carrier added, determine yields of both the comparator and un-

known samples. By comparing the activities of the comparator and unknown CuCNS precipitates determine the amount of copper in the unknown sample.

Notes:

1. When Method No. 5 11230 in the Master Analytical Manual of the Oak Ridge National Laboratory was written, no decontamination data was available using the holdback carriers given in Note 4. Since that time, decontamination data has been obtained using radiotracers and carriers of Zn^{++}, As^{++}, Ag^{+}, Cd^{+}, In^{+++}, Sn^{++++}, and Sb^{++}. Decontamination data for these elements in Method No. 5 11230 are shown below.

Tracer Used	% Followed Through
Sb	0.166
In	0.0928
Ag	16.0
As	0.285
Cd	1.24
Sn	0.137
Zn	0.0160

2. The sensitivity of this procedure is such that 5×10^{-8} g of copper can be measured. The sensitivity can be improved by the use of higher neutron fluxes.

3. The standard copper carrier solution recommended has a concentration of ~ 10 mg of Cu^{++} per ml.

4. Holdback carriers recommended are: Cd^{++}, Co^{++}, Fe^{+++}, Mn^{++}, Na^{++}, Sr^{++}, and Zn^{++}.

PROCEDURE 2

Source: Brooksbank, W. A., Jr., Leddicotte, G. W., and Dean, J. A., Anal. Chem. 30, 1785-1788 (1958).

Method: Precipitation

Element Separated: Copper

Target Material: Aluminum base alloys containing traces of Cu, Mn, Ni, Fe, Zn, Ti, Ag, Cr, Zr, Sb

Type of Bombardment: Neutron

Yield: Greater than 50%

Degree of Purification: Free from other radioactivities

Time for Separation: 2-3 hours

Equipment Required: Standard

Procedure

(1) Irradiate 30 minutes. Two hours after irradiation, dissolve sample (0.001-0.060 gram) in 3 ml of 19 M sodium hydroxide.

(2) Add 3 ml of distilled water, after reaction subsides, heat to boiling and maintain for 3 minutes, cool to room temperature, acidify with HCl, and dilute to known volume.

(3) Take aliquot, adjust acidity to 0.5 N, and bubble H_2S through the solution.

(4) Collect CuS ppt. and dissolve in HNO_3, add H_2SO_4 and evaporate to obtain fume of SO_3.

(5) Add solid ammonium sulfite and a solution of ammonium thiocyanate. Collect cuprous thiocyanate, dry at 110°C and weigh.

Note:

1. The source cited for this procedure also gives analyses for many of the other trace elements. Some of the elements, including copper, were determined nondestructively by gamma scintillation spectrometry.

PROCEDURE 3

Source: Kraus, K. A. and Moore, G. E., J. Am. Chem. Soc., 75, 1460, (1953). (See Note 1)

Method: Anion exchange

Element Separated: Copper

Target Material: Elements Mn through Zn

Type of Bombardment: Thermal neutrons

Yield: Exact value unknown

Degree of Purification: Good, but purification unknown

Time: ?

Equipment Required: Standard plus 26 x 0.29 cm ion exchange column containing 200 + 230 mesh Dowex-1 resin.

Procedure

(1) Dissolve target material in 1 ml of conc. HCl, add carriers to bring conc. of all elements to 1-6 mg/ml.

(2) Place solution on resin which has been pretreated with conc. HCl.

(3) Elute Ni, Mn, and Co with 4 M HCl, elute Cu with 2.5 M HCl leaving other elements on column.

(4) Use additional procedures which are necessary to get Cu into form for counting and/or weighing.

Note:

1. The Cu which was used in the source cited was not radioactive. The procedure would seem to be such an excellent one that it is reported here as if the copper were determined radiochemically.

PROCEDURE 4

Source: Meinke, W. W., U. S. Atomic Energy Commission Report UCRL 432 (Aug. 1949).

Method: Precipitation

Element Separated: Copper

Target Material: ~ 4 g U metal foil

Type of Bombardment: All high energy particles in 184" cyclotron

Yield: ~ 60%

Degree of Purification: Decontamination factor ~ 10^4 from fission and spallation products. ~ 10^6 from elements 38-56.

Time for Separation: 1-2 hours

Equipment Required: Centrifuge, cones, 110°C oven

Advantages: Good yield of Cu purified from all other elements.

Procedure

(1) Dissolve target in HCl or HNO_3, take aliquot, add 10 mg Cu, make basis with NH_3, centrifuge out $Bi(OH)_3$ and scavenge with $Fe(OH)_3$ and $BaCO_3$, $SrCO_3$ (add K_2CO_3).

(2) Make supn. 0.5 N in HCl. Bubble in SO_2, add KCNS until CuCNS precipitates (slight excess).

(3) Dissolve CuCNS in HNO_3 and make neutral. Add KCN and scavenge with CdS, As_2S_3 and TeS_2.

(4) Acidify and boil off HCN (caution!) add Sr, La, and Y holdbacks, ppt. CuS from 3 N HCl.

(5) Dissolve in minimum HNO_3, dilute to 0.5 N acid and scavenge twice with AgCl. (Boiling helps coagulate AgCl).

(6) Ppt. CuCNS from supn., filter, wash with H_2O and alcohol, dry 15 min. at 110°C. Weigh as CuCNS (19.2 mg per 10 mg Cu).

Note:

Scavenges made with 1-2 mg carrier.

PROCEDURE 5

Source: Meinke W. W., U. S. Atomic Energy Commission, Report UCRL 432 (Aug. 1949).

Method: Precipitation

Element Separated: Copper

Target Material: Ni (separated isotopes)

Type of Bombardment: Protons - 37" and 60", deuterons - 60" cyclotrons

Yield: 50-75%

Degree of Purification: Factor of 5

Time for Separation: 4-5 min.

Equipment Required: Small beakers, Hirsch funnel

Advantages: Speed of separation

Procedure

(1) Dissolve Ni foil (3-5 mg) in 0.5 ml of 6 N HNO_3 in 10 ml beaker, evaporate to dryness in preheated hotplate.

(2) Add 3-4 drops conc. HCl, evaporate to dryness. Repeat.

(3) Add following in succession, warming after each addition: 2 mg Cu and 2 mg Co or 2 ml of the chloride solns.; 0.5 ml conc. NH_4HSO_3 soln.; and 10% NH_4SO_3 N soln.

(4) Stir and warm slightly. Filter the sample through a No. 42 Whatman paper disc in a Gooch or Hirsch funnel and prewet with a few drops of 0.1 N NH_4SCN - 0.1 N NH_4HSO_3 wash soln.

(5) Wash with a small amount of 0.1 N NH_4SCN - 0.1 N NH_3HSO_3 wash soln., followed by a few drops of acetone. Mount for counting.

PROCEDURE 6

Source: Haymond, H. R., Maxwell, R. D., Garrison, W. M., and Hamilton, J. G., U. S. Atomic Energy Commission Report UCRL 639 (March 1950).

Method: Solvent extraction

Element Separated: Copper (See Note 1)

Target Material: Zinc

Type of Bombardment: Deuterons in 60" cyclotron

Yield: See Note 2

Degree of Purification: Quantitative separation from Ga

Time for Separation: ?

Reagents Required: Standard; plus dithizone and carbon tetrachloride

Equipment Required: Standard; plus muffle furnace at 500°C

Procedure

(1) Dissolve ~ 1 gm of target in minimum amount of 12 N HCl, dilute to 5.5 N HCl.

(2) Add 10 mg of $GaCl_3$ carrier and extract the Ga with ether.

(3) Evaporate almost to dryness, dilute to 50 ml, adjust pH to 1.0-1.2 with NaOH soln., and extract three times with equal volumes of CCl_4 containing 0.001% dithizone.

(4) Combine CCl_4 extractions, wash twice with 0.1 N HCl and evaporate to dryness in a porcelain dish.

(5) Heat to 500°C for 30 minutes to destroy copper dithizonate complex and obtain carrier free Cu^{64} and Cu^{67}.

Notes:

1. This procedure yields carrier free Cu^{64} and Cu^{67} which may be used in biological investigations.

2. No values for the yield, and time for separation were given in the source of this procedure. However, according to the data given by Geiger and Sandell(105) for the extraction constant for primary copper

dithizonate extractions into CCl_4, the yield of such extractions should be practically 100%. The time required for separation should be about 45-60 min. since the extractions only require 3-5 min.

PROCEDURE 7

Source: Meinke, W. W., U. S. Atomic Energy Commission, Report UCRL 432 (Aug. 1949).

Method: Precipitation

Element Separated: Copper

Target Material: ~ 1 g Bi metal

Type of Bombardment: All particles is 184" cyclotron

Yield: ~ 10%

Degree of Purification: ~ 10^4 from fission and spallation products

Time for Separation: 1-2 hours

Equipment Required: Standard

Advantages: Good yield of Cu from all other elements

Procedure

(1) Dissolve target, take aliquot of target soln., add 10 mg Cu, make basic with NH_3, centrifuge out $Bi(OH)_3$ and scavenge with $Fe(OH)_3$ and $BaCO_3$ (add K_2CO_3).

(2) Make supernate 0.5 N in HCl, bubble in SO_2, add KCNS until CuCNS precipitates (slight excess).

(3) Dissolve CuCNS in HNO_3 and make neutral. Add KCN and scavenge with CdS.

(4) Acidify and boil off HCN (caution!), add Sr and Y holdbacks, ppt CuS from 3 N HCl.

(5) Dissolve in HNO_3, add HCl and destroy HNO_3. Dilute to 0.5 N HCl and scavenge twice with AgCl.

(6) Ppt. CuCNS from supernate, filter, wash with H_2O and alcohol, dry 15 min. at 110°C. Weigh as CuCNS (19.2 mg per 10 mg Cu).

Note: Scavenges made with 1-5 mg carrier.

PROCEDURE 8

Source: Meinke, W. W., U. S. Atomic Energy Commission Report. UCRL 432 (Aug. 1949).

Method: Precipitation

Element Separated: Copper

Target Material: Copper

Type of Bombardment: 60", 184", linear accelerator - all particles

Yield: 80%

Degree of Purification: Factor of $\sim 10^3$

Time for Separation: 40 minutes

Equipment Required: Standard

Procedure

(1) Dissolve copper in as little HCl as possible adding H_2O_2 to speed up the solution. Add holdback carriers for necessary elements.

(2) Make 1 $\underline{N}$ in HCl. Reduce the Cu^{++} to Cu^{+} with Na_2SO_3, cool and add NaCNS until precipitation is complete.

(3) Centrifuge and wash precipitate with cold H_2O.

(4) The precipitate can be dissolved in concentrated HNO_3 or HCl.

(5) Reprecipitation can be accomplished by diluting to 1 $\underline{N}$ acid reducing with Na_2SO_3 and precipitating with NaCNS. Holdback carriers are again added before precipitation.

Notes:

1. Copper can also be precipitated as the sulfide from 0.5 $\underline{N}$ to 1.0 $\underline{N}$ acid solution, and the precipitate dissolved in fuming HNO_3.

2. A drop of wetting agent will prevent the tendency of the precipitate to creep.

3. In redissolving the precipitate, care must be taken since the evolution of gas is profuse.

4. Three precipitations of the Cu are enough to give a decontamination factor of $\sim 10^3$.

PROCEDURE 9

Source: Bowen, H. J. M., Intern. J. Appl. Radiation and Isotopes, 4, 214-20 (1959).

Method: Precipitation

Element Separated: Copper

Target Material: Biological materials containing copper

Type of Bombardment: Neutrons

Yield: 70%

Degree of Purification: ?

Time for Determination: 2 hours

Equipment Required: End window counter, centrifuge, drying oven plus standard laboratory ware.

Reagents Required: KCNS, HNO_3, carrier of Fe, Mn, and P, NH_4OH, alcoholic soln. of salicylaldoxime, acetone

Procedure

(1) Wet ash sample with hot fuming nitric acid and add 10 mg of Na, Ca, Sr, Cl, Br, K, Cu, Mn, Co, Y, and P carriers.

(2) Make the solution 1 N in HNO_3, reduce the Cu^{++} to Cu^+ with Na_2SO_3, add KCNS solution and centrifuge.

(3) Dissolve ppt in hot HNO_3, add Fe, Mn, and P carriers and make strongly alkaline to precipitate $Fe(OH)_3$. Recover $Fe(OH)_3$ ppt, dissolve in HNO_3, and reprecipitate with NH_4OH. Centrifuge and discard ppt.

PROCEDURE 9 (Continued)

(4) Combine the two supernatants, make 1 N in HNO_3 and add KCNS soln. Discard supernatant liquid.

(5) Add HNO_3 to ppt, boil to destroy thiocyanate, and bring soln. to pH of 5 with NH_4OH and acetic acid.

(6) Add alcoholic salicylaldoxime, boil to coagulate ppt., centrifuge, wash ppt. with water and acetone.

(7) Dry ppt., weigh and count in end window counter.

Notes:

1. Cu^{64} is produced by other nuclear reactions, e.g., $Zn^{64}(n,p)Cu^{64}$, but such reactions are probably insignificant compared to the $Cu^{63}(n,\gamma)Cu^{64}$ reaction.

2. The biological materials analyzed and reported in the source cited were blood, tomato seed, and red champion (silone dioica).

PROCEDURE 10

Source: Maddock, R. S. and Meinke, W. W., Progress Report No. 8, on Activation Analysis, Nuclear Chemical Research, and Radiochemical Separations, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, November (1959).

Method: Solvent extraction

Element Separated: Copper

Target Material: Biological tissue

Type of Bombardment: Neutron

Time for Separation: 8 minutes

Equipment Required: Standard

Yield: 80%

Degree of Purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure

(1) Irradiate sample for 5 min. at 1 Megawatt.

(2) Fuse in nickel crucible with 10 gms. Na_2O_2 containing 10 mg Cu carrier neutralized with 3 pellets of NaOH, cool crucible.

(3) Dissolve melt in 50 ml water and add 30 ml conc. HCl (caution!)

(4) Cool solution with 50-70 ml liquid nitrogen.

(5) Transfer to 150 ml separatory funnel containing 5 ml of equilibrated CCl_4 (1.2 $\underline{N}$ HCl).

(6) Add 10 ml 6% aqueous cupferron solution and extract for 1 min.

(7) Back extract cupferron layer with 10 ml conc. NH_4OH.

(8) Precipitate Cu with H_2S, and collect ppt. with filter chimney.

(9) Determine activity with 100-channel gamma scintillation spectrometer.

Note: Chemical yield may be determined iodometrically.

PROCEDURE 11

Source: Meinke, W. W., U. S. Atomic Energy Commission Report UCRL 432 (Aug. 1949).

Method: Precipitation

Element Separated: Copper

Target Material: Arsenic

Type of Bombardment: 190 Mev D^+

Yield: 90%

Degree of Purification: Factor of $\sim 10^3$

Time for Separation: 3/4 hour

Equipment Required: Standard

Reagents Required: Hydrochloric acid, nitric acid, carriers, H_2S

Procedure

(1) Dissolve As in HCl + HNO_3, evaporate off HNO_3, add 5 mg Cu carrier and 1 mg other holdbacks.

(2) Ppt. from 1 $\underline{N}$ HCl with H_2S. Wash with H_2O and treat ppt. several times with 1 $\underline{N}$ KOH. Wash out As and Ge, discard washes.

(3) Dissolve remaining ppt. in minimum conc. HNO_3, evaporate to dryness with HCl.

(4) Dilute with 1 $\underline{N}$ HCl, add small amounts of solid Na_2SO_3 and NaCNS.

(5) If ppt. is not pure white, add more Na_2SO_3. After two minutes, centrifuge.

(6) Dissolve with hot conc. HCl and repeat precipitation.

(7) Weigh as CuCNS.

Note: Holdbacks added are Cr through Sc, except As and Cu.

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